

Ceramic Materials

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1 Clay

Clay is a flexible and tough material that can be formed using many different techniques. Moist and soft clay becomes hard and brittle as it dries, and when fired it hardens and condenses into a very durable material, i.e. ceramics. Clay materials are the oldest construction materials developed by humans from natural raw materials and, as such, raw clay has been used long before firing it for durability was invented. *Fig 1*

Clay is a very fine, naturally occurring type of soil created by weathering of different types of rock. Clay can be found practically all over the world, in different places and in different colors. Different types of clay include e.g. kaolin, ball clays, red clays and other natural clays. Theoretically, geologists define clay as a type of mineral soil in which at least 30% of the particles are less than 0.002 mm. *Fig 2*



Figure 1. Clay construction, Burkina Faso

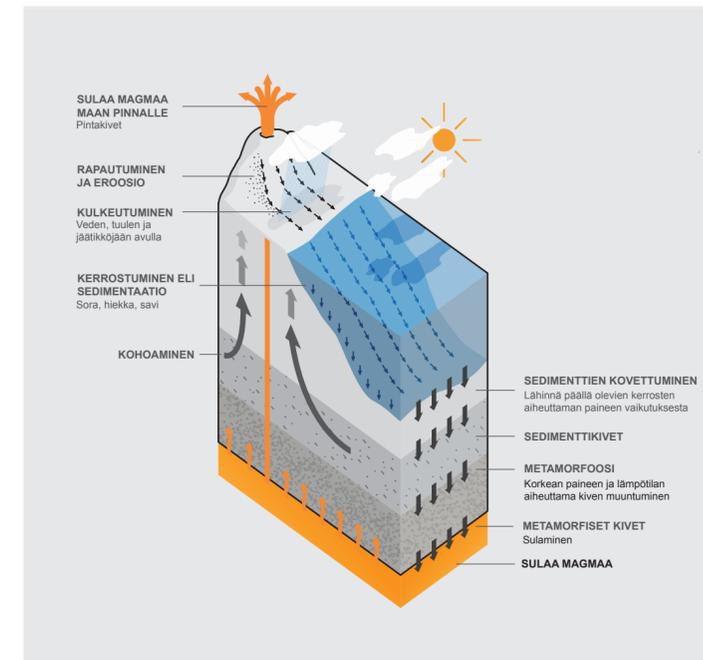


Figure 2. High circulation of a substance

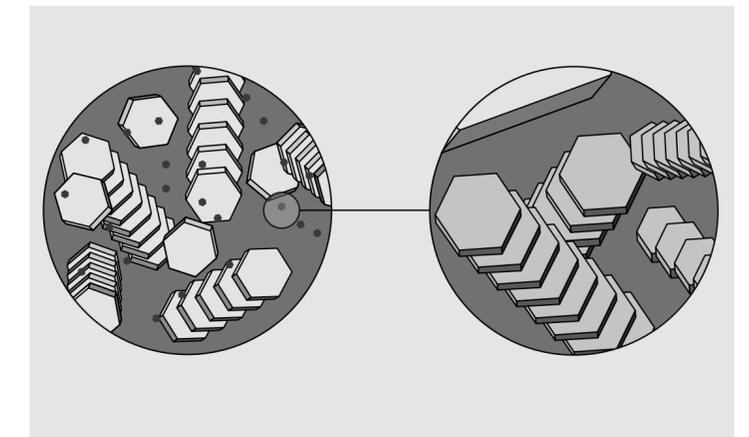


Figure 3. Clay crystal

Primary clays are residually deposited clay minerals, such as kaolin and bentonite. Primary clays are often the purest clays. Secondary clays are clay minerals that have migrated to other areas of origin and contain varying amounts of impurities. Secondary clays include, for example, ball clays and natural clays.

Most naturally occurring minerals are a combination of silicon (Si) and oxygen (O), but they often contain other common crustal elements such as iron and aluminum. These substances are called silicate minerals. Silicates are the key raw materials for ceramics. By combining them and firing them at high temperatures, different clay bodies and glaze surfaces are obtained.

Theoretically, the chemical composition of a clay crystal is expressed by the formula: $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Clay crystals are flat, hexagonal, microscopically small plates whose shapes and sizes vary according to different clay grades (Jylhä-Vuorio, 2003). *Fig 3*

1.1 Different Clay Bodies and Plasticity

A mixture of clay minerals and other raw materials is called a clay body. Clay bodies can be found directly in nature (red clay, natural stoneware clays), but in practice most clay body mixtures are industrially produced. Typical properties of clay bodies are plastic and non-plastic.

Plasticity in physics is a property of matter in which the effect of force on its shape results in irreversible deformations. The plasticity of clay means that the clay body can withstand stretching and machining without tearing. The smaller the clay particles, the greater the plasticity they provide in the clay body.

A fine, plastic body is called fat (versus short). Because the fat and fine-particle body holds a lot of water, its drying shrinkage is high. When drying, a body with a large shrinkage rate causes defects in the object, such as cracks. To avoid defects, the clay bodies can be adjusted with non-plastic raw materials such as quartz, feldspar and crushed clay, i.e. chip or chamotte. Non-plastic raw materials reduce shrinkage during drying, i.e. drying shrinkage (Jylhä-Vuorio, 2003).

Plastic or non-plastic clay bodies are suitable for

various manufacturing techniques. Plastic compounds are suitable for throwing, hand-building and molding. Compression powders and granules of non-plastic clay bodies are used in industrial production. Casting slip, or casting clays, are fluid mixtures, in which a form is usually made using a plaster mold.

The plasticity of different clay bodies is regulated by their raw material composition. Raw materials are divided into plastic and non-plastic raw materials. Plastic raw materials include, for example, kaolin, ball clays, red clays and bentonite. Non-plastic raw materials include feldspar, nepheline syenite, quartz, flint, grog and fibers.

Plastic raw materials:

- Bring the finest material to the body.
- Contain a lot of water, which causes severe drying shrinkage.
- Features are slow drying, good dry strength.

Non-Plastic raw materials:

- Bring coarser material to the body.
- Slimming, opening the clay body, water evaporation is easier, drying shrinkage decreases and distortion decreases.

Other possible raw materials for clay bodies:

- Whiting whitens the fired clay (low-fire clay below 1100°C).
- Wollastonite reduces the drying and firing shrinkage of the pulp and increases the strength and heat shock resistance of the fired product (low firing clay below 1100 ° C).
- Talc is used in refractory cordierite clays due to its good thermal shock resistance.
- Bone ash is used in bone china as a bleaching, filling and melting agent.

Additives for clay bodies:

- Deflocculants (e.g. Dolaflox, Dispex, Darvan) keep a clay slip flowing even with quite small amounts of water.
- Flocculants (vinegar, magnesium salts) or thickeners prevent, for example, sedimentation of glazes from the bottom of a container.
- Already fired pieces, grog, sand increase the stiffness of clays and reduce the drying shrinkage as well as the need for water in the clay body.

(Jylhä-Vuorio, 2003)



Photo: Anne Kinnunen

1.1.1 Plastic clay

Plastic clay bodies are solid and can be molded without cracking or breaking. Therefore, the clay must contain enough plastic raw materials. Plastic bodies can undergo plastic forming, i.e. shaping, while the molded shape is retained even after molding and machining are stopped. Plastic bodies contain 20-30% water and rarely any additives.

