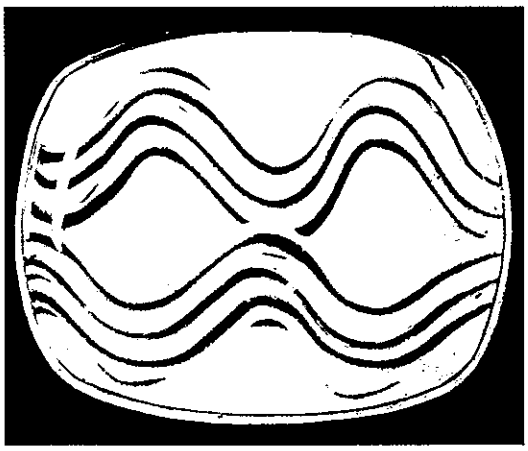


System of sedimentary rocks. A few deposits are residual clays similar to china clay. Fireclays are often refractory clays and are used for firebricks. The name gives this impression but there are fireclays which vitrify below 1300°C (2372°F). These are used for drainage pipes, building bricks, sanitary ware and stoneware. Grog is usually fired and ground fireclay.

Fireclays can be divided into the compressed rock fireclays and the underclays. The rock fireclays are both solid rocks and shales. The rock fireclays must be crushed in a mill before they can be wetted and pugged or even blunged. They are often mined rather than quarried and come to the surface as hard lumps which take twenty or thirty years to weather to a plastic clay. In contrast, the underclays have often remained damp. They are more obviously clays when won and can often be blunged without previous milling. They weather quickly, surprisingly quickly for their clay particle size, and produce plastic clays suitable for ovenware.

All fireclays are the seat earths of vegetation which grew during the Carboniferous Period over 280 million years ago. The underclays were the soil for the coal forests and this is why an underclay is found immediately under a coal seam. The coal forest vegetation has taken from the soil much of the potassium and other soluble salts. It may also have taken some silica but it has not taken aluminium oxide. Hence these clays are high in aluminium oxide and are refractory. The rock fireclays tend to be less refractory than the underclays. All contain organic impurities, some as much as 3% carbon and others actual carbonaceous matter as old root hairs etc. They also contain free quartz, which may be large visible grains; mica; iron pyrites; iron carbonate (siderite) and calcium carbonate (calcite).

The presence of impurities which are volatile, e.g. the carbon in the organic impurities, the sulfur in the pyrites, the carbon dioxide in the carbonates, dictates a careful firing of these clays if the impurities are not to be trapped. Trapped carbon and sulfur cause the most trouble. Even a relatively small amount, like 0·5% of the dry clay, is sufficient to cause a black core with attendant problems at higher temperatures. See ***Black core***. The carbon dioxide usually escapes without difficulty from the carbonates and also the bound water presents no difficulty. With fireclays more than with other clays, the bound water escapes over a long period of the firing starting around 350°C (662°F) and continuing up to 600°C (1112°F). This fact and the general coarseness and quick-drying nature of these clays often lead potters to think that they can withstand any treatment.

The fired colour of fireclays is pale buff. Some are nearly white. All tend to be speckled with iron particles which originally were pyrites. Well-weathered fireclays have often had the pyrites decomposed to carbonate, and fire to a more uniform pink colour. Fireclays associated with iron ore deposits are often red-burning and are used for making bricks.

Fireclays are various in chemical composition. It is usual to quote a fireclay by its aluminium oxide content and to relate this, with some justification, to a point of refractoriness. Whether a clay deforms at a low temperature or a high temperature is dependent equally on the amount of alkali present but it is true to say that a fireclay containing 40% aluminium oxide is unlikely to melt easily. Fireclays contain between 10% and 40% of aluminium oxide, between 40% and 80% of silica. Compare this with china clay, which contains 38% aluminium oxide and 46% silica.

Some fireclays are as refractory as china clay and are able to withstand 1700°C (3092°F) without deformation and probably melt around 1800°C (3272°F). In Britain these are the Scottish fireclays. It has been suggested that nearly all the fireclays originated in the north of the British Isles and were transported southwards. In so doing the impurities were collected. Certainly there seems to be some progression in the amount of impurities from north to south and a resultant drop in refractoriness.

