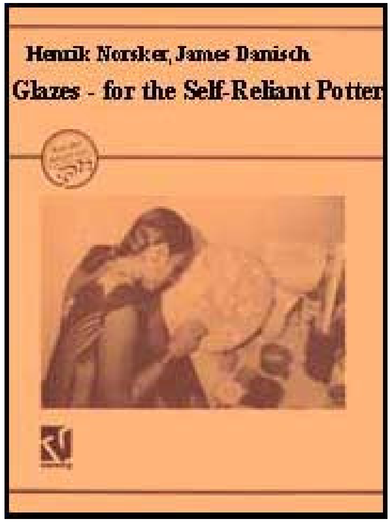

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Acknowledgements

Deutsches Zentrum fr Entwicklungstechnologien-GATE

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- Dissemination of Appropriate Technologies: Collecting, processing and disseminating information on technologies appropriate to the needs of the developing countries: ascertaining the technological requirements of Third World countries: support in the form of personnel, material and equipment to promote the development and adaptation of technologies for developing countries.

- Environmental Protection. The growing importance of ecology and environmental protection require better coordination and harmonization of projects. In order to tackle these tasks more effectively, a coordination center was set up within GATE in 1985.

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- provision of materials and equipment for projects, planning work, selection, purchasing and shipment to the developing countries

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Deutsches Zentrum fr Entwicklungstechnologien - GATE
in: Deutsche Gesellschaft fur Technische Zusammenarbeit (GTZ) GmbH
P. O. Box 5180
D-65726 Eschborn
Federal Republic of Germany
Tel.: (06196) 79-0
Telex: 41523-0 gtz d
Fax: (06196) 797352

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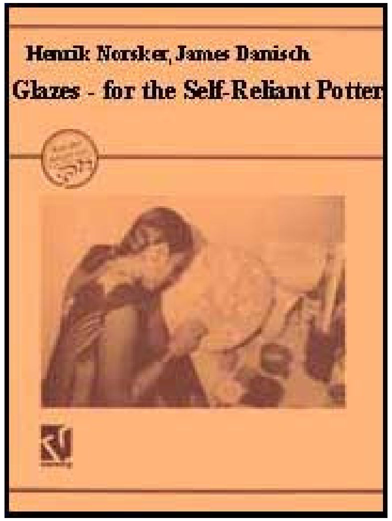

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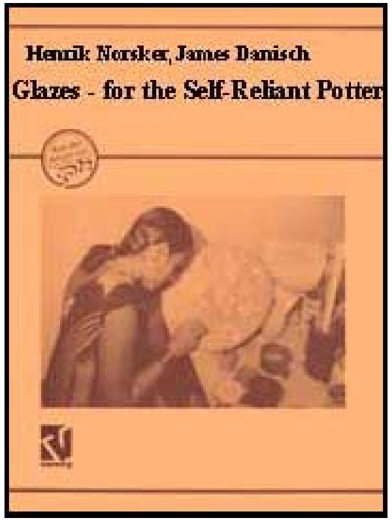

Glazes - for the Self-reliant Potter (GTZ, 1993, 179 p.)

1. Introduction and scope

There are already many books in the world on the subject of ceramic glazes. So the obvious question is: why yet another book on the subject? The authors have worked together for several years in a ceramics development project in Nepal, which is based on using local raw materials and resources. There are few existing books which offer much help in this area, especially working in the low

temperature range from 900°C to 1100°C, where lead glazes have been the tradition but which now, with greater understanding of health hazards, need to be replaced with lead-free glazes. This book is intended to provide practical information for ceramists working in developing countries, with little access to the prepared and controlled glaze materials available in industrialized nations.

Glazes are at one and the same time the area of most fascination and most difficulty for potters. Most potters have little inclination or time to devote to developing glazes, faced as they are by the daily need to produce for the market. However, there often are times when familiar glazes suddenly stop working correctly or special glazes are required for customers. This book offers guidelines for developing and altering glazes, understanding where problems with glazes come from, and standard procedures for testing and developing glazes when there is no laboratory equipment available. It has been written for potters who have little knowledge of chemistry and mathematics.

1.1. Glaze making using local materials as far as possible

Most small producers of glazed ceramics will use glazes that are prepared by a company specializing in supplying industry. However, these glazes are often unreliable, as big companies tend to serve large-scale producers and have little interest in the special glazes needed by small industries. For that reason, the small producer is often forced to rely on his own glaze production, with little or no laboratory equipment available. Additionally, the small producer does not usually have access to raw materials at reasonable prices, so he must use locally available raw materials that do not have an accurate chemical analysis.

1.2. Glaze and clay systems

The producer must think carefully before starting production. When a particular glaze is wanted, it must work with the available clay body, production system and firing system. For example, if you only have low-temperature red clay available, your glazes must work at around 1050°C. If you only have coal available for firing, you must make sure that it will work for your product. The following chapters provide information which will help you to make these decisions.

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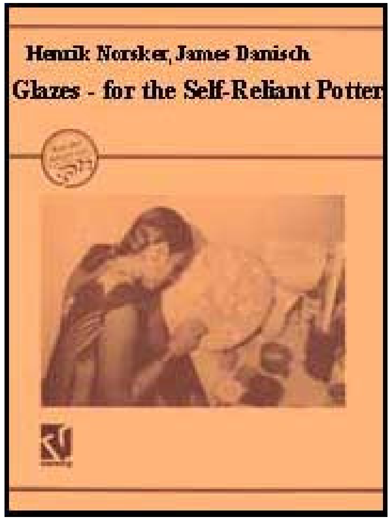

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2. The nature of glazes

2.1. Glass and glaze, benefit of glaze

Glass is a useful material that has been known for thousands of years. It can be produced in many different shapes for many purposes, and it has many useful qualities: it is transparent, hard, resistant to chemicals, and can have many colors.

Glaze is a special type of glass, made for coating ceramic products. Whereas glass is suitable for forming into bottles or windows, glaze is different because it is applied on a ceramic surface and must form a hard, durable coating after being melted in the kiln. It must not run off the product and must stay on the product after firing without cracking.

2.2. Glaze making is difficult

Because glaze before firing looks nothing like the finished product and because we are not able to directly understand what happens when glaze melts at high temperatures, making glazes is very difficult. We must try to understand which materials melt at certain temperatures and what happens when materials are combined. It requires a lot of direct experience before you start to understand causes and effects. In this way it is like cooking: we are familiar with cooking because we know the raw materials, and by trial and error we have a good idea of what the finished meal will be like. However, imagine that you are in a foreign country with unfamiliar food in the market and you want to make a meal: How do you start? The best way is with a cookbook full of recipes and a local friend to tell you if the result is correct or not. This book is intended as a cookbook for the independent potter.

Although by just reading this book and experimenting with it you will probably be able to make glazes after some time, there is no substitute for learning about glazes from an experienced teacher, who can save you a lot of time by guiding you in proven directions.

2.3. History of glazes

Unglazed ceramics have been in existence for over 10,000 years. It has only been in the last 2000 years that there have been glazed ceramics and only in the last 100 years that a scientific approach to glaze making was developed. For that reason, glazes still occupy a mysterious area somewhere between science and magic.

The first glazes were probably invented in middle eastern countries, where there naturally exist deposits of sodium and potassium compounds (soda ash and pearl ash) that melt at low temperatures (800°-1000°C). By chance, early potters discovered that some clays when put in the fire developed a shiny surface. These self-glazing clays are known as "Egyptian paste". They are not very useful for making household items, being difficult to form.

The next step was to develop these substances so that they could be applied to the surface of pottery clay in order to give it the desirable qualities of a hard, shiny, easy-toclean and durable surface. Because early potters did not have the technology to reach high firing temperatures, they had to use materials with low melting points, mainly sodium, potassium and lead compounds. Glaze development had to be done by trial and error, since these early potters had no idea of chemistry. This took a lot of time and effort, and naturally successful

glazes were closely guarded secrets. These early glazes were often soft and not durable, and had problems such as cracking and eventually falling off the pot. Additionally, glazes based on lead were poisonous both for the potters who worked with them and for users.

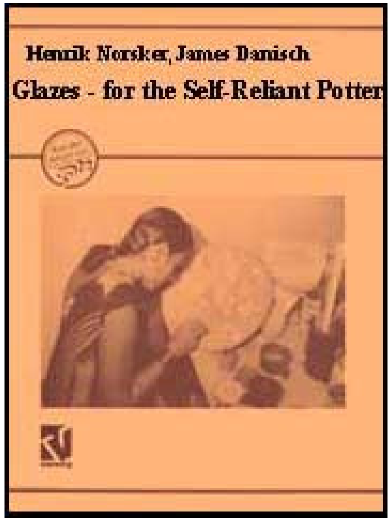
It was only when potters learned to reach high temperatures that truly permanent ceramics were developed. There are many more common chemicals and minerals that melt above 1100°C to form glazes, and clay that is fired to these high temperatures is also much stronger and resistant to water.

2.4. Classification (earthenware, stoneware etc.)

Although there are many different ways to classify glazes, the simplest way to understand them is according to the firing temperature. The useful range of temperatures for glaze melting is from 900°-1300°C. In this book, we talk about two different categories of glaze:

- low temperature from 900-1100°C, called earthenware;
- high temperature from 1100-1300°C, called stoneware.

These two categories are used because they require different raw materials as the main ingredients of the glaze.



Glazes - for the Self-reliant Potter (GTZ, 1993, 179 p.)

3. Temperature ranges and requirements

3.1. What is temperature?

Temperature means the amount of heat energy in a material. We raise the temperature of a material by providing it with heat energy, using a fire or electricity. What effect does this have on a material? We know that many familiar substances can exist in different states of solid, liquid and gas. For example, water can exist as ice, liquid water or steam. What is different about it? Only the temperature. All materials consist of atoms and molecules which are in constant motion. The amount of motion depends on the temperature. Cold materials have less motion and therefore appear solid to us (e.g. ice). When the temperature is increased, the motion of the molecules becomes greater and they can move more freely around each other (e.g. water). When the temperature is increased even

more, the molecules become very active, as we can see when water boils. Then the molecules are even less bonded together and we see gas (e.g. steam).

Similarly, glazes are solid when they are cold (at room temperature), liquid when they are heated sufficiently (in the kiln), and become gas when they are heated too much.

It is also important to understand the relationship between clay and glaze. Most common red clay (such as brick clay) melts by 1100°C. This makes it useful for forming low temperature products. 1200°C, it can be used as a glaze.

3.2. Low temperature range 900-1100°C

Products called earthenware, whiteware, low-temperature ceramics, and terra cotta are all fired in the range of 900-1100°C. We will call these products generally "earthenware". What they have in common are clay bodies that develop their maximum strength in this range, and glazes that are based on low-melting compounds such as lead, sodium and potassium.

3.2.1. ADVANTAGES/DISADVANTAGES

Advantages: low temperature ceramics have the advantage of easy firing -it is much simpler to construct kilns and burner systems that have to reach no more than 1100°C, and fuel costs are lower. Bright colors are possible in this range. Most common clays cannot be fired higher than this.

Disadvantages: earthenware is often not as strong as high temperature ware, because the clay does not become vitreous. This means that it also has some

porosity (the property of absorbing water) with the result that earthenware products often do not hold water unless the glaze is perfectly fitted to the body. Also, it is easier to chip the glaze away from the clay.

Historically, many earthenware glazes were based on poisonous lead because it is easy to melt: nowadays this is not a problem because lead can be replaced by non-poisonous materials.

Modern earthenware glazes are usually based on frits, which are expensive -the lower firing cost must be compared to the higher cost of the glaze.

3.2.2. APPROPRIATE PRODUCTS

Earthenware is used for all common household containers -cups, bowls, storage containers, oil lamps etc. Ordinary wall tiles, most low-cost tableware, sanitary ware, common unglazed containers, bricks, roof tiles etc. are all made in the low temperature range. Many countries have a long tradition of glazed red clay products, which are still useful in modern times. Most modern factories have changed their production to white clay products, which have become more feasible with recent developments of white bodies that become strong enough at low temperatures.