Various industrially made clay bodies can be purchased from retailers, but clay bodies can also be made in the studio. You can develop your own clay-body recipe (requires material research), or use a ready-made recipe found in the literature and distributed by potters. Table 1

Ball clay (Hyplas 64)	35%
Kaolin (Standard Porcelain)	25%
Feldspar (FFF K7)	30%
Quartz (FFQ)	10%
+	
Water	~30%

Table 1. TPP20 / Plastic stoneware body, 1250 °C (Pelkonen 2001)

Clay body production:

1. Add the weighed ingredients into hot water.
2. Stir vigorously with a drill or pug mill for at least an hour to make sure the ingredients mix well.
3. Leave the clay mixture in the tank to set. For example, a porcelain body can be left to age for years. The body contains a lot of water, so before use it must be dried on plaster slabs and wedged to get rid of any air bubbles. It is also possible then to put the clay at this more plastic stage into the pug mill to vacuum out the air bubbles, be compressed, and extruded and ready for the production of ceramics.

1.1.2 Casting-slip

Casting slip (casting clay) is prepared by adding water and adjusting agents to a mixture of raw materials. Adjusting agents (deflocculants) make the slip flowable at a lower than normal water ratio, which speeds up the drying of the object and improves its casting properties. This gives a flowable, liquid body which can be cast into a mold made of plaster. The plaster mold absorbs water from the casting slip into its capillary channels, as a result of which the clay slip begins to condense from the inner surface of the mold and solidifies into a casting wall. The thickness of the casting wall is adjusted by the length of the casting time. The longer the clay slip stays in the mold, the thicker the wall becomes. The Figure 4. illustrates the deposition of clay particles in the casting clay. In the casting slip in the plaster mold, the particles tend to settle so that the largest surfaces are perpendicular to the flow direction, i.e. parallel to the casting surface. An example recipe for making casting clay can be found in Table 2.

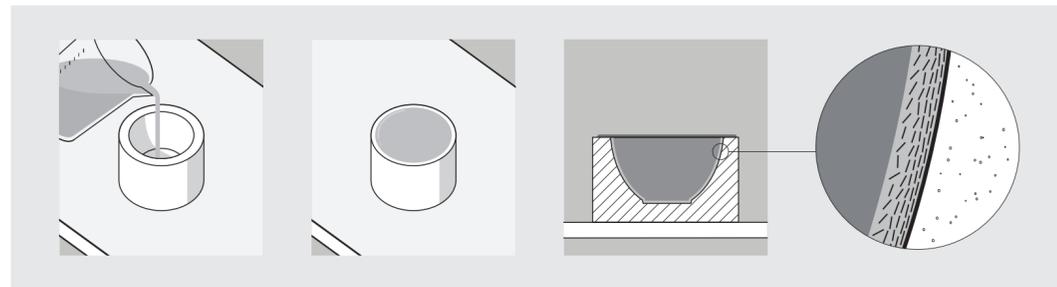


Figure 4. Settling of clay particles in casting clay

Kaolin (Super Standard Porcelain)	30%
Kaolin (Standard Porcelain)	10%
Feldspar (FFF K7)	30%
Quartz (FFQ)	20%
Molochite	10%
+	
Water	40%
Deflocculant (Dispex N40)	~ 0.3%
Liter weight	1760-1800g / L

Table 2: TPV20 / Porcelain casting clay, 1250 °C (Pelkonen 2001)

Mixing Casting-Slip:

1. Weigh the raw materials of the slip and mix them in hot water (about 95% of the water content of the final recipe) to which about 80% of the amount of deflocculant has been added.
2. After the slip materials have been soaking in a slurry at least overnight, mix vigorously with a drill for several hours to mix the ingredients, then let the slip settle and air bubbles to disappear.
3. Finally, adjust the slip to the desired composition using the remaining water and deflocculant. If the casting slip is familiar, visual evaluation of the composition is sufficient. If the slip recipe is new, it is a good idea to measure its liter weight and viscosity to ensure the correct composition.

1.2 Raw materials in ceramic production

In this subsection, we list the most common raw materials used in the production of ceramics and their properties. These raw materials are used to make both clay bodies and glazes.

1.2.1 Plastic raw materials:

Kaolin is a general term for primary and secondary clays consisting mainly of kaolinite. Pure kaolin clays are the whitest and finest clay grades used especially in porcelain casting slips. However, in addition to kaolinite, they always contain a small amount of other minerals.

Kaolin:

- Mineral, Kaolinite
- Melting range about 1750-1770 ° C
- Adds whiteness
- Low plasticity or non-plastic
- The main raw material of porcelain
- Raises the melting temperature of bodies and glazes
- The brand name of calcined kaolin is Molochite, which is a non-plastic raw material

Ball clays are originally kaolin-derived clays that have traveled long distances from their origins. They contain varying amounts of organic and inorganic impurities. The main mineral in ball clay is kaolin.

Ball clay:

- Minerals, kaolinite, montmorillonite
- Melting point 1200-1300 ° C
- Produces plasticity, toughness and dry strength in the clay
- Rich in organic matter, which improves the workability of the clay
- High drying shrinkage can cause cracking and warping in objects

Bentonite is a “superplastic” clay with a high water-binding capacity. Water not only goes between the clay particles, but penetrates the crystal structure, swelling them 4-5 times.

Bentonite:

- From volcanic ash
- Small particle size, high plasticity
- Prevents glazing from settling
- Lowers the combustion temperature of the pulp
- Increases drying shrinkage and dry strength

Red clay is a natural clay commonly used around the globe, the reddish-brown color is due to the high iron content in the clay.

Red Clay:

- Contains a lot of alkalis and heavy metals
- Low melting point
- Contains a lot of iron, which causes the fired object to turn red

1.2.2 Non-plastic raw materials

Oxygen (O) and Silicon (Si) are the most common elements in the earth's crust, with abundant compounds all over the globe. The most common of these is **quartz**.

Quartz:

- Sturdy and add firmness to over-plastic clay body
- Makes the body structure more transparent and facilitates drying
- Reduces the drying shrinkage of the clay body but reduces the dry strength
- Raises the melting temperatures of bodies and glazes
- Acts as a 'skeleton' in the clay and supports the structure of the fired body

Feldspar is the most common of the crystallized rock minerals. It is the most important raw material used by the fine ceramic industry after clays.

Feldspar:

- Acts as melters
- The most common types of feldspar are potassium feldspar, soda feldspar, lithium feldspar, calcium feldspar
- Molten feldspar is very viscous, i.e. stiff, which makes it a good melting agent

Alumina raises the firing temperature of the clay, lightens the firing color of the fired clay and increases the mechanical resistance of the clay body. In porcelain clays, alumina reduces the transparency of the body.

(Jylhä-Vuorio, 2003)

2 Ceramics

Ceramics are clay fired at high temperatures. After drying, the clay can be converted back to plastic form by mixing it with water countless times, but if the clay is heated to a temperature above about 600 ° C, it becomes a hard substance that is no longer soluble in water and does not return to its plastic form. Because of this hardening, pottery is called an eternal material because it never decays, but at most shatters and crumbles.

Ceramic change means that clay never ever returns to a plastic body, its minerals have changed their chemical crystal structure under the influence of heat and clay has changed into a new, durable material, i.e. ceramics.