It will be understood that it is impossible to give an accurate chemical formula for fireclay. In calculations one should correctly work from an analysis. However for the small amounts which may be contained in a glaze, and for quick calculations, the formula $Al_2O_3.4SiO_2.2H_2O$ will be found reasonable. The aluminous fireclays of Scotland approximate the formula for china clay: $Al_2O_3.2SiO_2.2H_2O$. With increasing free silica and proportionate decrease of aluminium oxide in the more southerly ones, an acceptable formula for south Wales fireclay is $Al_2O_3.5SiO_2.2H_2O$.

Firing

The process of conversion from clay to pot. It involves heat of at least 600°C (1112°F). Clay disintegrates in water but is changed by firing into a stone-like material, unaffected by water, and in some cases impervious to water. The change is called the ceramic change. Other changes occur during the firing, e.g. organic matter is burned away, the colour changes, a layer of glass is fused onto the surface.

The decorative effects which are used in pottery often require separate firings. The first firing converts the clay to pot. It is called the biscuit firing. Subsequent firings involve colour, perhaps underglaze colour, glaze, onglaze colour, lustre and are named after these purposes. They will vary in

temperature, speed of temperature rise and fall, and in atmosphere (oxidation and reduction). However, it is often possible to achieve a number of results from one firing. It is only the sophistication of potting methods, occurring in the last 300 years, that has resulted in the general practice of separate firings for biscuit, glaze and colours. Prior to this, the general practice was a single firing, although the use of subsequent firings for different effects was known to early potters around the Mediterranean. See ***Biscuit, Through firing, Onglaze, Lustre, Oxidation*** and ***Reduction***.

The stages of a biscuit firing are:
Water smoking
Decomposition of vegetable matter
Ceramic change
Burning out or oxidation of carbon and sulfur
Progressive vitrification

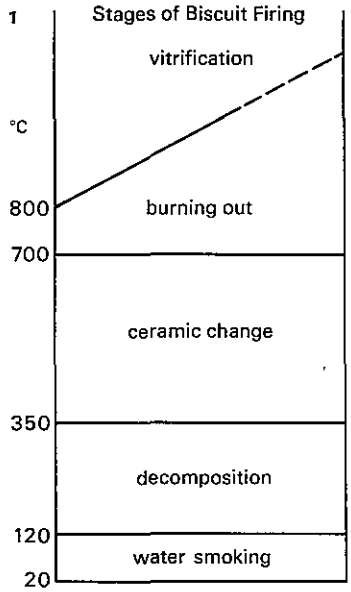
This achieves a strong and porous material: strong so that it may be handled, and porous so that it may be glazed. A summarized description is given in the next section and references made to other articles.

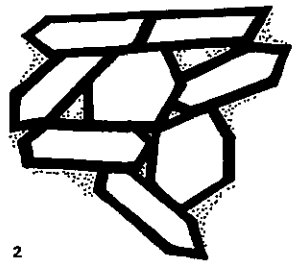
The stages of a glaze firing are:
Drying out
Start of glaze fusion
Continuation of vitrification of body
Integration of body and glaze
Completion of glaze fusion

The cooling which follows involves the growth of crystals within the body-glaze layer, in the glassy parts of the body and possibly in the glaze. The individual actions of the different glaze constituents are given under these materials. A summarized general description is given in the section following the summary of the biscuit firing.

BISCUIT FIRING. The progression is described under headings taken from the accompanying chart (fig. 1). The sectional diagrams here, showing clay particles, overlap with, and are a continuation of, those used in the article on ***Drying***.