3.2.3. CLAY/GLAZE CHARACTERISTICS

Earthenware clay

Common red-burning clay is normally used, often mixed with talcum powder to

increase its firing range. In many countries, red clay which contains lime is used because it makes it easier to formulate glazes that do not craze (crack). White firing clay bodies are often based on talc, ball clay and fluxes to make them harder.

Earthenware glaze

Earthenware glazes are based on low-melting materials, mainly lead oxide (white lead oxide, red lead oxide), sodium and boron compounds (soda ash, borax, boric acid) and potassium compounds (pearl ash, also known as potassium carbonate). Usually it is necessary to use these compounds in the form of frits (see chapter on frits).

3.2.4. RAW MATERIAL REQUIREMENTS

Most of the raw materials for low temperature glazes can be obtained from commonly available sources. They include: local clays, wood and rice husk ash, limestone, and even soap powder (based on sodium and boron compounds). Materials such as borax must be obtained from chemical suppliers. Ready-made frits can be obtained from glaze suppliers, but in many locations it is necessary to make them from raw materials.

3.3. High temperature range 1100-1300°C

Types of ware fired in this range are known as stoneware and porcelain.

3.3.1. ADVANTAGES/DISADVANTAGES

Advantages

High temperature products are generally stronger, more acid and abrasion-resistant. Raw materials do not require fritting. The clay is more vitreous and thus does not have problems of water seepage.

Disadvantages

Kilns for high temperatures require more sophisticated bricks and kiln furniture, and better burner systems. Fuel costs are higher.

3.3.2. APPROPRIATE PRODUCTS

High temperature products include stoneware utilitarian items, whiteware of various types, porcelain and electrical insulators.

3.3.3. CLAY/GLAZE CHARACTERISTICS

Clay

Clay body raw materials are limited to those clays which can withstand high temperatures without melting: fireclays, ball clays, china clays, "stoneware" clays. Most bodies also include feldspar to cause vitrification, which prevents water seepage through the body.

Glaze

High temperature glaze is easier to make than the low temperature sort, mainly

because it is not necessary to frit the ingredients.

3.3.4. RAW MATERIAL REQUIREMENTS

Most stoneware and porcelain glazes are based on feldspar, quartz, limestone and clay, with other ingredients to provide specific properties of surface, color etc.

3.4. Firing systems and glaze effects

Different types of kilns and fuels have specific effects on glaze color and surface.

3.4.1. OIL, GAS, WOOD, COAL, ELECTRICITY, OTHER

These are the main options for fuel. Each fuel requires a different kiln design and burner system. You must first decide which fuel is most available and most economical. The choice of fuel will determine whether products can be open-fired on shelves, or whether it is necessary to use saggers to protect the glaze from ash and contamination from dirty fuel.

The cost of fuel should be thought about very carefully. One kg of fuel produces a certain amount of heat. Heat is usually measured in calories or in British Thermal Units (BTU). One calorie is the amount of heat required to raise the temperature of one cubic centimeter of water 1°C. The table at page 170 shows the heat value of different fuels. Because a calorie is very small, the usual unit of heat is expressed as kilocalories (kilo = 1000, so 1 kilocalorie = 1000 calories).

A particular kiln, loaded with an average number of products and fired to a specific temperature, will usually require the same amount of fuel each time, since it

requires a specific number of calories to convert raw clay and glaze into finished ceramics. When you know the total kg of products and the total cost of one firing, it is easy to calculate the cost per kg of product:

Total cost/Total kg = cost per kg

You can also calculate the total number of calories required to do one firing. If you are using kerosene, you can find from the table that one lifer of kerosene supplies about 12,000 kilocalories of heat. So, if you use 80 lifers to do a firing, the calculation is:

(Total fuel) X (kilocalories per unit) = total kilocalories required

80 X 12,000 = 960,000 kilocalories

When deciding on the type of fuel to use, you should find out the cost per kilocalorie for different fuels in your area.

Oil

Oil is available in many different forms, all of which can be used by the potter, including kerosene, diesel, furnace oil, and waste crankcase oil. Kerosene is the most clean-burning (without too much smoke or impurities), and waste crankcase oil is the dirtiest to use. Normally, products can be open-fired, but oil will produce some discoloration. For high quality whiteware, saggars may be necessary. Oil is suitable for high or low temperatures.
Oil provides between 9000 and 11000 kilocalories per kg.

Gas

Gas is available as natural gas, producer gas or liquid propane gas. Where gas is available at a reasonable cost (compared to other fuels), it is the easiest fuel to use. Gas is very clean-burning, does not require saggars, and the burners are also simple to manufacture locally. It is suitable for any temperature.

Wood

Almost any kind of wood can be used for firing kilns. Nowadays, wood is a scarce resource in most countries and more and more it is being replaced by other fuels. Firing with wood is labor-intensive. Because it produces a large volume of ash, it is usually necessary to fire the ware in saggers. It is suitable for any temperature.

On the other hand, wood is a renewable resource and in many areas of the world it is produced as a cash crop, which makes it appropriate to use.

The calorific value of wood is difficult to calculate, because it depends on the type of wood, whether it is wet or dry, and the efficiency of burning. Dry wood can supply between 3000 and 4500 kilocalories per kg, whereas the same wood when wet may produce only half the calories.

Coal

Coal comes in many different grades, all of which are suitable for firing kilns. Firing with coal is labor-intensive, but in many countries it is the cheapest fuel available. Coal also produces ash and impurities, so it is usually necessary to fire the ware in saggars. It is best for high temperatures, but can be used at any temperature.

Coal can provide between 4500 and 7700 kilocalories per kg.

Electricity

Electric kilns are practical for the small producer where there is a reliable source of electricity. Because there is no combustion, electricity is the cleanest fuel of all. Electric kilns fire very evenly and do not require saggers. Electricity is best for temperatures up to
1100°C.

Other fuels

These include tires, which burn very well but produce a lot of smoke, and also produce poisonous gases. They can be used in kilns designed to burn wood or coal. Some brick industries use scrap asphalt from roads as fuel. Also in this category are such fuels as brushwood, sawdust and rice husk. Most of these are dirty-burning, so require the use of saggers. They are best for low temperatures.

3.4.2. OXIDATION/REDUCTION

To understand oxidation and reduction, it is necessary to know how fuel burns. All fuel produces heat when it combines with the oxygen in the air. As anyone knows who has made a wood fire, if there is plenty of air the fire burns hot and clean, with little smoke. This is called an oxidation fire. If the air is reduced, there will be less heat and more smoke. This is called a reduction (or reducing) fire, which simply means reducing the amount of oxygen. So:

- Oxidation firing means there is plenty of air and no smoke.
- Reduction firing means there is little air and more smoke.

Glazes will have different colors and surfaces depending on whether they are fired in oxidation or reduction conditions. Oxidation has its greatest effect on the metallic oxides that are used to create color in glazes. For example:

OXIDE	OXIDATION	REDUCTION
red iron oxide	brown	red-brown, black
copper oxide	green, blue	red

Iron also changes from a grey color to a red color when it rusts. This is because oxide from the air-combines with the metal and forms iron oxide.

In firing, it is difficult to exactly control the amount of oxidation or reduction. Many beautiful glazes can be obtained in reduction firing, so it is widely used for decorative stoneware, and for lusterware. However, the results are variable and difficult to reproduce every time, and even in one kiln-load there will be differences. For that reason, most producers who need to supply a uniform product use oxidation firing.

3.4.3. VAPOR GLAZING

In vapor glazing techniques, the glaze is not applied to the product before firing in the usual manner. Instead, glaze is introduced into the kiln through the firebox at the end of the firing, when there is enough heat to change the glaze into vapor form. The most common material for vapor glazing is ordinary salt. At

temperatures above 1100°C, salt breaks down into sodium and chlorine vapor, which circulates through the kiln. The sodium is attracted to silica in the clay and forms a strong, durable glaze. Salt glazing is used mainly for sewage pipes, because it is cheap and a perfectly glazed surface is not necessary. In Europe, it was once used widely for household items, even including beer bottles. Nowadays, salt glazing is less popular because it produces toxic smoke that harms the environment.

Salt is sometimes replaced by soda ash and sodium bicarbonate, which produce a similar vapor glaze without the poisonous side effects. Vapor glazing is not recommended for the small producer, except for making specialized art ceramics.

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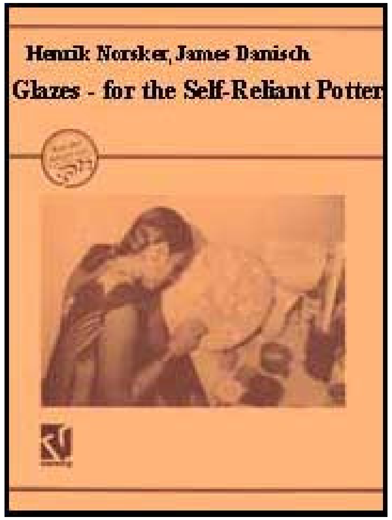

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4. Decisions

As a ceramics entrepreneur, you must start by making decisions: what product? what temperature? how much technology? These decisions depend on your market, raw material and fuel availability. In industrialized countries, where everything is easily available, the decision will usually be based first on the market, and then the best combination of clay body, glazes and kiln can be decided on.

In developing countries, it is usually necessary to start by thinking about raw materials and fuel. Then the product can be selected.

Usually, it is easiest to use the same technology as other producers, as most of the problems will have already been solved. On the other hand, a new type of technology can capture a new market sector with no competition. However, a new technology may cause technical problems that a potter cannot solve without outside help.

Some typical questions for the entrepreneur to answer are given below.

4.1. Selecting your best firing temperature

Is high-firing clay available?

If so, it may be best to decide on high temperature ceramics (stoneware or porcelain), as producing reliable glazes will be easier.

Is only low-firing clay available?

If so, it will be necessary to select a low temperature system and to make frits or purchase ready-made ones.

Are ready-made glazes available?

If there is a reliable source of glazes nearby, a lot of trouble can be saved by using these.

What are the fuel constraints?

If only electric firing is available, then only low temperature systems will be practical. If oil or coal is available, the additional costs of using saggers should be compared with the cost of clean-burning fuels.

4.2. Market factors

Most producers decide to enter the ceramics sector because there is already a good market and not enough local supply or because they think they can create a market for products that are not yet common in their area.

What is the existing market?

For example, if there is already a good market for glazed white earthenware (perhaps imported), the potential producer will have to find out if he can produce similar products at competitive prices. If he wants to compete directly, he will have to take up the same clay/glaze/firing system.

Is there a possible new market?

On the other hand, it may be possible to produce a product with the same function, but using a less costly technology. For example, it may be possible to produce glazed red clay earthenware cheaper than the whiteware on the market and thus to create a new market.

Small-scale vs. large-scale

Large-scale ceramics industries are able to produce a large volume at a low profit margin. For this reason, it is difficult for the small producer to compete directly. The small producer has an advantage of flexibility - he can produce a variety of products on demand and thus can supply local customers with special requirements.

For example, the modern tile industry is mostly very large-scale and can supply very cheap tiles of a uniform quality. The small producer can never compete directly with this. However, there is a growing market for specialty tiles, with decorations or relief designs, which the large producers cannot make. Many customers are interested in small quantities of special decorative tiles made according to their own design, even if the price per square foot is higher than mass-produced tiles.

Ceramics substituted for products made from other materials

In some countries, products like glasses for drinking tea may be produced more cheaply in ceramics. Or cement sewage pipes and toilet pans may be replaced by longer-lasting, more hygienic ceramic products.

4.3. Strength requirements

Household items

Most common tableware items (cups, plates) can be made satisfactorily using either high or low temperature systems. Low temperature ceramics are more easily chipped and broken, but their low cost may be an advantage. High temperature products are stronger, and most hotels and restaurants will prefer them, unless the lower cost of earthenware makes up for the higher rate of breakage.

Electrical insulators

Low tension insulators, fuse holders (kit-kats) etc. do not have to be very strong, so can be made in the low temperature range. High tension insulators have special requirements for porosity and strength, so must necessarily be made at high temperature.

Tiles

Glazed tiles are most commonly produced at low temperatures, which gives them sufficient strength for wall and floor applications.