The term ceramic is used for inorganic materials made at high firing temperatures. In everyday language, the word ceramic often refers to the so-called technical ceramics, which are new materials developed in recent decades. Technical ceramics include very strong materials that are used to replace e.g. metals.

The term ceramics is used for objects made from clay-based raw materials that have undergone a ceramic firing process. Ceramics can be divided into two groups according to the degree of processing of the raw materials used: coarse ceramics and fine ceramics. Conventional coarse ceramic products include various bricks and brick elements. Fine ceramics can be considered to include, for example, household and sanitary ceramics.

2.1 Grouping of ceramics

Fired products can be divided into different groups based on their manufacturing technology and properties: porcelain, stoneware, red clay, earthenware, faience, raku and paper clay. These have strong cultural and historical traditions and traditions of pottery making. However, various clay bodies and ceramic manufacturing techniques can also be freely experimented with, thus developing means of design and artistic expression as well as producing new aesthetic solutions.

Porcelain was developed in China during the Tang Dynasty. About a thousand years ago, kaolin (china clay) was first discovered in eastern China, which, mixed with another raw material containing quartz-containing feldspar, created a new kind of milky material resembling white glass. Porcelain became an admired material that was attempted for a long time without imitation in Europe. Kaolin is the main raw material for porcelain. In Europe, it was discovered in Germany in the early 18th century, and in 1709 Meissen porcelain was developed. Genuine hard porcelain is fired at a temperature of 1300-1450 °C in a reduction firing, it is a very hard, white and translucent material. However, porcelain is also made at a lower firing temperature by adding meltable ingredients to the clay body. Such porcelain is called soft porcelain. Soft porcelain is usually not quite as translucent as hard porcelain and the hardness of the body is weaker than hard porcelain. Bone china, on the other hand, is one form of soft

porcelain in which bone ash, for example ground from bovine bones, is used as the translucent ingredient and melting agent.

Stoneware is a ceramic product fired at a temperature of more than 1200 °C which is almost as dense as porcelain but not transparent at all. The color varies from grayish and yellowish white to dark. Unlike porcelain, stoneware contains larger clay materials such as ball clay or natural stoneware clay. These make clay more plastic and easier to mold compared to porcelain and are therefore an excellent sculptural material.

Red clay and other low-fired natural clays can be found almost everywhere in the world. The reddish-brown color of Finnish red clay is due to the large amount of iron compounds in the clay. Iron melts the clay body, which is why, for example, the combustion temperature of Finnish natural clay is low, about 1020-1080 °C. The red clay quickly melts into a lava-like puddle if the temperature is raised above the sintering point of the clay body. For this reason, it is important to make sure that the red clay is not fired above the recommended temperatures, as the molten, lava-like body easily drains from the kiln shelves to the bottom of the kiln.

Earthenware is the general term for a clay body that remains porous after firing and is fired at a temperature below 1200 °C. The color of the pottery after firing is often yellowish, orange or brick red.

Faience or majolica was originally a decoration technique developed in the city of Faenza in Italy. The slightly reddish, iron-containing, unprocessed, and porous body was covered with white tin glaze or white engobe. The name Faience spread in Europe to mean white or colored, porous and brittle earthenware. It was the most common ceramic pottery material in Central Europe from the Middle Ages to the 19th century.

Raku's roots are in artefacts made for a Japanese tea ceremony. Raku is a firing technique in which ceramic objects are lifted red-hot from a kiln and smothered with organic materials to create a smokey and blackening environment and then quickly immersed in still water to maintain reduction, and to provide a cracking glaze. Raku clay is a low-firing and porous clay that is very resistant to sudden changes in heat.

Paper clay is made by mixing paper with clay. Adding

paper to the clay brings fibers into the clay structure, which makes it durable in the raw phase, and therefore very thin and bulky walls can be built from the paper clay. Organic burns out during combustion, leaving a thin and light ceramic structure.

3 Glaze

Glaze is a thin layer of glass on the surface of the ceramic body. Glazes are named according to their composition, appearance, firing temperature and firing method. They can be glossy, matte, translucent or opal in visual properties. The glazes may have crystals or may be completely clear. Glazes can be stained with metal oxides and pigments. The raw materials they contain or clay base can affect the properties of the glaze. Firing conditions also affect the appearance of the glaze.

The glaze is selected according to the firing temperature of the clay body used. For example, low-fire bodies are glazed with low-fire glazes (900-1180 °C) and high-fire clay bodies are glazed with high-fire glazes (1200-1400 °C).

Glaze is used for many different reasons. In utensils, the glazed surface is more hygienic and easier to keep clean than the unglazed surface. In addition, the glaze improves the wear resistance of the object and makes the object waterproof. There may also be purely aesthetic reasons for using glaze. For example, it can improve the appearance of an object and smooth out defects visible in the body. In art ceramics, the visual properties of the glaze can go beyond usability requirements.

The properties of the glaze are substantially affected by the raw materials used, the clay body used, the firing method, the firing temperature, the thickness of the glaze layer and the composition of the glaze mixture. By their nature, glazes are not precise chemical compounds, but mixtures whose melting is affected by several simultaneous eutectic reactions. The properties of the glaze are regulated by changing their chemical composition, i.e. the amount of compounds in relation to each other. The basic raw material and glazing agent of the glaze is silica SiO₂ obtained from quartz sand. In addition to quartz, fluxes are added to the glaze to lower the melting temperature, usually in the form of feldspar minerals and frit. In addition to these, many other ceramic oxides act as glaze fluxes.

Glazes are divided into two groups according to the firing temperature: low-fire glazes 900-1180 °C and high-fire glazes 1200-1400 °C. The breakdown is indicative. Both groups include glossy, matte, and matte glazes depending on the surface melt.

Glossy glaze is clear, translucent, very meltable and often very smooth.

Matte or semi-gloss glaze is poorly transparent, even and smooth.

Matte glaze is a flat, opaque glaze which, depending on its composition, can be weakly meltable and unbalanced or well melted and crystallized to a matte surface when cooled.

By adjusting the firing program, the melting and appearance of the glaze can be greatly affected. If the soaking time is long, some matte glazes may turn shiny as they melt. In addition, how the oven is stacked and how many objects are fired in the kiln affect the melting of the glaze ([Hortling, http://www.airihortling.fi/Lasite_ja_lasittaminen.pdf](http://www.airihortling.fi/Lasite_ja_lasittaminen.pdf)). For example, a fully stacked kiln prolongs cooling time and can promote the crystallization of glossy glazes to a matte finish.

All semi-matte and matte glazes will melt to shine if the firing temperature is high and the brewing time is long enough. In other words, all opaque and matte glazes are suspended melting reactions of the glaze. Small bubbles in the matte glaze prevent the transparency of the glaze, in matte glazes the glaze materials contain a lot of small crystals that form the matte surface (Hortling, http://www.airihortling.fi/Lasite_ja_lasittaminen.pdf).

3.1 Raw materials used in the glaze

In this subsection, we list the most common raw materials used in the formulation of glazes.