Water smoking. The remainder of the pore water, which has been unable to dry out because of atmospheric humidity and pressure, is now driven out by heat. The action takes place between room temperature (20°C or 68°F) (fig. 2) and boiling point of water (100°C or 212°F). It is usually considered to be completed by 120°C (248°F) (fig. 3). This period of a firing must be taken cautiously. Two hours is usual for general ware up to 2 cm in thickness. Thicker ware will require proportionately longer. Too rapid a rise in temperature will cause steam pressure to build up and possibly shatter the clay. The water-smoking period is over when the kiln vents are dry. During water smoking there will be water vapour escaping from the chamber. This can be seen or, if not visible, can be detected by condensation onto

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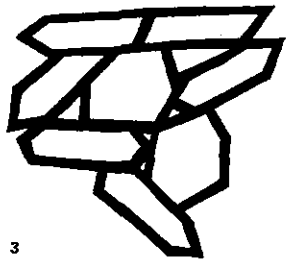
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a cold glazed surface held near the vent. This test is effective with electric and wood-fired kilns but, with kilns fired by natural and liquid petroleum gas, the test needs interpretation because these gases produce water as they burn. See ***Water smoking, Drying*** and ***Water***.

Decomposition. Many clays contain vegetable matter which breaks down at approximately 200°C (392°F). This is the same action as the compost heap and with surface clays the effects can very occasionally be detected by smell. This is not a burning process. The burning out of carbon comes later. This part of the firing can be taken quickly because there are no changes to cause trouble.

Even the presence of cristobalite makes no difference at this dry clay stage although the cristobalite dunting point is passed. There is a very slight expansion of the ware over this

period. It rarely amounts to more than 1% linear and, since the kiln props and shelves have similar expansion, it is unlikely to cause trouble. However, large pots set close to the kiln arch have been known to break their rims against the roof. In such cases the kiln structure is probably expanding inwards to meet the pots and it is advisable to leave about 2 cm clearance between pot and kiln arch.

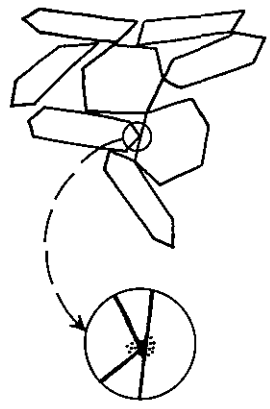
Ceramic change. The bound water which is part of the crystal structure of clay is driven off at this stage (fig. 4). The result is a change, from clay to pottery body, known as the ceramic change. This action begins very gently between 350°C and 450°C (662°F and 842°F) and increases to a maximum at 600°C (1112°F), after which the action quickly fades away before 700°C (1292°F). There is little danger from the escaping steam and the firing can be taken quickly. Water vapour will be seen escaping from kiln vents which have been dry during the decomposition stage.

Dunting point (573°C, 1063°F) is passed during this period, but the open texture of the body enables adjustments of size to be made without rupture.

Theoretically, the now thoroughly dried particles are only just touching, as shown in fig. 4. However, the body retains its form and does not collapse as a pile of dust, because the particles are fastened to each other by a process called sintering. This is not fusion in the vitrification sense but a welding of similar particles at points of extremely small contact as shown in fig. 5. It is as if a vibration at these points creates an incandescence of sufficient heat to fuse the tips together.

The strength created by sintering is sufficient to hold a pot in one piece while allowing adjustments of size caused by the silica inversion. Dunting is therefore very unlikely to happen. However, there is insufficient strength to allow a pot to be held for glazing and so it is necessary to take the firing to a higher temperature. A partial vitrification is necessary to give a satisfactory biscuit ware and it is also necessary to burn out the carbon and some of the sulfur content from the body.

There is a very slight shrinkage over the period of ceramic change.



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Burning out. Carbon and sulfur are present in clays and remain to be burnt out by the process sometimes called oxidation. They combine with oxygen to form monoxide, dioxide and trioxide gases (CO, CO_2, SO, SO_2, SO_3). This process requires at least the dull red heat of 700°C (1292°F) and reaches its climax around 800°C (1472°F). Most of the carbon has been burnt out by 900°C (1652°F) but some sulfur lingers until 1100°C or 1150°C (2012°F or 2102°F).