Cold climates

Ceramic products to be used outdoors in freezing temperatures have special requirements, because of damage that can come from water freezing inside the product and causing it to break. These products are generally made at high temperatures, which make it possible to control water absorption.

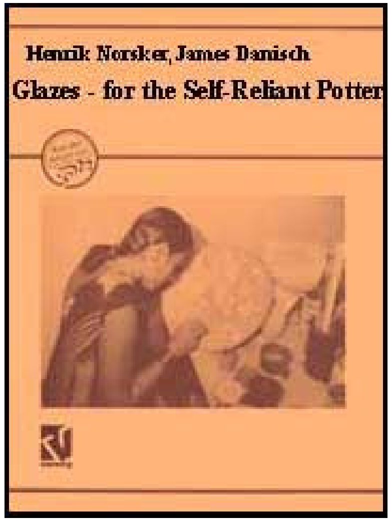
4.4. Investment and production costs

After considering the above decisions, the entrepreneur must then make an analysis of investment and production costs. These calculations are not easy to do, as the production of ceramics depends on so many complicated factors. For the new entrepreneur, it is important to start small and as simply as possible.

Low temperature systems usually require a lower initial investment, as kilns and burners will be cheaper. Fuel is usually the highest cost of production, and firing at low temperatures can save production costs. On the other hand, the cost of high temperature glazes is lower, as it is not necessary to use expensive frits.

In preparing a scheme for a new business, it is best to get help from a ceramics expert' who can help to figure out the comparative costs of the various options. Besides the usual overhead costs, it is necessary to consider:

- cost of clay body
- cost of glaze
- labor costs in production
- capital investment for equipment
- fuel costs
- working capital requirements.



Glazes - for the Self-reliant Potter (GTZ, 1993, 179 p.)

5. Simple glaze theory

5.1. Basic chemistry

Chemistry is the science which describes what substances are made of and how they combine with each other. This science uses special names and symbols which are described below.

5.1.1. ELEMENTS/COMPOUNDS

Elements

An element is made of only one kind of atom. It cannot be broken down into more simple substances. Oxygen (O) is the most common element on earth.

Compounds

A compound is composed of more than one element combined chemically. Water (H_2O) is a compound made up of two atoms of hydrogen (H) and one atom of oxygen (O). Silica (SiO_2) is another compound and consists of one atom of silicon (Si) and two atoms of oxygen (O). This is the most abundant material in the earth's crust. Two or more atoms combined form a molecule.

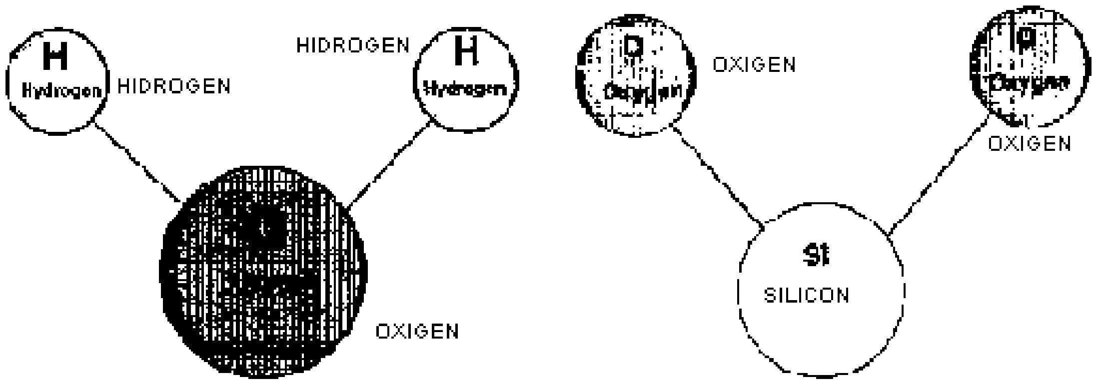


Figure 5.1.1.A. Water is two elements combined. A molecule of water consist of two atoms of hydrogen and one of oxygen. Figure 5.1.1.B. A molecule of the compound silica (sand) has two atoms of oxygen and one of silicon

Ceramic raw materials are usually in the form of oxides: an oxide is a compound that includes oxygen (O). Minerals are compounds.

5.1.2. SOLID, LIQUID, GAS

Solid, liquid and gas are the three states of matter. Most materials can exist in all of these states, depending on their temperature. A familiar example is water, which is solid below 0°C, liquid from 0°C to 100°C, and gas above 100°C.

Making glaze depends on mixing solids together, applying them on a pot and then changing them to liquid in the kiln. Some of the glaze materials also become gas during firing and leave the glaze. On cooling, the glaze again becomes solid.

Mixture

A mixture is a physical, not chemical, combination of compounds (and sometimes elements) and each compound remains chemically unchanged in the mixture. Air is a mixture of oxygen, carbon dioxide, nitrogen and other gases. A glaze made of feldspar, quartz and lime is prepared by combining the compounds as a mixture, but during firing a chemical combination takes place and the fired glaze becomes a compound.

Chemical symbols

There are about 100 elements, and each of these has a name and a chemical symbol, which is used as an abbreviation of its name. Some of these symbols are the same as the first letters of the English name, but some are not!

For example:

Oxygen is "O"
Hydrogen is "H"
Silicon is "Si"

Alumina is "Al"
Sodium is "Na"
Lead is "Pb"

Compounds are written in a similar way with capital letters marking the individual elements: for example, water is "H_2O" and salt is "NaCl"

The small number "2" in "H_2O" indicates that there are two atoms of hydrogen for each atom of oxygen in water. If there is no number, it is understood that there is only one atom -so salt is one atom of sodium and one atom of chlorine.

The formulas of complex ceramic materials are written as compounds of oxides with a raised period (·) between them to show they are chemically combined. For example potash feldspar is written:

$K_2O\ Al_2O_3\ 6SiO_2$

In the appendix the chemical formulas of other materials are listed.

5.1.3. CHEMICAL REACTIONS

The formation of clay from feldspar can be written in chemical symbols:

$K_2O\ Al_2O_3\ 6SiO_2 + H_2O$
(feldspar) + (water)

$\rightarrow Al_2O_3\ 2SiO_2\ 2H_2O + K_2O + SiO_2$

(clay) + (potash) + (silica)

All materials are built up of elements which are chemically bonded together. When heated to a high temperature, chemical bonds can break down and the material will change its properties. The production of quicklime by heating limestone to 900°C is an example of this:

$CaCO_3 \rightarrow$	CaO	$+ CO_2$
(limestone)	(quicklime)	(carbon dioxide)

Carbon dioxide (CO_2) goes into the air, and the remaining quicklime (CaO) is slaked with water and can then be mixed with sand to form mortar for house construction. The mortar sets when the calcium oxide (CaO) takes back carbon dioxide (CO_2) from the air and thereby regains the hardness of the original limestone ($CaCO_3$):

CaO	$+ CO_2$	$\rightarrow CaCO_3$
(soft mortar)	(from air)	(set mortar)

5.1.4. SOLUTION/SUSPENSION

Solution

A solution is a mixture of molecules. For example, sugar completely dissolves in

water: the separate particles consist of molecules of sugar and water. Sugar and water remain a solution until the water evaporates.

The higher the temperature of the liquid, the more solid material can dissolve in the liquid. When no more solid can be dissolved the solution is called "saturated".

Suspension

In a suspension the particles are bigger than molecules. A mixture of clay and water is a suspension. The clay particles are not changed by the water, and after some time the clay will settle at the bottom of the vessel. The clay is insoluble in water.

5.1.5. CRYSTAL STRUCTURES

Crystal structure

If we heat water to 90°C and add salt (NaCl), it will become dissolved in the water. If we continue to add salt until no more salt can be dissolved, the suspension is saturated with salt. If we let the solution cool to room temperature (20°C) the water can hold much less salt in solution, with the result that some of the salt will separate in the form of salt crystals.

All minerals have the form of crystals. When the water cools, the excess salt molecules start to combine with one another in regular patterns like small building blocks. The way the salt molecules connect to one another is very orderly and produces a cube-shaped crystal. Different materials will produce crystals of different shapes. The shape of a mineral's crystal is used to identify it.

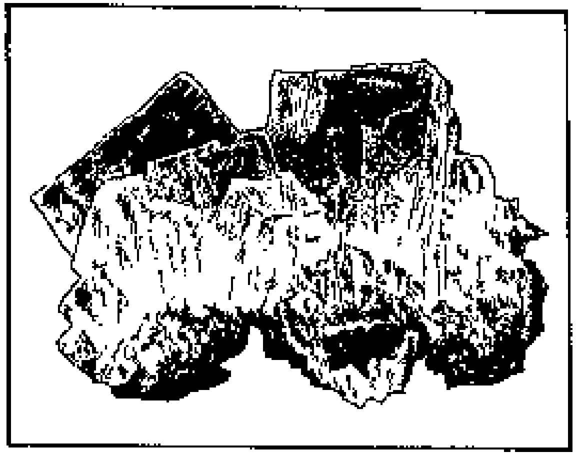


Figure 5.1.5.A. The cubic shape of a salt crystal.

5.2. Glaze structure

Glaze is similar to glass. Making glazes is confusing because there are so many raw materials that can be used. However, all of these raw materials can be broken down into three categories:

- flux
- glass former
- stabilizer.

All glazes require these three components. The main glass former is silica, the main stabilizer is kaolin, and the rest of the glaze is composed of one or more fluxes.

5.2.1. GLASS STRUCTURE

Silica (SiO_2) alone will make an excellent glaze if it is fired to its melting point (1715°C). Since this temperature is too high for ordinary kilns, other materials are added to lower the melting point of silica. Quartz is a crystalline form of silica found in nature. If a glaze forms quartz crystals when it cools, it will not be transparent, since light is refracted in many different directions by the crystal faces. Because glass or glaze is not usually crystalline, this does not happen.

A glaze or glass is a mixture of compounds that melts when heated. The melted liquid glass is like a solution. When the liquid cools, crystals start to form in a similar way as in a salt solution. However, the liquid glaze is very viscous (meaning sticky and semifluid) and the molecules cannot easily move around to form a regular crystalline pattern. So normally no crystals form during cooling, and the glaze remains clear like a liquid.

Glaze is, therefore, like a solid solution and is sometimes called a supercooled liquid.

5.2.2. FLUXES

Fluxes are the materials which lower the melting point of a glaze. They can be called melters.

Silica melts by itself but at a very high temperature. Therefore it needs additions of flux to make a practical glaze. The most common flux for temperatures below 1100°C is lead oxide (PbO), but since it is poisonous it is no longer used in modern crockery glazes. Another powerful flux is boron or boric oxide, B2O3, which is not poisonous and is used in glazes in the form of borax or boric acid.

There are many other fluxes which contribute various properties of hardness, opacity, color response etc.

Fluxes are also called basic oxides or network modifiers.

5.2.3. GLASS FORMERS

Silica forms the main part of all glazes and is called a glassformer. The other glass-former is boron. Silica and boron are the building blocks of a glass or glaze. Other materials are only used to modify their behavior in the glaze.

Titanium oxide (TiO_2), tin oxide (SnO_2) and zirconium oxide (ZrO_2) also belong to this group. Sometimes they are called the acidic oxides or network former, or the acid portion of the glaze.

5.2.4. STABILIZERS

Aluminum oxide, Al_2O_3, is added to make the melted glaze stiffer, so that it will not run off the pots during firing. It is called a stabilizer. Other words for stabilizer are: amphoteric, neutral or intermediate oxide.

Aluminum oxide has a high melting point and will increase the melting point of the glaze. It is usually added to the glaze as kaolin (china clay).

(Boron is termed a stabilizer in the USA but a glass former in Europe.)

5.3. Effect of heat

As heat is increased, the molecules in the glaze move faster, resulting in drying, sintering, melting and gas escape. All of these effects occur when the glaze molecules move so fast that they start to break down, releasing some of their atoms and combining with other molecules to form the glaze.

5.3.1. DRYING

When the powdered glaze on the surface of the ceramic ware is heated, the water evaporates above 100°C (no matter how dry the glaze seems to be, there will always be some water remaining in it). The glaze layer should be as dry as possible before setting in the kiln. If the glaze layer dries too fast when firing starts, it may crack. This can cause crawling of the glaze after it melts.