SiO₂ Silica

- Is the main glass former, (60-80% of the composition of glazes)
- Improves the durability of glass and glaze
- Raises the melting point
- Reduces the flowability of glazes
- Extends the melting range
- Reduces cracking
- Increases thermal expansion
- Increases acid resistance
- Reduces the dissolution of lead in lead-containing glazes
- The most common raw material is quartz sand
- The most common impurity is iron oxide

Al₂O₃ Alumina

- Refractory
- Improves the chemical resistance of the glaze
- Clearly raises the melting point
- Increases the stiffness of the glass melt
- Prevents crystallization and cracking in the glazes
- Makes the glaze harder
- Allows the formation of a matte surface
- Obscures many colors, but helps in the formation of black

Na₂O and K₂O Sodium and Potassium Oxide

- Are the main ceramic fluxes
- Significantly reduce the viscosity of the glass melt
- Narrow the melting range
- Increase the thermal expansion and cracking of the glaze
- Impair chemical and mechanical resistance, especially acid resistance
- Increase crystallization
- Increase the dissolution of lead from the glaze
- Expand and enhance the color spectrum available from metal oxides
- Raw materials: feldspar (k-, na-), nepheline syenite, alkali melt and ash

Li₂O Lithium Oxide

- Acts as an efficient melter
- Generates new color shades from ordinary metal oxides and forms crystals in crystal glazes
- Increases fluidity in the glass melt
- Increases the gloss of the glaze
- Impairs mechanical and chemical resistance
- Raw materials: petalite, Li₂CO₃, lithium feldspar, spodumene, lepidolite, lithium melts

B₂O₃ Boron Oxide

- Toxic
- Effective melting agent
- Glaze chemical balancer
- Glass former
- Properties of each of the three oxide groups
- Fired in a glaze does not pose a health risk, is used to replace the more toxic lead oxide
- Increases the smoothness and gloss of the glazing surface
- Usable raw materials: colemanite, calcium borates and boron melts

CaO Calcium Oxide

- Belongs to the group of alkaline earth oxides
- Good high combustion flux
- Forms a matte surface
- Improves the scratch resistance and hardness of the glaze
- Calcium oxide is obtained for glazing from lime or chalk
- Calcium oxide is also obtained from wollastonite for glazing

SrO Strontium Oxide

- Belongs to the group of alkaline earth oxides
- Corresponds in nature to calcium oxide
- Not used very much because of its expensive price
- Increases the power of colors, enhances red tones
- Improves acid resistance
- Promotes the formation of a translucent matte surface
- Introduced into the glazing as carbonate

MgO Magnesium Oxide

- Belongs to the group of alkaline earth oxides
- In small amounts promotes melting, use increases as the combustion temperature rises
- Raw material for refractory products: low thermal expansion
- Increases the mechanical and chemical resistance of the glazing surface
- Prevents cracking
- Increases the stiffness of the glass melt
- Obtained from magnesium carbonate, talc and dolomite

BaO Barium Oxide

- Toxic
- Effective co-melting agent at all temperatures
- Replaces lead oxide in glazes
- Barium matte glazes are not suitable for food storage containers
- Reduces the viscosity of the glass melt
- Hardens the glass surface
- Introduced into the glazing as barium carbonate

ZnO Zinc Oxide

- Raw material harmful to health: occupational safety must be remembered
- Efficiently melts at temperatures above 1100 °c
- Forms a matte surface in large amounts
- Improves the hardness and gloss of the glass surface
- Prevents the glazing sludge from settling

(Jylhä-Vuorio, 2003)

3.2 Properties of glazes

In this subsection, we discuss the various properties of glazes and the factors that affect them.

The most important properties of glaze are:

- Melting
- Viscosity or flowability of the glaze melt
- Glaze surface melt surface tension
- Thermal expansion
- Coloring properties
- Mechanical resistance
- Chemical resistance
- Toxicity / non-toxicity
- Glaze structure
- Optical properties

Factors affecting glaze properties include the following:

- Chemical composition of glazes (oxides)
- Used glaze raw materials
- Clay body composition
- Firing method and firing temperature
- Degree of finesse of glazing
- Glazing layer thickness

(Jylhä-Vuorio, 2003)

Viscosity refers to the internal friction of a substance against an external force. High viscosity is referred to when liquids flow poorly, i.e., they are stiff, and low viscosity, when liquids are more fluid. The viscosity of the glaze is dependent on the firing temperature and the viscosity is determined at the peak temperature of the glaze. In the glaze, alumina (Al_2O_3) increases the viscosity and alkali oxides decrease it. By controlling the viscosity of the glaze, the maturity range of the glaze can be increased.

When the glaze has a high surface tension, the glaze melt does not level off as it melts, but the runoff traces and glazing layers left over from the glazing application remain visible. If the glaze has too low a surface tension, it will cause the glaze to ripple. Magnesium oxide (MgO), calcium oxide (CaO), alumina (Al_2O_3), zinc oxide (ZnO) increase the surface tension. Surface tension is reduced by boron oxide (B_2O_3) and alkali oxides.

Thermal expansion is an event in which the volume of a material increases as the temperature increases and the volume decreases correspondingly as the temperature decreases. When cooled, the glaze is subject to either compressive or tensile stress in relation to the body below. Cracking is a sign of poor tensile strength, in which case the glaze shrinks more than the body below. The thermal expansion of the glaze should be lower than that of the body, because the glazes withstand the compressive stress better, i.e. the body shrinks more than the glaze during cooling (Jylhä-Vuorio, 2003).

3.3 Glaze-making

Glazes can be made yourself or purchased ready-made from retailers. There is a wide range of commercial glazes. Commercial powder glazes should be mixed with water, but liquid glazes (so-called brush-on glazes) are also available, which are applied with a brush to the surface of a bisqued object. If you make the glazes yourself, below you will find in Table 3. a recipe for bright, shiny high-fire glaze, which is a modification of Kyllikki Salmenhaara's and Airi Hortling's KX series (Salmenhaara 1983) and widely used in Aalto University's ceramics studio.

Feldspar (FFF K7)	45%
Quartz (FFQ)	25%
Whiting (FC 7)	18%
Kaolin (Super Standard Porcelain)	6%
Zinc oxide	6%
=	100%

Table 3: KXX5 / Clear, glossy high-fire glaze, 1200-1300 °C

Finely ground raw materials (200 mesh) are used for the glass mixture. The target thickness of the glaze is determined by the product to be glazed and the thickness can vary from extremely thin to a very thick layer.

Step by Step Glaze Mixing

1. Glaze recipes are usually delivered as a percentage recipe, where the amount of each raw material is expressed as a percentage by weight of the entire formula. Knowing the total amount of glaze to be produced, the amount of individual raw materials in the glaze can be calculated.
2. The raw materials are carefully weighed. Prior to weighing, it is important to ensure that all equipment used for weighing is clean.
3. Carefully weighed glaze raw materials are added to water and mixed. Water is usually added in an amount of 1-1.3 x dry matter. Glazes containing a lot of clay raw materials require more water.
4. The liquid glass mixture is sieved through a 100-200 mesh screen. The purpose of this step is important, in addition to mixing, to ensure that there are no coarse particles among the glaze and that the glaze mixture becomes consistent.
5. The glaze should be stored in a lidded container that is carefully marked with the name, composition, firing temperature, and date of the glaze. If the glaze settles to the bottom of the container during storage, a material can be added to prevent the settling of the glaze mixture, e.g. bentonite 1-2%.

When preparing or mixing glazes, always remember personal working safety! Always wear a respirator when working with dusty materials. It is also important to keep the surfaces clean by wiping them with a damp cloth and making sure that any raw materials or crumbs that have fallen to the floor are cleaned with a damp cloth so that walking traffic does not make small particles airborne dust. Likewise, work clothes should be washed often enough so that the clay or glaze that has adhered to the clothes does not start to dust. Dust is the worst health hazard in the ceramics industry and repeated wet wiping is the most effective way to prevent health problems.