It is essential that this process is thoroughly completed. With thick pieces of work this may take a number of hours. Some potters slow down the rate of firing or try to hold the temperature steady at 800°C (1472°F) for a couple of hours. With normal potting clays made into tableware, the thickness is not great and the usual hour taken from 750°C to 850°C (1382°F to 1562°F) is satisfactory. Surface clays and present day estuarine muds require more care because they contain a lot of carbon and sulfur respectively.

These volatiles cause trouble at a later stage if they are not removed from the body. The vitrification of the body begins at 800°C (1472°F) and, from this point, the body progressively loses its pervious nature. A body will bloat if the outer part becomes impervious by the action of heat while there is gas attempting to escape from the inner part. The impervious outer part is soft and glassy by vitrification. Bloating usually occurs at the upper temperatures of a stoneware firing and is often a sign of overfiring of the body. However, the causes of premature bloating lie with a hurried burning-out period in the biscuit firing. At biscuit stage the fault is not visible on the outside of the body, but, in broken section, a black core will be found. See ***Black core***, ***Breakdown*** and ***Bloating***.

Clearly, different clays require different treatments because the amounts of carbon and sulfur vary from clay to clay. The coarser clays, like fireclays and brick shales, often contain a lot of carbon which takes a few hours to burn out in spite of the open texture of these bodies.

A problem arises in the through firing of these clays, that is, when firing these clays with glazes in one firing. The glaze must not melt before the burning out is completed or else the outer pores of the body will be sealed. Some fine slips can cause trouble in this way and it is noticeable that on much of the traditional slipware, which was once-fired with soft lead glazes, the pieces are slipped and glazed on one side only. Plates and dishes were glazed top side only, and jugs etc were glazed inside and just over the rim. Potters with less troublesome clays were able to decorate and glaze all over but this achievement was limited to a few localities.

During the burning-out period there will be no change in body size. Any slight expansion is countered by the sintering and incipient vitrification.

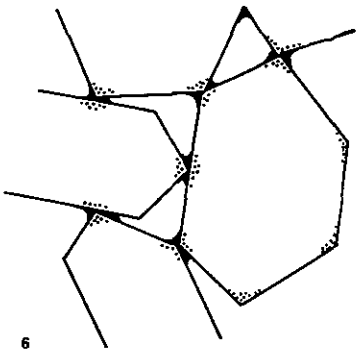
Vitrification. This begins at 800°C (1472°F) when the sodium and potassium oxides within the body start to flux the free silica. Vitrification progresses throughout the firing, filling the pores between the alumino-silicate (original clay) particles and eventually involving these also. The body shrinks during vitrification. See figs. 6, 7 and 8 which show

the effects of vitrification but do not show the original fluxes and free silica. For simplicity these have been omitted from all the diagrams overleaf.

Vitrification strengthens the final product by welding the particles together with glass. If the firing were to continue, then the vitrification would be completed to the point where the whole body melted to a glass.

Above 1000°C (1832°F), the fused alumino-silicate is able to form mullite. Mullite crystals are long needles which considerably strengthen the final body. See ***Mullite***.

The temperature chosen for a biscuit firing depends upon the balance required of the properties of strength and porosity. See ***Biscuit***. Strength is also required to withstand the shock of the silica inversion during cooling. See ***Dunting: biscuit dunts***.



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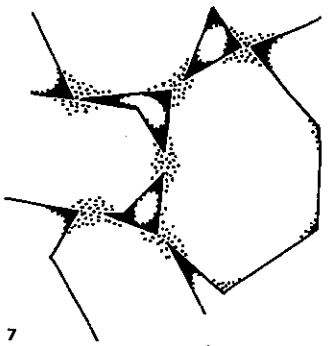

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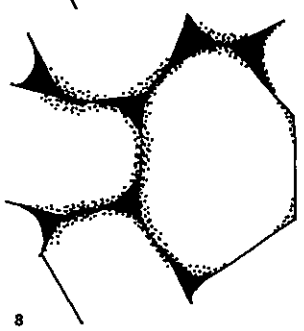

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Cooling. During cooling, the biscuit contracts at a regular rate except for the sudden contractions occasioned by the quartz and cristobalite inversions. The glassy parts of the body set solid, possibly with crystals, binding the whole into a strong unit.