5.3.2. SINTERING, MELTING, GAS ESCAPE

Sintering

As the temperature rises above 600°C, the sintering of the glaze powder starts. Sintering also takes place in the clay at this temperature. Sintering means that the glaze (or clay) particles start to stick to one another where they touch. The finer the glaze particles are ground, the earlier the sintering will start and the stronger the bond will become.

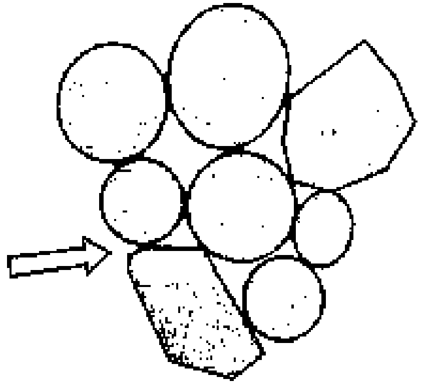


Figure 5.3.2.A. The glaze particles are enraged many thousand times showing sintering in a glaze heated to 600°C. At the points of contact (arrow) a weak bond is formed.

Fusion

As the temperature rises further, the most fusible (easy melting) materials in the glaze start to melt. This is celled fusion. The refractory (hard melting) particles are surrounded by the liquid materials and are slowly included in the liquid.

The temperature at which melting starts depends on the materials in the glaze. Silica alone melts at 1715°C, but with additions of other materials the melting point will go down. Aluminum oxide (Al_2O_3) melts at 2050°C and calcium oxide (CaO) at 2570°C, but a mixture of 62% silica, 14.75% aluminum oxide and 23.25% lime melts at only 1170°C. A mixture which has a lower melting point than any of the single materials in the mixture is called an eutectic.

A mixture with many different materials will form eutectics (and will melt) at a lower temperature. Fine grinding of the glaze materials and prolonged firing time above the sintering temperature will also lower the melting point.

When fusion starts, the compounds also start to change. The chemically bonded water in clay has already been released. Around 900°C, limestone ($CaCO_3$) releases carbon dioxide (CO_2) and so do other materials containing carbonates, like barium carbonate ($BaCO_3$). Gases of sulfates, oxides etc. are also released both from the glaze and from the body. These gases have to pass through the glaze layer. This action mixes the glaze, helping it to become homogeneous.

In the beginning the melted glaze is very stiff (high viscosity), but as the temperature keeps rising the glaze becomes more fluid and, when watching the melting glaze surface through a spyhole in the kiln, bubbling or even boiling can be seen. When the glaze reaches its maturing temperature, the reactions stop and the glaze becomes smooth.

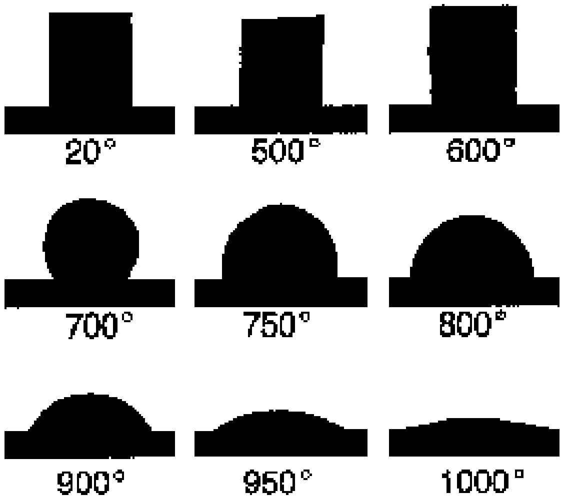


Figure 5.3.2.B. A cube of glaze is gradually heated up to 1000°C. At 500°C the glaze shrinks slightly (sintering), but at 600°C it swells as gases develop. Melting starts before 700°C and is completed at 1000°C.

5.3.3. MATERIALS WHICH INCREASE/LOWER MELTING POINT

This chart shows the oxides according to their influence on melting temperature:

OXIDES WHICH RAISE MELTING TEMPERATURE

Al_2O_3 High

SiO_2

MgO |

Cr_2O_3 |

SnO_2 |

ZrO_2 |

NiO |

Fe_2O_3 |

TiO_2 |

CaO |

ZnO |

BaO |

FeO |

CoO |

CuO |

MnO |

PbO |

B_2O_3	|
Na_2O	|
K_2O	↓
Li_2O	Low

Note this scale is not linear and depends on firing temperature and amount of oxide in the glaze

OXIDES WHICH LOWER MELTING TEMPERATURE

5.4. Melted glaze behavior

Fluid state

The fluid state of the glaze should be maintained long enough to allow all bubbles time to escape, so the glaze layer can heal over the holes left by the escaping bubbles. If a glaze tends to produce pinholes and craters, it can be given a soaking period (keeping the kiln at maturing temperature for some time) or the firing temperature can be raised in order to make the glaze more fluid (reduce viscosity).

If the glaze is too fluid, it will run off the pot or the fluid glaze will soak into a porous body leaving matt, dry spots on the surface.

The following chart shows materials which increase or decrease viscosity.

MATERIALS THAT INCREASE VISCOSITY

Al_2O_3	High
ZrO_2	
SiO_2	|
Cr_2O_3	|
SnO_2	|
NiO	|
Fe_2O_3	|
TiO_2	|
CaO	|
MgO	|
ZnO	|
SrO	|
BaO	|
CoO	|
MnO	|
PbO	|
K_2O	|
Na_2O	|
B_2O_3	↓
Li_2O	Low

Materials at top increase viscosity most. Note these materials are mainly stabilizers and glass formers. (Scale is not linear.) Most materials in this group are fluxes. Materials at bottom decrease viscosity most.

MATERIALS THAT DECREASE VISCOSITY

5.4.1. SURFACE TENSION

To understand surface tension, fill a glass with water to the rim and look at the water surface. The middle of the water surface will be higher than the rim, but the water will not run over. The surface tension of the water holds it as if it were held by a plastic membrane.

A small amount of water forms a spherical drop. Larger amounts of water flatten the spherical form because the force of gravity increases with the weight of water. The fluid glaze behaves in a similar manner, and if the surface tension of the fluid glaze is too high the glaze will pull itself into small islands, leaving the clay body uncovered. This is called crawling.

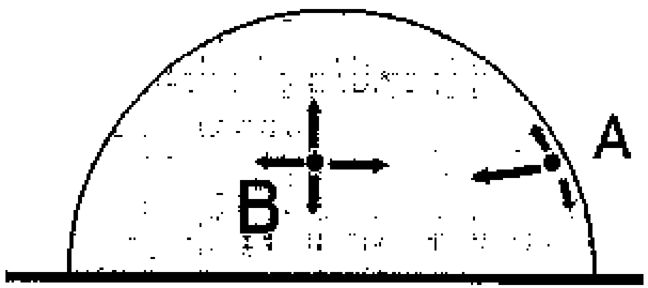


Figure 5.4.1.A. Surface tension is created by the difference of forces acting on

water in the center (B) and at the surface (A). A water particle at B has forces of traction of the water around it evenly distributed. But at A the force is mainly directed away from the surface. This difference causes water to from itself ion spherical drops.

Increasing temperature lowers the surface tension as Fig. 5.3.2.B illustrates. At 800°C the glaze forms a half globe but at 1000°C it

has completely flattened out. Different ceramic oxides influence the surface tension as listed in this chart:

MATERIALS THAT INCREASE SURFACE TENSION

MgO	High
Al_2O_3	
ZrO_2	|
ZnO	|
CaO	|
SnO_2	|
Cr_2O_3	|
NiO	|
BaO	|
SrO	|
Fe_2O_3	|
SiO_2	|

TiO_2	|
Li_2O	|
Na_2O	|
K_2O	|
B_2O_3	↓
PbO	Low

Note the scale is not linear and the sequence of oxides may change due to other factors like viscosity, flue gas

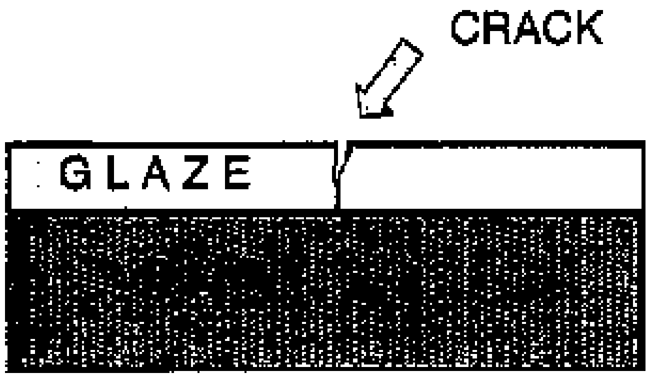
MATERIALS THAT DECREASE SURFACE TENSION

5.4.2. CRAWLING

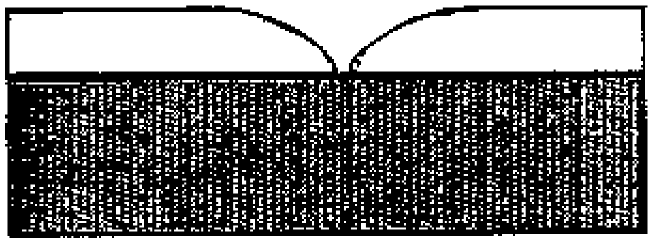
Crawling is caused by two factors:

- **high surface tension of the glaze;**
- **difficulty for the glaze to stick to the body.**

If the body surface is greasy or dusty the problem is aggravated. Crawling may also happen if the glaze layer cracks before it is sintered. This happens if the glaze contains a high amount of clay or has been ground for too long in the ball mill. The surface tension will then pull the glaze away from the cracks.



a) An enlarged section of body and glaze shows that a crack has developed in the dry glaze layer.



b) Glaze starts to melt and surface tension causes the glaze to pull away from the crack.

c) The body is left exposed. If the temperature is raised further the surface tension will be lower and the glaze might flow back and cover the body.

Figure 5.4.2.A. Crawling

5.4.3. CRATERS, PINHOLES

The lower the surface tension, the shinier the surface of the glaze becomes and the easier it is for the glaze to heal over craters, bubbles and pinholes.

Interesting effects can be obtained by applying glazes with different surface tensions on top of each other (see page 80).

Surface tension, viscosity and melting temperature are interrelated, so when replacing materials all three will be affected.

5.5. Interface between glaze and body

During firing the glaze interacts with the clay body. Some of the glaze will sink into the body and some of the body material will mix with the glaze so that an intermediate layer is formed between the body and the glaze. This layer bonds the clay and glaze together. It is called the glaze/body interface or "buffer" layer.

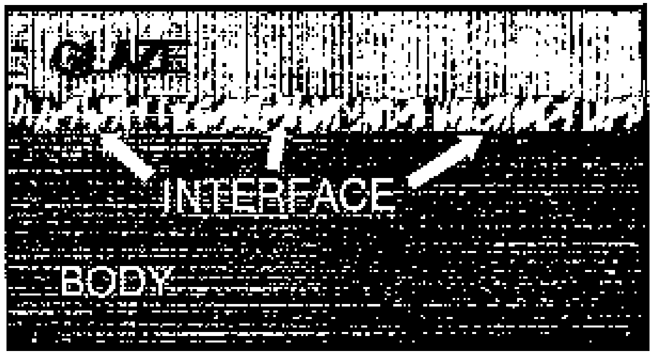


Figure 5.5.0.A. Interphase layer created during firing by mixing of materials in the body and the glaze.

Effects of interface

Some of the coloring oxides in the body may enter the glaze and change its colon The higher the firing temperature the stronger the interface layer. The interface layer produces a strong bond between glaze and body that reduces the tendency to craze or peel.

Glazing on greenware (raw glazing or green glazing or single firing) promotes interaction between body and glaze. If too much of the glaze's flux combines with the refractory materials in the body, the glaze may become matt or dry.