3.4 Glazing techniques

Glazing refers to various methods of applying a glaze coating to the surface of an object. The most commonly used techniques in glazing are dipping, pouring, and spraying. Prior to glazing, objects are usually fired to make them durable enough to be handled during glazing. When glazing, a porous, bisque-fired object absorbs water from the glaze liquid, and a layer of glaze forms on the surface. The thickness of the glaze is determined by the speed of work, the porosity of the object, the viscosity of the glaze and the specific gravity.

It is important to remember that before firing the glaze, be sure to carefully wipe the bottom of the bisque-fired object so that they do not stick to the kiln shelf when the glaze melts. The objects are stacked in the kiln so that they do not touch each other.

Dipping or immersion means that the object is quickly immersed (approx. 2 seconds) in the glaze solution. Then, the object is lifted from the glaze, the excess glaze is drained off and an even layer of glaze remains. The thickness of the glaze is determined by the immersion time, i.e. the longer the object is immersed, the thicker the glaze layer. The benefits of dipping are e.g. low glaze waste and working is quite dust-free. Be sure to mix the glaze well just before dipping. When the glaze liquid settles, the “surface water” formed on the top can prevent the glaze from evenly sticking and the result is a layer of glaze that is too thin and inconsistent.



Glaze is poured on the outside or inside of an object. When glazing the interior, the glaze is poured back into the container. The thickness of the remaining glass layer is determined by the speed of work, i.e. the longer the glaze liquid remains inside the object, the thicker the glaze layer. In pouring, the glaze waste is also small when pouring is done above a container and the excess glaze is recovered.

Figure 5. Pouring technique in glazing



A glaze spray-gun is used for spraying. Glaze and compressed air are fed from a tank to the nozzle of the gun, after which a layer of glaze is sprayed on the surface of the object. The thickness of the glaze layer depends on the spray time. The advantage of spraying is to obtain a uniform layer of glaze, easy protection of details and the possibility of partial glazing. Care must be taken to achieve the correct glazing thickness. It is important to spray in a glass cabinet to prevent glass dust from spreading into the room air.

Figure 6. Spraying technique in glazing

3.5 Ceramic clay-based coatings

A simple surface treatment for ceramics can be done by burnishing. Burnishing takes place when the object is in the raw or greenware stage and the surface is dry. The surface is rubbed, for example, with the bottom of a spoon or a smooth stone. In this way, the porous surface of the clay becomes shiny and dense as the smallest particles pack in a dense layer on the surface of the object. (Salmenhaara, 1983). Polishing with burnishing is only suitable for low temperatures, as at high temperatures the melting reactions of the clay body remove the resulting shiny effect.

A slip called **Terra Sigillata** is closer to an engobe than glaze, although it sometimes resembles a very thin layer of transparent glaze. Terra Sigillata is made by separating the finest part of the clay. (Salmenhaara, 1983). It was used to decorate high-quality pots in ancient Greece. The result was a dense, glossy, water- and dirt-repellent surface with very precise, detailed illustrations.

Engobe is a generic name for clay slip, which often consists essentially of the same raw materials as the clay body of the object itself. An engobe has a wide range of applications and is suitable for both low and high fire. Engobes can, for example, be painted, sprayed or dipped for surface application of an object. It is colored by mixing metal oxides or pigments. (Salmenhaara, 1983). An engobe can be added to the surface of an object when it is leather-hard, completely bone-dry, or bisque fired. The range of possibilities of engobe surface decoration are very wide, and it is possible to layer different colored translucent glazes to create a wider range of colors and surfaces.



Figure 7. Traces from the Antropocene exhibition in Venice Biennale in 2019.
Photo: Tzuyu Chen

3.6 Glazing at different stages of production

An object can be glazed by various methods during many different steps of production: raw or green, when bisque fired or after the glaze firing. The most common way is to glaze the object after the bisque firing and then glaze-fire the object after glazing.

The purpose of bisque firing is to strengthen the durability of an object for processing in glazing. In addition, the bisque fired object is more porous than the unfired object and therefore the glaze liquid is better absorbed on its surface.

Once-firing refers to a process in which bisque and glaze firing take place simultaneously. In this case, the raw dried clay object is glazed, after which it is fired only once to a high temperature. One-time incineration brings significant savings in firing costs, as the bisque firing is completely eliminated. However, once-firing is only suitable for objects with good dry greenware strength that can withstand glazing. This also requires that the objects are glazed either by spraying or with a brush, not by dipping.

Sometimes it is necessary to first fire the ceramic objects to a higher temperature than what the glaze firing itself is. With this method, objects can be fully supported during the first firing to full maturity, thus avoiding sagging and warping of the shape. An already sintered object must first be heated below 200 ° C for application glaze so that the water in the glaze evaporates immediately and the glaze adheres to the hard and dense surface of the object. Adhesives can also be added to the glaze to provide better adhesion.

More information on glaze and glazing can be found in Finnish, for example on the Airi Hortlinging website <http://www.airihortling.fi/> (retrieved 27.11.2020).



Figure 8. Test pieces, photo Anne Kinnunen

4. Ceramic colors

In ceramics, glazes and clay bodies can be colored by adding metal oxides and pigments. Usually, even a few percent of a glaze recipe is enough to color a glaze.

Because ceramics are fired at high temperatures, considerable heat resistance is also required for dyes used in ceramics. Therefore, the dyes used in ceramics must be inorganic. Metal oxides are mainly used as raw materials for ceramic colorants.



Figure 9. Photo: Anne Kinnunen

4.1 Metal oxides

Metal oxides are sensitive to glaze raw materials unlike pigments or stains, which can result in more versatile and surprising results compared to stains. However, the use of crude metal oxides in large-scale production can be problematic, as their color properties may vary depending on the quality of the batch used. Some metal oxides are toxic, causing rashes, for example, and some have been found to be carcinogenic. Therefore, special care is required in handling them. However, in the finished fired and melted glaze, the harmful substances have formed new compounds and may no longer be in a dangerous form. It is advisable to use glazes that have been found to be safe for surfaces intended to come into contact with food, or to test, for example, with an acid test, whether the glaze can withstand food use.

By mixing metal oxides in different proportions and also in different glazes, a large number of different color shades are obtained. It must be remembered that different oxides melt glazes in different ways. The raw material composition of the glazing base, such as its alkalinity, also greatly affects the color properties of the oxides. For this reason, complimentary colors, for example, can be obtained by using the same oxide. Likewise, the firing temperature and the firing method affect the final result.