GLAZE FIRING. There are two types of glaze firing: the one in which glaze and body mature together; and the one in which the body is already matured and only the glaze is affected. Both types have advantages and disadvantages.

An example of the first type is porcelain. With porcelain, the body matures and becomes translucent during the glaze firing. At the same time the glaze matures and together body and glaze create a thick body-glaze layer which is often thicker, in section, than the pure glaze layer.

An example of the second type is raku. Here the body is already fired to a temperature equal to or higher than the glaze firing. It is therefore unaffected by the heat of the glaze firing but the glaze changes completely. There are obvious advantages in this. The biscuited ware can be inspected with the knowledge that it will retain its biscuit properties of soundness and shape through the glaze firing. Delicate ware is easier to handle. With the English industrial earthenware method, the differences in temperature between biscuit and glaze are marked. The biscuit temperature may be in excess of 1250°C and the glaze below 1080°C (2282°F and 1976°F respectively). The terms bisc and glost are used for these firings to indicate this temperature difference. See ***Bisc*** and ***Glost firing***.

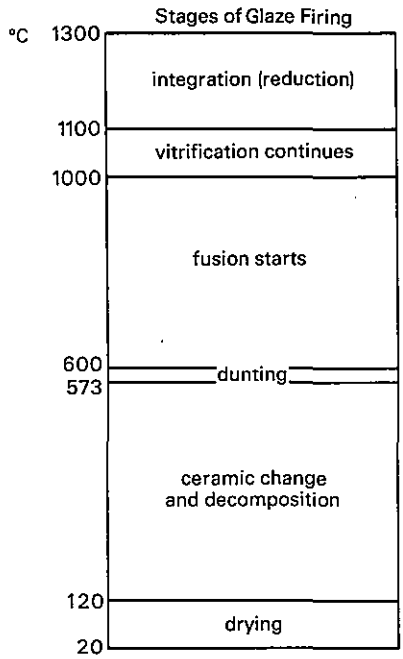
The disadvantage of a glost firing is that there is little body-glaze layer established. Glaze fit must therefore be accurate. Without it, the glaze readily crazes or flakes.

Returning to the first type, in which body and glaze mature together, one can see that the advantage is in the establishment of a sound body-glaze layer. The integrated ware has a soundness which can be related in terms of strength in comparison with unglazed ware. For example, a piece of glazed porcelain can be twice as strong as its unglazed counterpart. The strength lies in the integrated bonding of body and glaze with the slight compression of the glaze by the body. Integration also gives integrated colour, a fact made full use of in reduced stoneware. Earthenware, although not reaching the vitrified state of stoneware, can still make use of this integration if the biscuit firing is around 950°C (1742°F) and the glaze firing around 1100°C (2012°F).

The disadvantage of this combined maturation is that the body or glaze might be affected adversely. Fluid glazes are absorbed by porous bodies and can cause over-fluxing which results in warping, bloating and deformation, although the glaze effects themselves are interesting. Stiff glazes, like lime and dolomite matts, do not integrate well on some buff bodies. The body inhibits the glaze's fusion unless reduction can be used to create fusion with iron oxide at the body-glaze interface. Body and glaze must be matched to achieve maximum benefit from the body-glaze integration.

The combined maturation can occur in a glaze firing which follows a soft biscuit or in the firing of a glaze applied to raw ware. See ***Raw glazing***. In the following description, it is assumed that there has been a biscuit firing to 1000°C (1832°F). The glaze firing is a stoneware glaze firing to 1300°C (2372°F). The stages are described under headings taken from the accompanying chart.

Drying. The first 100°C (180°F) of the firing, from room temperature to beyond the boiling point of water, is a drying period. Most glazes are applied as suspensions in water and this water must be driven out of the absorbent biscuit. It must be done slowly. Many potters do it prior to kiln packing by a system of open, slatted shelves and a moving current of warm, dry air. There is an advantage in this when one has to fire the glaze within a tight schedule but a slow warm-up to the glaze firing is acceptable. Too rapid a warm-up will not burst the pots as with raw ware, but it will loosen the glaze from the biscuit. Loose glaze either falls off or crawls when it starts to fuse. The defect is known as wet ware.