5.6. Cooling and crystal formation

Glaze or glass is called a supercooled liquid because, during cooling, crystals have no time to form in the rather sticky mass, and glass by definition does not contain crystals. But some matt glazes and opaque glazes depend on the formation of crystals. For these, cooling should be slow to allow the crystals to grow. ZnO, BaO and TiO2 are used for making matt glazes, but if cooling is rapid the glaze will become glossy instead of matt.

To avoid crystal formation, glossy transparent glazes should be cooled quickly after the maturing temperature has been reached.

5.7. Transparency and opacity

Transparency is the property of allowing light to pass through the glaze to-the clay below. Transparent glazes may be colorless or have color in them - transparent blue, green, brown etc. It is necessary to use transparent glazes in

combination with underglaze decoration. Transparent glazes are always shiny.

Opacity is the property of not allowing light to pass through the glaze. Colorless opaque glazes usually look white or gray. When coloring oxides are added, they can be any possible colors. They generally are used with overglaze or on-glaze.

It is possible to make glazes with every degree of transparency or opacity, such as semitransparent or semiopaque.

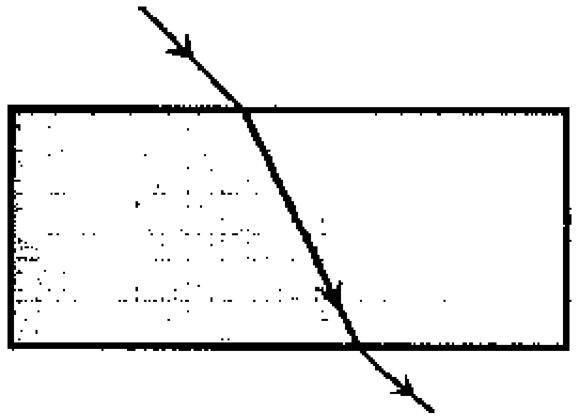


Figure 5.7.0.A. Section of a window glass. A beam of light passes through it - it is transparent. The lights dissection is slightly bent when passing from one medium (air) to another (glass). This is called refraction.

5.7.1. REFRACTION OF LIGHT

Transparency and opacity are determined by the glaze's ability to transmit light. When light strikes a transparent glaze, most of it passes through the glaze layer to the clay underneath, and the color we see is determined by the color of the clay. Thus, a transparent glaze on a brown clay body will look brown whereas the same

glaze on a white clay body will look white. If the transparent glaze is colored, the clay body color will be changed by the fact that the glaze is green or blue, etc.

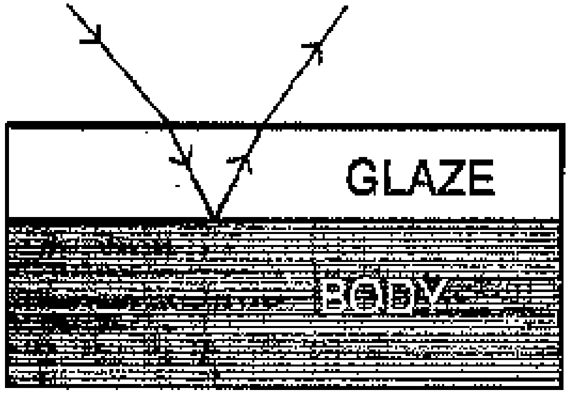


Figure 5.7.1.A. A transparent glaze reflects the color of the underlying body.

Opaque glazes have a large number of particles in them that reflect light, without allowing it to pass through the glaze. So we are not able to see through the glaze. Thus what we observe is only the surface of the glaze, which is not affected by the color of the clay underneath.

Semitransparent glazes have smaller numbers of light-reflecting particles, so they look cloudy or milky, and their color will be affected by the clay color underneath.

Transparent glazes can be made opaque by the addition of opacifiers, which are finely ground particles that do not enter into the melting of the glaze. These particles stay suspended in the glaze and reflect light. This is similar to mixing clay with water, which makes the water opaque.

Opaque glazes cannot be made transparent without changing their formula (unless they are transparent glazes with opacifier added).

The causes of opacity in glazes can be divided into 4 groups:

1. Presence of very fine particles, which do not dissolve in the glaze melt. The light going through the glaze is scattered by the fine particles. Tin oxide (SnO_2) and zircon ($ZrSiO_4$) are used for this.

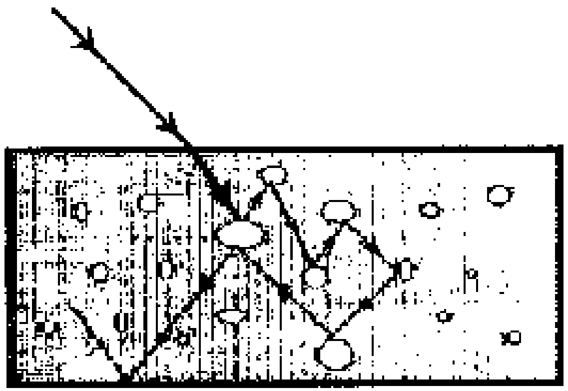


Figure 5.7.1.B. Fine particles of zircon or tin oxide in the glaze scatter the light and produce opacity.

2. Crystals formed in the glaze during cooling will scatter the light, causing opacity. Titanium dioxide (TiO_2) recrystallizes if the cooling is slow and can make glazes opaque.

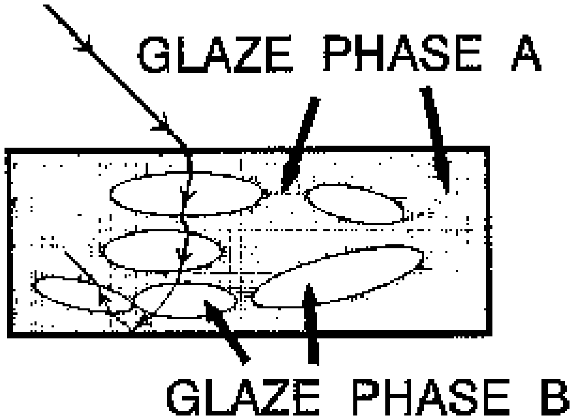


Figure 5.7.1.C. Two glaze phases, A and B, in the melt cause opacity. Both glaze phases may be transparent but the light gets lost passing from one phase to the other.

3. Opacity is also caused when two melting phases of the glaze do not mix. The light will be scattered when it passes through the border between the two different melts. This takes place in boron glazes and with calcium phosphate (bone ash).

4. Gas bubbles scatter the light and produce opacity. This type of opacity is difficult to control and the method is not recommended.

In practice, a combination of the four methods is used. For example, an opaque glaze can be made with boron and additions of lime, zinc oxide and zircon.

5.7.2. MATERIALS CAUSING OPACITY

The best opacifier is tin oxide, which will make most glazes opaque in additions of up to 7%. However, it is a very expensive material and today is only used for

special high-cost products.

Commercially available opacifiers are based on zirconium silicate, prepared with other additions such as magnesia and zinc oxide. They are marketed under names such as "zirconium opacifier", "zirconium silicate", "zinc zirconium silicate" and "magnesium zirconium silicate". Most of these are added to glazes from 5 to 10% and produce different results depending on the type of base glaze. They also vary widely in quality, and it is important to test them before ordering a large quantity. Zirconium opacifiers have the disadvantage of making glazes more refractory and often cause pinholing problems.

The main opacifiers are:

Tin oxide, SnO_2
Zircon, zirconium silicate, $ZrSiO_4$
Titanium dioxide, TiO_2
Alumina, Al_2O_3 (high content in boron glazes will reduce opacity)
Calcium oxide, CaO (improves opacity in boron glazes)
Zinc oxide, ZnO
Calcium phosphate, bone ash, $Ca_3(PO_4)_2$.

Particle Size

The finer the particle size of the opacifier, the better it works. Zircon is often included in the frit batch for greater opacity. In this way opacity is obtained with less zircon, thus reducing some of zircon's bad side effects like high viscosity and

the tendency to cause pinholes. Unfortunately the addition of zircon to the frit increases its melting point, making it more difficult to run it off the frit kiln. It also increases the hardness of the frit so much that it may be difficult to grind it with ordinary pebbles and ball mill lining.

It is important to make sure that the opacifier is well dispersed in the glaze. The fine particles tend to lump together. This reduces the opacity effect. By ball milling the opacifier together with the glaze a good dispersion is assured.

5.8. Shiny or matt glaze

Glazes are also defined by the way they reflect light: they may be shiny or matt or in between.

Shiny

Shiny glazes are also known as "glossy" or "bright". They have the property of reflecting light like a mirror. They are best for utilitarian wares, sanitary ware and insulators, as they are easy to wash and do not scratch easily.

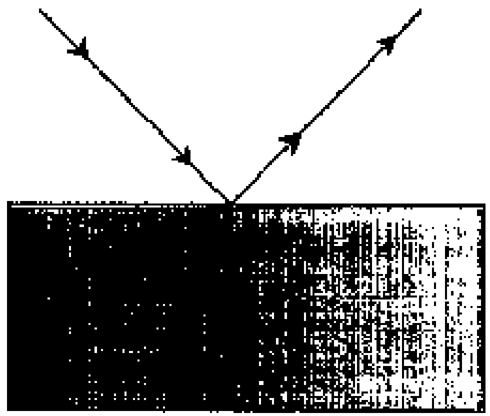


Figure 5.8.0.A. A glossy glaze with a smooth surface reflects the light without scattering it.

Matt

Matt glazes are also known as "dull" or "non-reflective". Their surface can vary from smooth to very rough. They are useful for decorative wares and are very popular for floor tiles, which need to be beautiful but not slippery. The matt surface is not functional for dinnerware, because used with cutlery it makes an unpleasant sound and scratches easily.

5.8.1. MATERIALS CAUSING MATTNESS

There are several ways to produce a matt glaze:

Underfiring

As glaze begins to melt, it becomes glassy. If the firing is stopped before the glaze is completely melted, even glossy glazes will appear matt. Often these underfired glazes will have other problems such as blisters and pinholes, but some glossy glazes make very good matt glazes if fired a few cones below their normal temperature. Similarly, adding refractory oxides to a glaze (such as china clay or calcium carbonate) will produce a matt glaze that really is just an underfired glossy glaze.

Crystalline matt

Crystalline matt glazes develop small crystals which break up light (Fig. 5.8.1.A).

This type of matt glaze usually produces a more smooth surface than underfired matt glazes. Some matt glazes depend on slow cooling to have time for the crystals to develop.

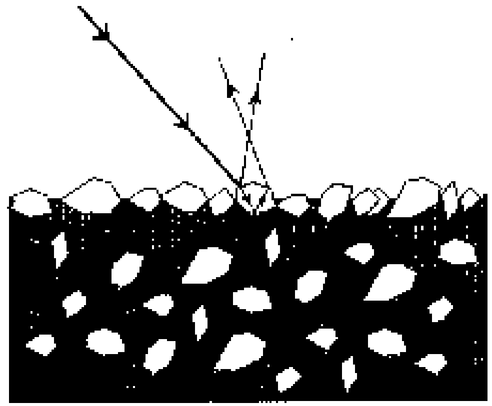


Figure 5.8.1.A. Surface of crystal matt glaze enlarged several hundred times. Crystals in the glaze scater the light by sending it in many different directions.

Barium carbonate, zinc oxide, titanium dioxide, magnesium oxide and calcium oxide are the agents for crystal matt glazes. For more details see page 113.

5.8.2. OTHER CAUSES

Sometimes glazes that should be glossy will become matt. Some of the reasons are:

- **Some of the flux materials may evaporate during firing, leaving a matt surface.**
- **Sulfates from fuel may settle on the surface of the glaze.**
- **The glaze is applied too thin.**
- **The glaze was not mixed sufficiently or not sieved finely enough.**

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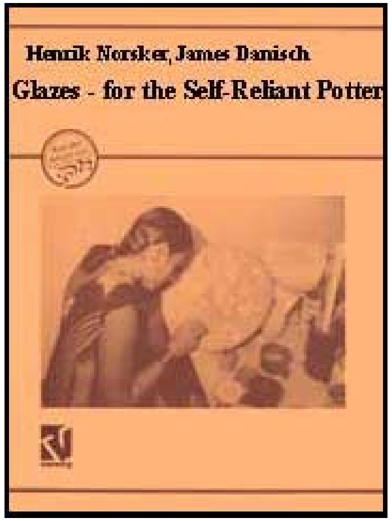


Glazes - for the Self-reliant Potter (GTZ, 1993, 179 p.)