List of the most common metal oxides used in ceramics:

Iron compounds

- Reliable raw materials, are used a lot in their raw form
- Color formation properties very versatile
- Efficient melter
- Main color brown
- Iron compounds are present as an impurity in many ceramic materials

Cobalt compounds

- Harmful to health
- Has the strongest dyeing power
- Very reliable blue color generator
- In clear glazes, an increase of approx. 5% Gives maximum color darkness
- Powerful melter
- The glaze containing cobalt oxide must be ground (such as in a ball mill) well if inconsistencies are to be prevented

Copper compounds

- Harmful to health
- Versatile ceramic colorant
- Basic green color
- Used in so-called ox-blood glaze to make red color (reduction firing)
- An increase of less than 2% already gives a strong color
- At high temperatures, color formation becomes more unstable

Chromium compounds

- Toxic
- Base shade grass green, other main colors lemon yellow, bright red and intense pink
- Use is limited by evaporation at temperatures above 1200 °C

Manganese Compounds

- Kiln firing fumes or gases from manganese compounds are very harmful according to a new study and can cause damage to the central nervous system. Therefore, good ventilation in the oven compartment is important
- The range of colors is not very wide
- Complements the brown color chart most commonly obtained from iron oxide with dark brown and purple-brown tones
- Powerful melter at temperatures above 1080 °C

(Jylhä-Vuorio, 2003)

Tin compounds

- Used mainly for opalescent glazes, as the opalescent glaze with tin oxide is pure white in color
- Tin white is beautifully soft in color
- Combined with other metal oxides to create new color tones
- Opaque white is usually produced by an increase of 8-12%

Zirconium compounds

- Opalescent glaze over white, although the tone is opaque and more paint-like
- Zirconium glazes are chemically and mechanically very durable, widely used in sanitary ware
- Important role in the production of ceramic color pigments: a number of yellow, blue, green, pink and gray pigments are obtained

Titanium compounds

- Used sometimes as a substitute for tin oxide
- Weaker than zirconium, easily turns yellowish
- Catches even small amounts of iron from the clay body and forms yellowish crystals on the glaze surface
- Rutile is a natural titanium oxide that contains a small amount of iron oxide as an impurity. It gives soft shades of pink and cream yellow and improves the evenness of the glaze surface
- Titanium oxide promotes crystal growth in crystal glazes

4.2 Colored stains

Colored stains are usually purchased ready-made, consist of complex crystal structures, and require careful technology to manufacture. Colored stains are insoluble in glaze, they are independent glazing agents, therefore their color does not react much with different raw materials when mixed, which makes them more homogeneous than metal oxides. The greater the amount of pigment added, the more saturated the color tone. The color pigments can also be mixed together, so that the color scale they give can be expanded.

Stains can be used in ceramics in various ways, such as for coloring glazes, engobes, underglaze paints and china paints (see <http://www.airihortling.fi/>). Color pigments can also be used to color clay bodies, for example by adding metal oxides or pigments to the solids during the weighing step or to the finished casting body. When adding pigment to clay, it is a good idea to first mix a small amount of water before adding it to the clay mixture. Once the pigment has been added to the clay, it is best to sieve it to obtain a uniform color. In a light fine body, 2-8% pigment is sufficient to give color. When coloring the clay body, the particle size and base color of the clay body must be taken into account. If the clay contains coarse grog, it can cover the finely ground pigment particles and the color will lose its effectiveness.



Figure 10. Nathalie Lautenbacher, Coquillages

5. Chemistry of ceramics

There are various ways to gain a deeper understanding of the behavior of glaze. In the design of glazes, it is essential to know how each raw material and the oxide it contains behaves, i.e. what roles different raw materials play in the glaze. A more scientific examination of the glazes is achieved by examining the chemical analysis of the raw materials, which expresses the amounts of substances contained in the raw material as a percentage by weight. On the other hand, the evaluation of the properties of the glaze requires detailed information on the 'potency' of each raw material and oxide in relation to the other substances. This can be aided by the so-called Seger formula, i.e. an empirical calculation formula that also takes into account the molecular weight of the oxides contained in the raw materials. There are easy-to-use calculation programs for researching glaze properties and calculating recipes, such as the Glazy database <https://glazy.org> and the Online Glaze Calculator <https://www.online-glaze-calculator.com/Calculator/fr2.php>.



Figure 11. Material test

Useful ceramic chemistry concepts:

A **mineral** is an element or inorganic compound that occurs naturally in solid form and has a certain composition and usually a regular crystal structure. Minerals are the materials that make up rock types and Earth's solid crust.

Silicate is a metallic element, a compound of silicon and oxygen. Silicate minerals are a broad and diverse group of minerals that make up 90% of the earth's crust. Silicate minerals form the most significant rock species in the earth's crust.

An **oxide** is a compound of oxygen and another element. In ceramic materials, usually a compound of oxygen and metal.

An **element** is defined as a substance that cannot be broken down or converted into another substance in a chemical process. Elements can be divided into metals and non-metals. Elements are made up of atoms.

An **atom** is the chemically smallest part of an element.

A **molecule** is a combination of two or more atoms bound by chemical bonds. A chemical compound cannot be divided into units smaller than a molecule; a molecule is the smallest part of a substance that retains its composition and chemical properties.

Molecular weight is the total weight of the atoms present in the molecular formula = molecular weight.

For example:

K_2O consists of two potassium atoms and one oxygen atom

Potassium has an atomic weight of 39.1 and oxygen 16.0

The weight of one K_2O molecule is thus $2 \times 39.1 + 16.0 = 94.2$

For practical weighing, a large mole (mol) has been developed, which is a unit indicating the number of atoms, ions, molecules, etc. One mole of a substance is obtained by weighing it in grams of its own molecular weight. The molecular weight or molecular weight (g / mol) of a substance is the weight of one mole in grams.

For example:

The atomic weight of potassium is 39.1. One mole of potassium weighs 39.1 g

The molecular weight of K_2O is 94.2. One mole of potassium oxide weighs 94.2 g

Potassium feldspar $K_2O \cdot Al_2O_3$. The formula weight of $6SiO_2$ is 556.8.

Thus, one mole of potassium feldspar weighs 556.2 grams

(Jylhä-Vuorio, 2003)

A chemical formula indicates the composition of a chemical compound, i.e., the number and order of atoms in a molecule. Each element has its own symbol, or chemical sign, with one uppercase letter or one uppercase and lowercase letter. The number of atoms of each element in a compound or formula unit is indicated by a subscript.

Chemical analysis indicates the amounts of substances contained in the raw materials as a percentage by weight.

For example:

Table 4. Chemical analysis of Lohja FFF feldspar

Oxide	%
SiO	267.5
Al_2O_3	18.05
K_2O	7.75
Na_2O	4.75
CaO	0.65
Fe_2O_3	0.15
P_2O_5	0.10
=	98.95
LOI	1.05

LOI = Combustion loss (gaseous substances such as hydroxified water, carbonates, chlorine, nitrogen, fluorine)

From the chemical analysis, the chemical formula of the raw material can be calculated by dividing the percentage of each oxide in question with the molecular weight of the oxide.

Table 5. Oxide formula

	%	g/mol	=	mol
CaO	0,65:	56,1	=	0,012
K ₂ O	7,75:	94,2	=	0,082
Na ₂ O	4,75:	62	=	0,076
Al ₂ O ₃	18,05:	102	=	0,177
Fe ₂ O ₃	0,15:	159,7	=	0,001
SiO ₂	67,5:	60,1	=	1,123
P ₂ O ₅	0,10:	141,9	=	0,0007

The resulting oxide formula expresses the molar amounts of different oxides from Lohja FFF potassium feldspar. It can now be seen from the formula how much of the raw material contains molecules of different oxides. For example, for each Fe₂O₃ molecule, the FFF potassium feldspar contains 177 Al₂O₃ molecules and 82 potassium oxide molecules.

The molecular weight of this formula is 98.95. The formula can be multiplied or divided by any number without changing the ratios between its oxides. One only has to remember to divide or multiply the molecular weight of the formula by the same number.