Ceramic change and decomposition. A final glaze requires a number of oxides but these oxides do not necessarily appear in the glaze recipe. The recipe includes raw minerals and prepared materials which are also carbonates, sulfates and clays. This use may be for a special effect, ease of handling before firing or for economic and supply reasons. The firing converts these minerals to oxides. Clay is converted to alumino-silicate by the ceramic change between 350°C and 700°C (662°F and 1292°F). Carbonates and hydrates decompose at various temperatures up to 900°C (1652°F). Each compound has its own decomposition temperature. Sulfates often require the presence of other minerals to assist their decomposition. See ***Ceramic change*** and the individual mineral concerned. Resist waxes burn out between 200°C and 300°C (392°F and 572°F).

Dunting. The biscuited body is subjected to a sudden expansion because of its crystalline silica content. This occurs at 573°C (1063°F). A temperature rise which is too rapid could create a large temperature difference across a pot causing a stress which results in a crack. See ***Dunting: firing dunts.***

Fusion starts. Some fusion starts at 600°C (1112°F) with sodium and potassium oxides. Also the earthenware glaze fluxes, lead oxide and boron oxide, start their work here. By 1000°C (1832°F) most earthenware glazes are semi-molten but stoneware glazes, although bonded like a biscuited body, are rarely as vitrified as the body at this point.

Vitrification continues. Up to the biscuit temperature, the body is unchanged. But from that temperature upwards, the arrested vitrification continues. It is here that the body fusion actually assists the slow fusion of the glaze. But while the body makes a slow but steady maturation towards the final temperature, the glaze makes an increasingly rapid one. The glaze fluxes start their action at different temperatures and therefore, as the temperature rises, more fluxes become involved in active fusion. The oxides of calcium, magnesium and zinc are notable examples. See ***Fluxing action*** and ***Viscosity of molten glazes.***

Integration. During the later stages of firing, the body and glaze flux each other to produce a body-glaze layer. This is the period of the active glaze fluxes. It is the period over which the glaze truly melts to a glass. Previously the body has been susceptible to reduction. Now the glaze too is affected by reduction. The use of reduction to assist creation of the body-glaze layer in stoneware and porcelain is most effective as the glaze starts its fusion. Once the glaze has fused, the effects of reduction are limited to the surface.

Part of the body-glaze layer begins to crystallize as it forms, encouraged by the formation of mullite. Some glaze crystals, notably wollastonite, also begin to devitrify from the melt during this period.

Cooling. At the top temperature of the firing, there are a number of crystals growing or establishing nuclei for later growth. Upon cooling, growing crystals establish a firm bond between body and glaze, and in some glazes create a crystalline opacity or matt surface for the glaze. Cooling is part of the firing 'cycle' and its rate affects glaze shine, colour and mattness by allowing or hindering reoxidation and the formation of crystals.

Even the relatively refractory stoneware glazes do not set solid until about 500°C (932°F). Crystals are able to grow during cooling down to about 700°C (1292°F), after which, the glaze slowly sets, becoming stiffer and stiffer. The final colour is not reached until below 150°C (302°F).

During cooling from 1300°C (2372°F) to room temperature, a body and a glaze contract about 3% volumetrically. If a glaze contracts more than the body, it is put under tension and might break to accommodate the stress. This is called crazing. If a glaze contracts less than the body, shivering might result. See ***Glaze fit.***

Two temperatures at which trouble can occur are the dunting points of 573°C and 226°C (1063°F and 439°F).

Here, the free crystalline silica in the body is subjected to a sudden decrease in size. Wide bowls and thin pots on thick shelves are prone to cracking if the temperature-fall rate is too rapid. The 226°C (439°F) decrease in size is unusual in stoneware but often present in earthenware where it helps to compress the glaze and prevent later crazing. See ***Cristobalite*** and ***Glaze fit***.