6. Obtaining glaze materials

6.1. Materials suppliers

In countries with large ceramics industries, there are suppliers that specialize in collecting and distributing raw materials. These may be mining companies that can supply specific items like clay and feldspar. If these can be obtained directly, it saves the costs of middlemen. However, these companies often deal only in large quantities. For the small producer, it is often best to get supplies from reliable distributors.

6.1.1. LOCAL SUPPLIERS OF CHEMICALS

General chemical suppliers or pharmacies often have many of the necessary ingredients for glazes (which are often used in other industries). They are useful for obtaining small amounts of chemicals, but often their prices are high.

6.1.2. SUPPLIERS OF OTHER INDUSTRIES

Glaze materials are often available from other types of suppliers. For example, agricultural suppliers can provide calcined limestone. Paint industries use materials such as iron oxide and opacifiers.

6.1.3. IMPORTED MATERIALS

Imported materials should only be considered if there are no local sources, as they are expensive and often customs and import regulations make it difficult or impossible for the small producer to obtain them. On the other hand, it is often worth paying the additional price, if it makes possible production of special glazes or decoration effects that are in demand in the market.

In Thailand, for example, where there is a large export market for decorative ceramics, many producers import clay, glazes and overglazes from Japan. Their profit comes from cheap labor and high value added.

6.2. Materials from natural sources

Small producers can mine their own materials if these are available in the area. Historically, pottery centers located themselves where the necessary clay and glaze materials were available. Where stoneware clay and high temperatures are used, it is possible to make glazes from low-temperature clay alone. Generally, stoneware glazes are made from the basic ingredients of feldspar, quartz, limestone and clay, which are quite common. Wood ash is another common base for high temperature glazes. The process of mining, selecting and grinding is quite time-consuming, and with the advent of modern transportation it is often cheaper to purchase materials from suppliers.

In Nepal, we developed low-temperature glazes based on borax, which must be imported. The bulk of the glaze is composed of local materials such as rice husk ash (for silica), limestone and local clay, which are all easy to get and cheap.

6.2.1. CRYSTAL ROCKS

Igneous rocks

When the young earth slowly started to cool, different minerals formed crystals in the mass of molten rocks (magma). A variety of crystalline rocks were formed differing in composition according to their locality. For example, the igneous rock called basalt was created at a great depth and contains little feldspar compared to granite, which formed near the surface.

If rock cools very slowly, crystals have time to grow large, whereas rapid cooling produces small crystals. This process is still going on today where movement in the crust of the earth causes deep layers of molten materials to rise to the surface.

An erupting volcano lets out hot magma, which cools quickly. The resulting volcanic rocks have microscopic-size crystals, since the rapid cooling allows little time for crystals to grow.

The most common crystal rocks used in glazes are feldspar and quartz. If a piece of granite is picked up and broken in two, the fresh faces of the stone will show a shiny surface and the crystals of the different minerals can be identified. The black crystals are mica or tourmaline. The yellow, white or red colored crystals with a pearly shine are different types of feldspar. The clear colorless crystals are quartz. The weathered surface of the granite will most probably show a rough surface with many holes, where the soluble feldspar crystals have been washed away by rain, whereas the less soluble crystals of mica and quartz remain. Coarse granite (known as pegmatite) often breaks up in weathering, leaving large pieces of quartz and feldspar lying on the ground. These can be collected, ground and used in glazes.

Volcanic rocks

These are rocks formed by the action of volcanoes, often in the form of molten lava that flows out of the volcano. The crystals in the rock are extremely small because the lava cooled very fast. Lava is essentially a glaze and can be used as the basis of high temperature glazes.

6.2.2. SEDIMENTARY ROCKS

Sedimentary rocks are made of materials produced by the crumbling of old rocks. All rocks eventually break up in the course of time when exposed to weather, and

the broken-up rock particles are carried away by water. These particles of clay and sand are transported to lower lying areas or to the sea where they settle one layer upon the other. In the span of millions of years, the growing weight of sediments causes the deeper layers to compact and gradually turn into rocks, called sedimentary rocks. Much later, the movement of landmasses sometimes turns the whole area upside down, so that the old sea floor, with its sedimentary rocks, becomes a new range of mountains.

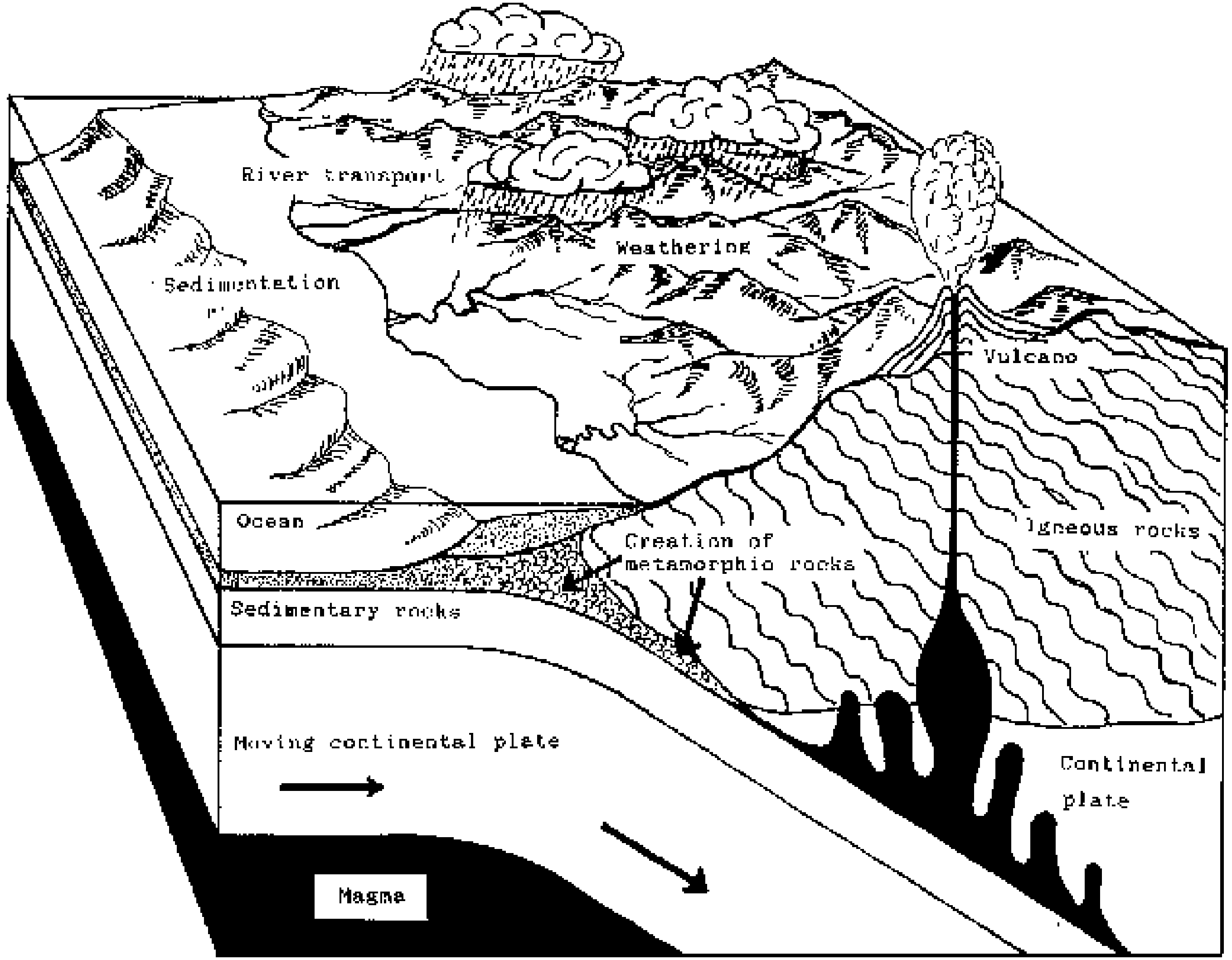


Figure 6.2.1.B. A coutout of a section of the crust of the earth shows a continental plate moving under another. The friction of the plates generates heat, which melts rocks and feeds a volcano. Rain falls and old rocks are weathered and washed to the sea creating new layers of sediments. Later the sediments are compressed into rocks.

The upper part of new mountains consists of sedimentary rocks resting on deeply set igneous rocks. Sedimentary rocks like sandstone, shale and slate can often be recognized by their layered structure. Limestone is a sedimentary rock created by the skeletons of billions of small animals that lived in the ancient seas. Gypsum is formed by chemical sedimentation in areas where seawater evaporates on a large scale. This produces a high concentration of gypsum which forms crystals like the formation of salt crystals in a glass of salty water.

For the glazemaker, sedimentary shale can be a source of glaze. At high temperatures, shale melts and with a few additions will produce glazes that are usually brown. Although shale often does not slake in water, it can be ground in a pan mill and used in glaze.

6.2.3. METAMORPHIC ROCKS

Igneous and sedimentary rocks are sometimes changed into new forms by high temperature and pressure. Marble is an example of a metamorphic rock formed from the sedimentary rock limestone.

6.2.4. HOW TO GET INFORMATION

Local authorities

First of all, information about the geology and the minerals of the region should be gathered from local authorities, like industrial development organizations, agricultural institutions, National Geological Institutes or mining corporations. They may have little information and the authorities may even say that no

materials are available in the region. However, that is often not true and should not keep anybody from looking on his own.

Practical people

It is worth talking to people who make water wells, and builders of dams and roads. They sometimes have useful information about the minerals of the region. Farmers in the area will know about the upper layers of soil on their fields and about local rocks. Sometimes glaze minerals are used for other purposes, like whitewashing houses or medicine.

The best source of information is often other potters.

6.2.5. LOOKING FOR MINERALS

Good places to look for minerals are in riverbeds, where many different types of rocks will wash down from the mountains above. Although most of these may not be useful, it is often possible to find quartz and feldspar. Any rock with an unusual color is worth testing. Rocks that are unusually heavy may contain metallic oxides. For the potter, however, there are few rocks that are directly useful, other than quartz, feldspar and limestone, and some of the volcanic rocks.

Other minerals that are useful in glazes are sodium and potassium compounds, which sometimes form on the edge of lakes, particularly in desert areas. These usually look like a white powder and are soluble in water.

6.2.6. TESTING

To begin with, the most useful test is to take a small sample of the material, place it in a clay bowl and fire it in a regular glaze firing. This will indicate if it melts or not. If it melts, it certainly can be used in a glaze. Materials that do not melt should not be automatically rejected, as many useful glaze materials (such as calcium carbonate and quartz) only melt when combined with other materials. The simplest way to find out if they are of use is to make a line blend of one of your standard glazes, combined with the unknown material.

Rock minerals can be identified by their crystal shape, color, specific gravity and hardness. If you are seriously looking for rock minerals there are good books presenting most common minerals with color photos.

Hardness

Mohs' scale of hardness is based on the hardness of 10 different minerals:

1 Talc
2 Gypsum
3 Calcite
4 Fluorspar
5 Apatite
6 Orthoclase feldspar
7 Quartz
8 Topaz
9 Corundum (pure alumina)
10 Diamond

Window glass and a penknife are about 5.5 and a metal file about 6.5.

Two materials have the same hardness if they cannot scratch each other. Quartz can scratch feldspar but not topaz. In the field a piece of glass and a penknife are used to find out if the hardness of a rock is higher or lower than 5.5.

Chemical analysis
If a testing laboratory is available, samples can be sent there for chemical analysis. This is usually expensive but may be helpful if the material looks useful after firing.

6.3. Other sources of materials

Recycled materials are often useful in glazes. These may be by-products from other industries, such as rice husk ash or bone meal, or waste materials. Some other sources of useful materials are discussed below.

6.3.1. METALLIC OXIDES

Metallic oxides are used as coloring agents in glazes. Commonly available are:

Iron oxide, which can be obtained by scraping rust from old steel. It is often possible to get this from paint and hardware suppliers, who use "red oxide" for coloring paint and cement.