(Jylhä-Vuorio, 2003)

Eutectic is a key phenomenon in ceramic chemistry that affects the melting of glazes. Eutectic mixture means a mixture containing different substances in a certain proportion and having a certain melting point. The melting point of a eutectic mixture of two substances is lower than the melting point of each pure substance. The eutectic mixture may contain two or more substances. Glazes are eutectic mixtures containing aluminosilicates of both alkali and alkaline earth oxides.

Eutektia

- Eutektia on kahden tai useamman aineen seossuhde, jolla saavutetaan alhaisin mahdollinen lämpötila

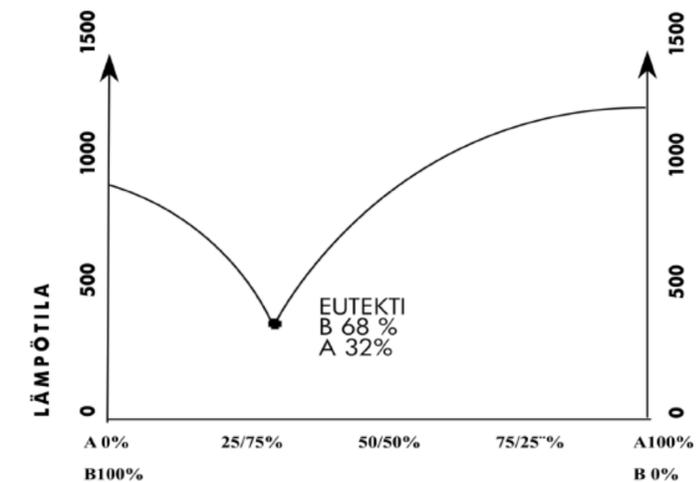


Figure 12. An eutectic is a mixture of substances having a melting point lower than that of any of its components

5.1 Classification of oxides

Glaze oxides are divided into three groups with different chemical properties: alkaline, neutral and acidic. Each group has its own role in the glaze: the oxide belonging to the alkali group acts as a melter, the oxide belonging to the neutral group balances and stiffens the glaze and the actual glass formers found in the acidic group, but also the opalescents of the glaze.

In the production of glazes, minerals containing oxides from several of the above groups are often preferred. It has been found that when a mineral is already a combination of several oxides when extracted from nature, it generally performs better in ceramics (e.g., melts at a lower temperature) than if those oxides were added as separate 'pure' oxides to the glaze. An excellent example of such a mineral is potassium feldspar ($K_2O - Al_2O_3 - 6SiO_2$), which contains oxides from all three groups and which is very similar in composition to the glaze itself.

RO(R ₂ O)-group (basic)	R ₂ O ₃ - group (neutral)	RO ₂ -group (acidic)
Li ₂ O	Al ₂ O ₃	SiO ₂
Na ₂ O	Fe ₂ O ₃	B ₂ O ₃
K ₂ O	Cr ₂ O ₃	TiO ₂
CaO	Mn ₂ O ₃	ZrO ₂
MgO	Bi ₂ O ₃	SnO ₂
BaO	Sb ₂ O ₃	MnO ₂
ZnO	V ₂ O ₅	SeO ₂
PbO		P ₂ O ₅
FeO		Sb ₂ O ₅
CoO		As ₂ O ₅
CuO		
MnO		
NiO		
SrO		
BeO		
MELTER	BALANCER	GLASS FORMER

5.2 Empirical formula

The empirical formula, i.e. the Seger formula, is a formula for calculating the composition of glaze, which is used internationally in the study of ceramics as a common language. It takes into account the molecular weight of the oxides contained in the raw materials of the glaze, i.e. the actual weight value. In addition, the different substances are grouped into the RO groups presented earlier (Table 4), which greatly facilitates the comparison of the glaze properties with each other. This way of expressing the content of the glaze is much more accurate than a normal weighing recipe, as the amount of different minerals is looked at molecule by molecule. The composition of the raw materials varies around the world, the empirical formula allows the raw materials to be exchanged without changing the chemical formula of the glaze at all. It can also be used to predict or identify the appearance and firing temperature of fired glaze.

There are easy-to-use calculation programs for researching glaze properties and calculating recipes, such as the Glazy database <https://glazy.org> and the Online Glaze Calculator <https://www.online-glaze-calculator.com/Calculator/fr2.php>.

Using Seger's formula, you can always make glazes similar to recipes from the available ingredients. You will also be able to evaluate the firing temperature and other properties of the glaze by looking at the oxide ratios, as well as make small changes to the glaze in a controlled manner. In the Seger formula, the weights of the oxides are taken into account, so that the actual amounts of substances in the different mixtures can be reliably compared. Therefore, changes to the glazes should be made to the glaze formula, not the weighing recipe.

The advantages of the Seger formula are:

- The mutual comparison of the composition of the glazes is reliable and reproducible.
- Recipes can be repeated with different ingredients (in the rest of the world, different ingredients are used than in Finland).
- Recipes can be modified: e.g. lower melting temperature, from glossy to matte, replacement of missing raw material with another.
- From the empirical formula one can deduce the properties of glazes, by practicing it one can see a lot of glaze at a glance even before it is made and fired.

5.3 Making your own glaze test kit

There are many ways to explore glazes. The easiest way is to change the amount of some raw material in the glaze and compare the result to the original.

The Line Blend method gradually varies one raw material into another, revealing a change in appearance. For example, it can be used to test the effect of different stains in a glaze. More information about the Line Blend method can be found on the Ceramic Art Network website <https://ceramicartsnetwork.org/daily/ceramic-glaze-recipes/glaze-chemistry/line-blends-a-surefire-way-to-build-your-understanding-of-ceramic-glaze-materials> / (retrieved 11/27/2020)

The Triaxial Blend method tests the effects of three different raw materials on a three-axis system. The corners of the triangle have the so-called starting materials, and the quantities of variable raw materials are calculated between the triangles. Often, for example, the mixing of stains can be studied in this way. More information on the Triaxial Blend method can be found, for example, on the Ceramic Art Network website <https://ceramicartsnetwork.org/daily/ceramic-glaze-recipes/glaze-chemistry/triaxial-blend-test-pottery-glazes> / (retrieved 11/27/2020)

The Grid method, a glaze calculation program and glazing table developed by Canadian potter Ian Currie, can be used to vary glazes by changing two raw materials. In this way, the effects of the gradual addition of raw materials on the appearance and composition of the glaze can be studied. The site has a counter that generates a recipe table, as long as two ingredients are provided you want to start varying (Currie, I. (e.p.), see <http://glazes.org/>).

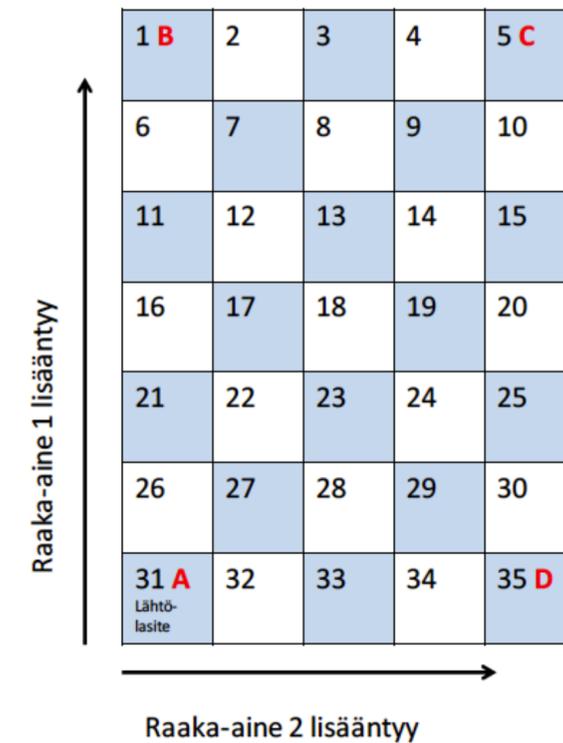


Figure 13. Grid test set

In the original Grid method, 35 glaze mixtures are made, but the amount can also be cut in half and 18 mixtures are prepared.