Firing cycle

The time and actions of firing and cooling pottery. The term is used in relation to graphs or other information about the rate of temperature rise and fall. The word cycle implies that it is repeated but it is really only a part of the larger kiln cycle which also includes packing, drawing, cleaning up and sorting the ware.

First red

Description of the incandescent glow of the pots in a kiln. The temperature is about 600°C (1112°F) and is an indication that dunting point 573°C (1063°F) has been passed and that the ceramic change is almost complete. Where open flames are concerned or electric elements may be glowing, the first red is about 500°C (932°F).

Fishout

Draw-out test. Trial. Draw ring. Any object taken out of the kiln during firing to determine what is happening within. Buller's rings are fishouts. Loops of clay are often used and glazed appropriately. These are easily withdrawn by a hooked rod. The effects of glaze fusion and reduction can thus be considered during firing and appropriate action taken. They are particularly useful in determining the glaze layer in salt glazing. Note that there is a danger in using a metal rod for fishouts from an electric kiln.

Fit

See ***Glaze fit***.

Flaking

See ***Shelling***.

Flambé

Rouge flambé. Iridescent red glaze produced by transmutation of colloidal copper into a relatively transparent glaze.

Flameproof ware

Fireproof ware. Ware capable of withstanding the extreme thermal shock of direct flame contact. Ovenware withstands a temperature of about 300°C (572°F) all over. To be flameproof a pot must withstand 500°C or 600°C (1112°F) in direct contact at one point only. Another part of the pot may be quite cool. Extremes of heat expansion must take place and very few bodies are capable of absorbing the difference.

Primitive cooking pots are sometimes flameproof. The globular form of these pots is strong and resilient to thermal shock. The extra flameproof quality can be attributed to careful selection of materials, empirically discovered, which contain a high proportion of micaceous sand. Also, an extremely low firing was used which achieved the ceramic change but did not flux any free silica to form a glassy matrix. The body particles are held together by sintering of the particles which leaves the mass extremely elastic. In addition, porous pots are often soaked in oil. The oil assists the heat transference by filling the pores which are otherwise an insulation.

Some high-fired porcelains are also flameproof. They have achieved a state where they contain negligible crystalline silica. Free silica has been fused and so rendered of low expansion rate. See ***Table 26***. These porcelains are almost glasses but do not contain any of the oxides of high expansion rate which have low resistance to thermal shock. They are fired at over 1400°C (2552°F) which is necessary to vitrify the extremely pure form of china clay which is used.

Some medieval cooking pots were used on the fire but it is unlikely that they withstood the flames or direct contact with the hottest parts of the fire. For cooking there is sufficient heat if the pot is near to the fire or amongst the hot ashes. Today it is occasionally possible to make a soft-fired redware which is capable of withstanding a gentle flame.

Since the making of the first cordierite body by Felix Singer in 1926, many ceramicists have tried to produce a commercial cordierite body. Cordierite is a magnesium alumino-silicate of low expansion and cordierite bodies withstand flames. The difficulty lies in producing a sufficiently plastic body which is free from catalysts that upset the equilibrium of the cordierite. There are also lithium-based bodies which have extremely low expansions. These are very difficult to match with a suitable glaze.

Flashing

The interesting or annoying colouration and fusion which occurs when volatiles settle on pots and produce unexpected ceramic combinations during the firing. Firing by wood produces fine ash which settles on pots and gives flashing. The reducing action of a flame can also increase the fusion of a pot on one side giving a scorched appearance. Salt-glazing is deliberate flashing. The term flashing is sometimes used to describe the process of alternate short periods of reduction and oxidation, one result of which is the movement of colour from the area where it was applied to surrounding areas of a glaze surface.

The volatiles involved are sodium, lead and boron oxides and to a lesser extent barium, zinc and potassium oxides. These oxides produce shiny glaze surfaces by fluxing unglazed parts. The effect is often an attractive toasted colour.

Some colouring oxides are also prone to volatilization which thereby distributes colour to other glazes in the same kiln. Small amounts can give surprising results on what was intended to be a pure white ware. The oxides concerned are chromium oxide, copper oxide, cobalt oxide and manganese oxide.