Manganese dioxide, which is the main ingredient in torch batteries (the black substance which can be removed from old batteries).

Copper oxide, which can be collected from makers of copper pots. The oxide is the black powder that forms on the surface of copper when it is heated. Another way is to fire copper wire in the kiln and to use the resulting black copper oxide.

6.3.2. ASHES

Wood ashes are used as the basis for high temperature glazes, since they contain sodium, potassium, silica and other ingredients. Early glazes were often simple mixtures of wood ash and clay. Most wood ash is suitable for this purpose, but each type of wood will produce different characteristics and will have a different melting point. So it is important to have a consistent supply. Ash must be sieved to remove unburned material and is usually washed in water and dried before use. If it is not washed it contains more fluxes but they are soluble and make the glaze slip caustic.

At cone 8 to 11, a good starting point is 2 parts ash, 2 parts feldspar and 1 part clay. Ash glazes have the following general limits:

Ash	20-70%
Feldspar	20-70%
Whiting	5-20%
Flint	15-25%
Clay	5-20%

Rice husk ash contains more than 90% silica, so it can be used instead of quartz in many cases. For accuracy, it should be burned white - if there is much black

carbon in it, it will make calculations incorrect. In the Appendix the chemical composition of different ashes is given.

6.4. Storing, packaging and labeling

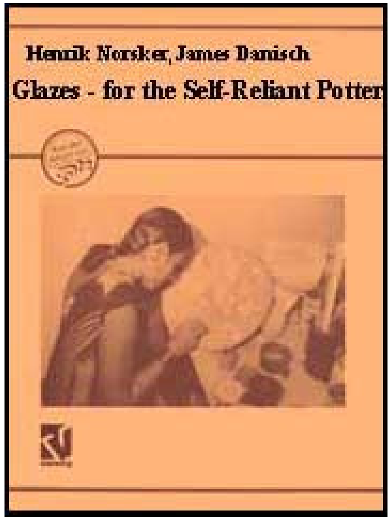
If you use local materials, they will change from time to time. For this reason, it is best to store as much material as possible and to check each new batch by trying it in a standard glaze. For example, feldspar tends to be variable and, as the mine is used, the chemical composition will change. Suppliers of feldspar usually keep several large storage areas of material from different parts of the mine. In order to keep it uniform, they mix the different feldspars together when supplying.

Some materials are damaged by water. Borax, boric acid, soda ash and plaster of parts should all be kept in a dry place. In particular, soda ash absorbs water (up to 7% after one year, 11% after two years) and will thereafter no longer be effective as a slip deflocculant; and plaster will not set correctly after damp storage.

When you get local materials, each batch should be kept separately and labeled with date and source. It is often a good idea to purchase more material when your old supply is about 50% finished and to test it to see if it is the same or not. If it is not greatly different, the new material can be mixed with the old and your glaze will not change unexpectedly.

A good labeling system is very important, as most glaze chemicals look rather alike. Never depend on your memory - keep a permanent label on the bag or jar of material. Additionally, if you order bags of material from a supplier, ask him to

label the outside of the bag, and also to put a label inside the bag as labels are often lost in shipping.



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7. Frits and fritmaking

Most low-temperature glazes require fluxes that are either poisonous (lead) or water-soluble (sodium and potassium). Traditionally, these materials were used raw, but this is not satisfactory for modern potters. Raw lead is poisonous and sodium/potassium are water-soluble. Borax is sometimes used raw in glazes, but these glazes cannot be stored for a long time, as the borax will go into solution or form crystals.

The principle of fritmaking is very simple: molecules of poisonous or soluble fluxes should be chemically combined with glass-making materials to eliminate these undesirable characteristics.

A frit is a combination of a flux or several fluxes (lead, borax, boric acid, potassium carbonate) that is combined with other insoluble materials (quartz, feldspar, lime etc.), melted in a kiln to form an insoluble glass, and ground to be used as the base for making glazes. (Many low temperature glazes are simply 90% frit and 10% china clay).

Fritmaking is not usually practical for the small producer, as it takes time and requires a special kiln and a ball mill for grinding. On the other hand, if reliable frits are not commercially available, the potter may have to produce his own. Frit glazes are more expensive than raw glazes, but their convenience usually makes up for the additional cost.

There are many different commercially available frits, all designed for different temperatures, surface qualities, coefficients of expansion, and color responses. The potter trying to decide which frit to use must depend on the supplier, as formulas are usually kept secret. Suppliers will give advice on which frit is best for the potter's purpose. There are two main types of frit:

Lead frits

These are all designed to provide lead in a nontoxic form. Lead oxide is combined with other materials to give desired properties of surface, opacity, and color response. The standard lead frit is called lead bisilicate and is simply a

combination of lead oxide and silica, which combines the lead in an insoluble form. This can be used as the base for a large variety of lead glazes.

Other frits used commonly in the tableware industry are called lead-borosilicate frits, which combine the desirable properties of both lead and boron and are generally safer to use.

WARNING! Lead frits can still be poisonous, and glazes made from them can be poisonous if they are not combined with sufficient silica to combine with all the lead molecules.

Leadless frits
These are based on boron compounds, again combined with other materials. Because glazes compounded with lead are difficult to control for lead release, leadless frits are recommended for small producers.

7.1. Why make frits?

Frit making is only suggested if reliable commercial sources are not available. Often frit manufacturers are not interested in supplying small amounts. Dishonest frit manufacturers sometimes sell bad batches of frit to small producers. Even though frit making is complicated, the small producer who makes his own frits at least has the process under his own control.

Raw borax glazes can be used, but they must be used immediately after mixing or problems will result from the soluble borax. This may be satisfactory for art pottery but, if consistent results are needed, it is better to use fritted glazes.

Similarly, raw lead glazes are widely used. This is a danger for the workers, who will eventually develop lead poisoning unless they take extreme care in handling the glaze. Modern industries never use raw lead glazes, and industrialized countries all have severe restrictions on the use of lead in glazes. In developing countries, workers in industry suffer from lead poisoning, and it is the responsibility of the industrialist alone to take care of the workers' health. As lead poisoning takes several years to develop, many factory owners do not understand the seriousness of the problem and continue to harm their workers. IT CAN TAKE UP TO 20 YEARS TO DEVELOP SYMPTOMS OF LEAD POISONING!

7.2. Frit production

Frit composition

All the soluble materials are included in the frit batch along with silica, in order to form a glass when fired in the frit kiln. Other ma" serials may be included for modifying the frit or helping to melt it.

The main frit raw materials are:

Silica sand, SiO_2
Rice husk ash, almost 95% SiO_2
Borax, or sodium borate, $Na_2B_4O_7\ 10H_2O$
Boric acid, H_3BO_3
Limestone, $CaCO_3$
Feldspar, soda and/or potash, K_2O & Na_2O

Al_2O_3 $6SiO_2$

Clay, Al_2O_3 $2SiO_2$

Zinc oxide, ZnO

Zircon,$ZrSiO_4$ (opacifier)

Red lead oxide, Pb_3O_4

Other materials like talc, barium carbonate and bone ash may be added.

In order to have a frit with low viscosity that easily runs out of the kiln, the clay or alumina of the glaze is not added to the frit. However, in order to make the ingredients insoluble, 2-3% kaolin should be included in the frit.

Work flow

The work flow for frit production is shown in Fig. 7.2.0.A. It is better economy to prepare large frit batches when firing a continuous-type frit kiln.

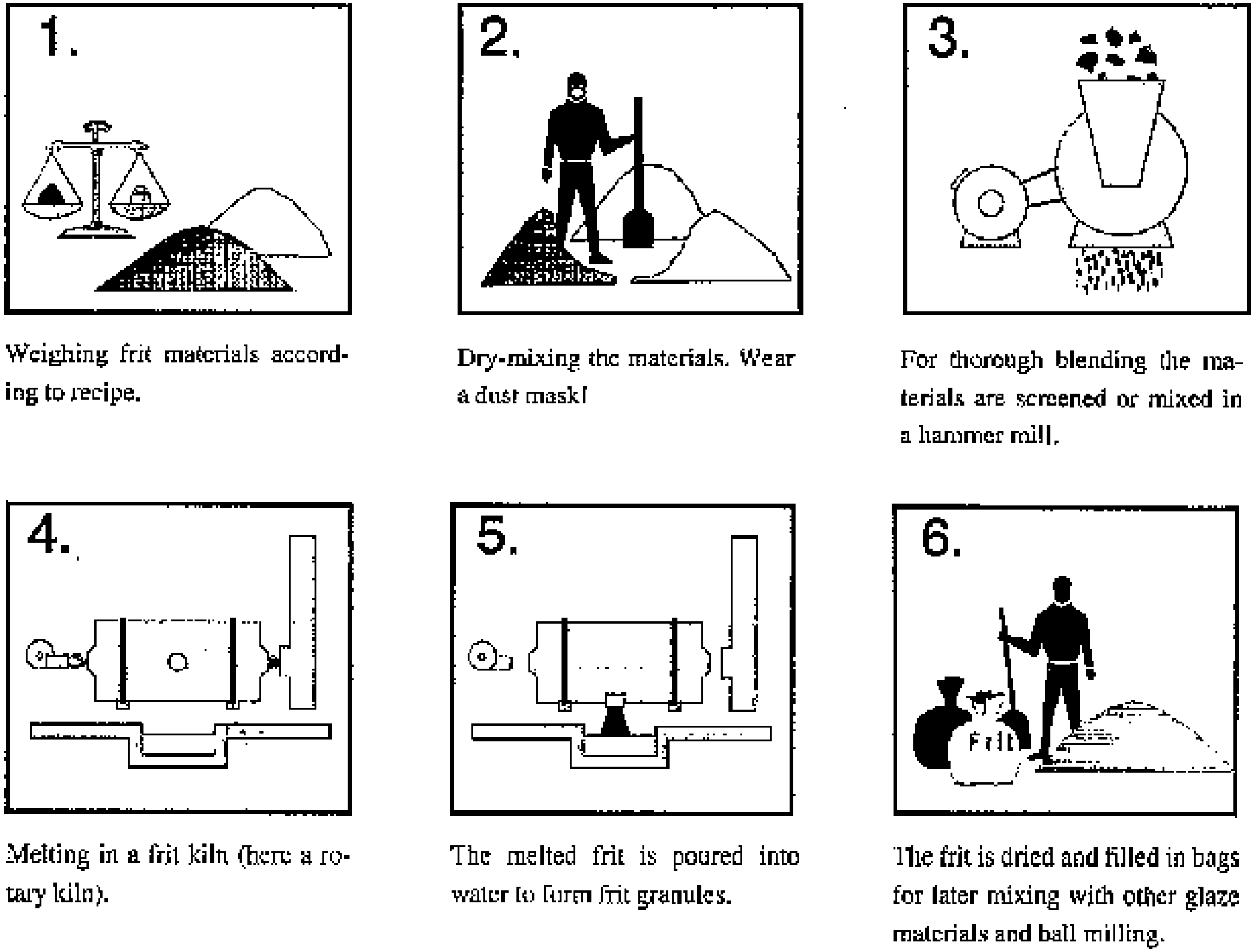

Figure 7.2.0.A. Work flow of frit production.

Prepare materials

All materials for frit need to be clean, dry and ground to pass through a 60-100-mesh sieve. The finer the material, the easier it will be to melt it. If rice husk ash is used as the source of silica, it should be well-burned to a white color, so that

unnecessary carbon is not introduced. If there is a large amount of black carbon, this will decrease the amount of silica available. The content of carbon in rice husk ash may vary more than 30% from batch to batch. If materials are wet, they should be dried completely so that the weight of water is not included in the recipe. In frit calculations, the loss on ignition (see page 146) needs to be included to account for loss of material during firing.

Blend materials

Weigh the materials accurately and blend them together dry. WEAR A DUST MASK! Small amounts can be mixed by hand in a bucket, and larger amounts can be mixed with a shovel on a clean cement floor. After mixing the frit materials they are screened through a 16-mesh sieve (mosquito net) to ensure thorough blending or the materials are run through a hammer mill.