How to Get Started

1. Think about which two ingredients you want to start varying. For example, kaolin and colorant. Currie most often varied the amounts of quartz and kaolin on his own tests. The relationship between them has the greatest effect on the balance of the glaze, and the glazing series uses melting oxides and variables to reveal the eutectic points and appearance of the glaze outside the glaze firing range.

2. What is the typical amount of colorant in the glaze? Are there any additives present in the glaze that bring color? Decide if these are standard with the melter.

3. Mixture ratios are calculated with a counter: http://ian.currie.to/original/calculation_page.htm

Copr8

Maasälpä	78 %
Alkaalifritti	9 %
Tinaoksidi	1 %
Liitu	1 %
(Kuparioksidi)	1 %
<hr style="border-top: 1px dashed black;"/>	
	99 %
	(100 %)

Figure 14. Oxblood glaze recipe, a starting point

Lasite nro.	Maasälpä	Alkaalifritti	SnO ₂	Liitu	CuO	TiO ₂	Yhteensä (%)
1	75,72	8,73	0,97	0,97	3,88	0,00	100
2	74,29	8,57	0,95	0,95	3,80	1,90	100
3	72,9	8,41	0,93	0,93	3,74	3,74	100
4	75,72	8,73	0,97	0,97	2,91	0,97	100
5	74,29	8,57	0,95	0,95	2,86	2,86	100
6	77,22	8,91	0,99	0,99	1,98	0,00	100
7	75,72	8,73	0,97	0,97	1,94	1,94	100
8	74,29	8,57	0,95	0,95	1,90	3,80	100
9	76,09	8,78	0,98	0,98	1,46	0,98	100
10	75,36	8,70	0,97	0,97	1,45	2,90	100
11	78,00	9,00	1,00	1,00	1,00	0,00	100
12	76,47	8,82	0,98	0,98	0,98	1,96	100
13	75,00	8,65	0,96	0,96	0,96	3,85	100
14	77,42	8,93	0,99	0,99	0,74	0,99	100
15	75,91	8,76	0,97	0,97	0,73	2,91	100
16	78,40	9,04	1,01	1,01	0,50	0,00	100
17	76,84	8,87	0,99	0,99	0,49	1,97	100
18	75,36	8,70	0,97	0,97	0,48	3,86	100

Figure 15. Calculated glaze recipes

Manufacture of glazes and test pieces:

1. Carefully prepare the glazes, weigh the raw materials carefully and make sure that the equipment used for weighing is clean. In the test series, the 100g batch is a functional amount. In the half-Grid series, 18 mixtures are created.
2. Test mixtures should be glazed on test pieces. In order to cope with the changes in the test series at different temperatures, each test mixture is fired at three different temperatures, so a total of 54 test pieces are made.
3. The goal is to have a layer of glaze of the same thickness on each test sample. The test pieces are glazed twice so that the first layer covers almost the entire test piece and the second layer half of the first layer. It is important to remember to mix the glaze mixture before each glazing so that the glaze liquid is as even as possible.
4. Carefully record test numbers and firing temperatures on test pieces and notes.
5. Firing is done in an electric or gas furnace according to the type of glaze to three different temperatures, for example in the high-fire glaze tests 1200 ° C, 1240 ° C and 1280 ° C.

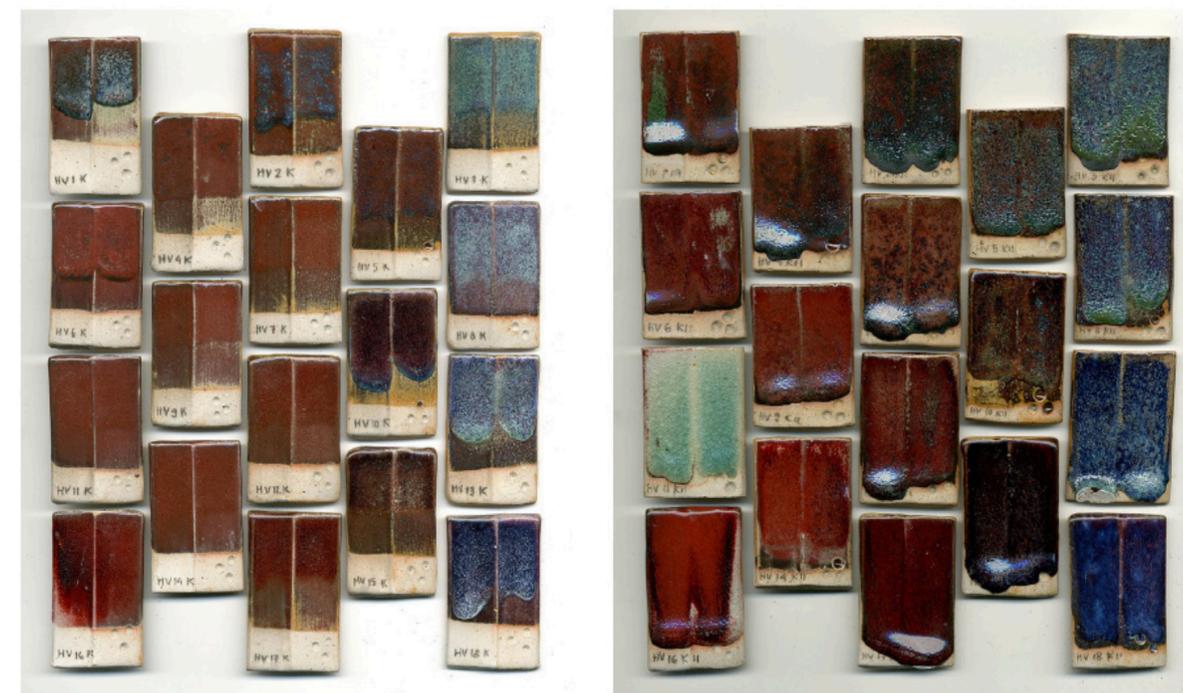


Figure 16. Oxblood glaze variations by Grid-method. Gas firing 1220°C ja 1260°C, test pieces by Jenny Lagus

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Table 2. Table 2: TPV20 / Porcelain casting clay, 1250 °C

Table 3. Table 3: KXX5 / Clear, glossy high-fire glaze, 1200-1300 °C

Table 4. Chemical analysis of Lohja FFF feldspar

Table 5. Oxide formula

Table 6. Grouping of ceramic oxides

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Special thanks to Aalto Online learning/Yulia Guseva
and Aalto Studios/Ikkamatti Hauru



Figure 17. Stock VI, Nathalie Lautenbacher and Naoto Niidome.
Photo by Naoto Niidome