Melt the frit in a kiln

There are many different systems for melting frit, which are described below in section 7.2. In each system, the principle is to thoroughly melt the frit until all ingredient! are combined. Most frit is melted at 1150°C to 1250°C.

Check the frit

A sample of molten frit should be taken and examined to see if the melt is complete The frit should be uniform, without particle! of unmelted material.

With continuous frit kilns, the rate of feeding raw frit and the speed of the melted frit must be adjusted so that all the material melts completely and has time to mix'

properly.

Quench the frit in cold water

The molten frit is poured into cold water, which "shatters" it into small pieces that can easily be ground. With continuous melting and discharging it is necessary to let fresh cold water run continuously.

Grind the frit

If the frit is quenched correctly, it will be easy to put it directly into a ball mill and grind it until it can be passed through a 100-mesh sieve. The granulated frit may be first dried and then stored in bags until it is needed for glaze making. Then it is ball-milled together with clay and other glaze materials. Alternatively, the still wet frit is ball-milled first.

Sieve the wet frit

When the frit is removed from the ball mill, it should be sieved through 100 mesh to remove any large particles that were not ground.

Dry the frit

The wet frit is settled, excess water is poured off, and the remaining frit can be spread out to dry, either in the sun or in a dryer.

Test the frit

Each batch of frit should be tested for correctness. The simplest way is to fire it in a kiln on a specially made flow tester, along with a sample of correct frit (page 131). If the frit flows evenly to the control sample, it will probably be correct but should be double-checked by trying it in a standard glaze.

Additionally, the frit should be tested for solubility in water. A sample amount is boiled in water for several hours, then allowed to sit for 2 weeks. If crystals do not form during this time, the frit can be considered stable. If crystals form, it means that there is not enough silica/alumina in the frit and the composition will need to be changed (frit calculations page 144). The causes of crystal formation could also be with the frit firing, e.g. overcharging, too short a firing time and improper mixing.

The finished tested frit may be sold to other ceramics producers either as a milled powder or in granular form.

7.3. Frit kilns

There are many different kinds of frit kilns, which are selected according to the amount of frit that needs to be regularly produced.

Normally, each type of frit -transparent, opaque, lead - requires a separate kiln to prevent contamination. When one kiln is used for several frits, it must be cleaned out before each different batch by melting frit in it to remove most of the old batch. This contaminated frit is then kept separately, to be used as "clean-out" frit before changing to different compositions.

7.3.1. CRUCIBLE FRITTING

Small amounts of frit for testing are easily made in a fireclay crucible. The crucible with frit is fired together in a glaze firing, which will melt the frit into a solid block of glass. After firing, the crucible is broken away from the frit and the frit can be crushed and ground. It is a good idea to first paint the inside of the crucible with china clay slip, as this will make it easier to separate the frit. NOTE: Frits containing boric acid often cannot be melted successfully this way, as the boric acid melts at a very low temperature and flows to the bottom before the rest of the ingredients melt. Frits with rice husk ash may also be difficult to melt in this way, because the upper layer of the frit melts first sealing off the frit mixture so that the carbon remaining in the ash cannot burn out. Carbon is highly refractory and it will prevent the frit from melting.

This is only suitable for test production and is not a safe method, since the pot often cracks, resulting in frit running out, destroying other ware, kiln furniture and the kiln lining.

CAUTION: Borax frits boil during melting with a great increase in volume. The crucible should be filled only half with frit, and a tile placed over the top to prevent boiling over.

7.3.2. CRUCIBLE KILN

For fritting small amounts of frit a simple frit kiln is shown in Fig. 7.3.2.A. It can be fitted with several crucibles arranged in a row for melting different frits at the same time. The crucibles can be loaded with raw frit from the top. The fuel

economy of this type of kiln is less than for the other kilns.

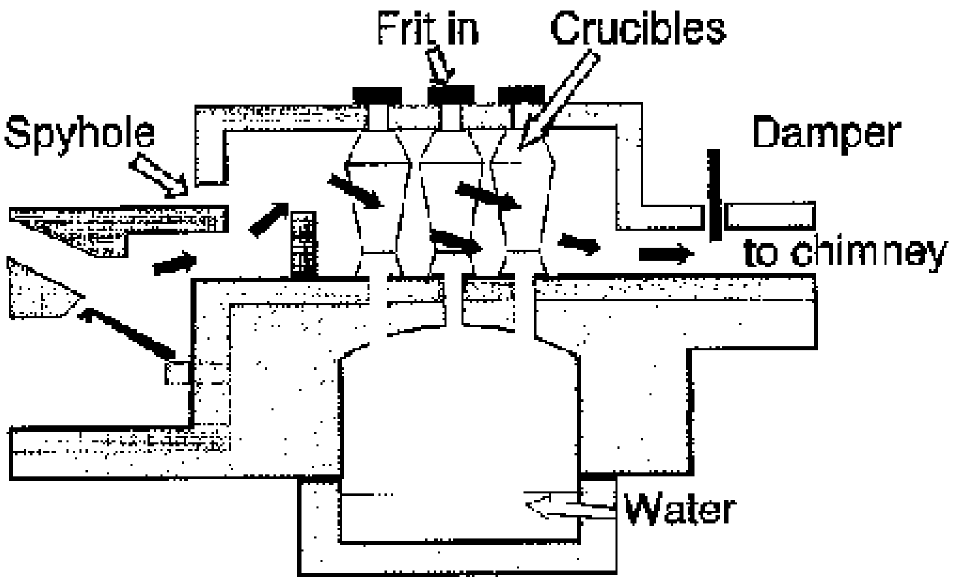

Figure 7.3.2.A. Coal-fired frit kiln with three crucibles.

7.3.3. OPEN HEARTH KILNS

Open hearth kilns consist of a tank made of firebricks, which is set in a crossdraft kiln. The kiln may be fired by coal, firewood, oil or gas. The hot flue gases heat the arch over the frit. The arch in turn heats the frit. In batch-type frit kilns, the frit melt is checked by drawing out some melted frit with an iron rod for inspection.

After the frit is completely melted, a hole at the bottom of the tank is opened and the frit flows out into cold water. Then another batch of frit may be charged from an opening in the arch.

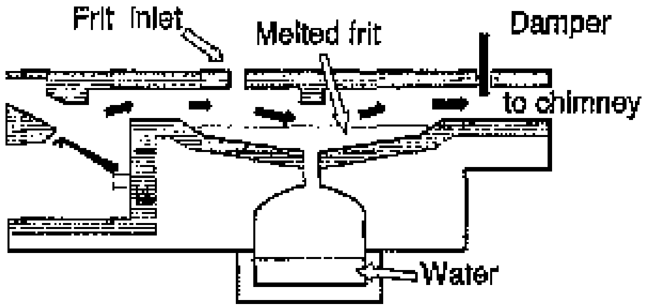

Figure 7.3.3.A. Open-hearth frit kiln for coal firing.

The melting of several tonnes of frit may take 6-12 hours consuming 1-1.5 tonne coal per 1 tonne melted frit.

7.3.4. CONTINUOUS FLOW

The continuous-flow frit kiln uses a kiln with a sloping floor, made of fireclay refractories. The raw frit is introduced at the upper end and, as it melts, it flows down while mixing to an exit chute by the burner and then into cold water. The kiln shown in Fig. 7.3.4.B was developed in Nepal. It uses a steam/kerosene burner, but any forced draft oil or gas burner can be used.

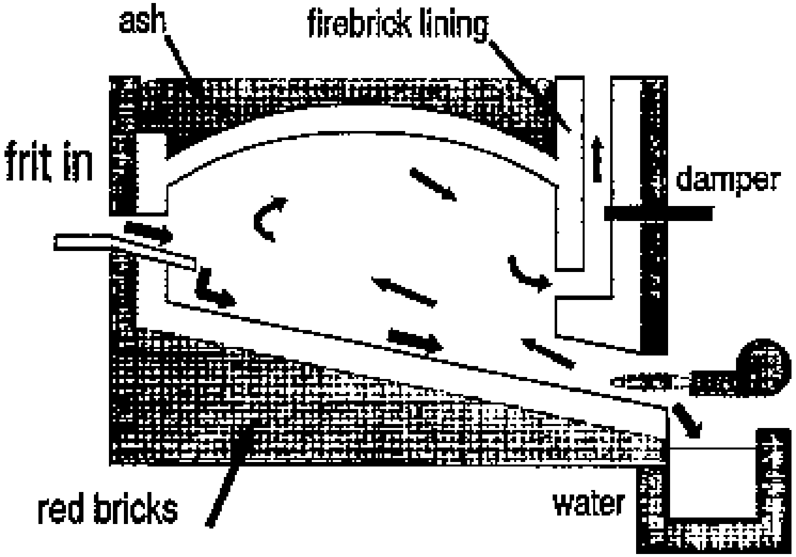

Figure 7.3.4.B. DSide elevation of a continuous flow kiln.

The rate of flow is controlled by introducing limited amounts of raw frit. Too much frit at one time may result in incomplete melting. If the frit runs very fast through the kiln, the low melting materials will not melt properly together with the silica. This may be a cause of water-soluble frit.

The frit can be slowed down in the kiln by making less of a slope and by putting some obstacles in the way (like kiln shelf supports).

7.3.5. ROTARY

Rotary frit kilns are large refractory-lined cylinders, which have a burner (gas or oil) that passes through them. The raw frit is introduced, and the kiln rotates full turns (or back and forth) as the frit melts. This has the double purpose of ensuring good mixing and of transferring the heat of the firebrick lining to the frit as this

constantly moves over it. When the frit is completely melted, the kiln is turned so that the frit flows out through an opening into cold water.

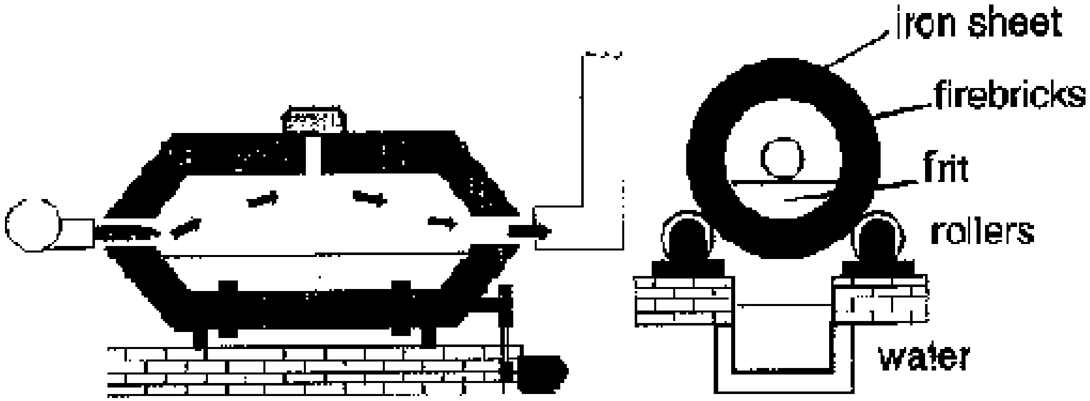

Figure 7.3.5.A. Front and side elevation of a rotary frit kiln. It consists of a firebrick-lined steel drum resting on rolers. It is gas-or oil-fired.

7.3.6. FUEL ECONOMY

If much frit is to be produced, fuel economy is an important factor. In general, the more frit that can be made at one time, the lower will be the fuel cost. In a continuous frit kiln, it takes several hours to heat the kiln sufficiently to melt the frit at maximum speed -this preheating period consumes a lot of fuel. It is best to fire several hundred kg of frit at the same time to reduce firing costs.

Frit industries generally use rotary kilns, as they are the most economical for long, continuous use. However, the continuous kiln developed in Nepal by the Ceramics Promotion Project compares favorably with standard fuel/frit ratios obtained with rotary furnaces.

Examples of fuel to melted frit ratios are:

Frit kiln type	Batch amount	Fritting time	kcal/kg melted frit
Open hearth coal	1 - 2 tones	6 - 12 hours	7500 - 11250
Nepal, continuous flow	1.5 - 2 tones	48 hours	5150
Rotary, India	300 kg	2 hours	5700