8. Glazes

The books tell us that all matter exists in one of three possible states: solid, liquid or gaseous, or as mixtures of these. Generally the more pure a material is, the simpler its behaviour in this respect will be. The foundryman heats his solid material till it becomes a liquid, casts it in a mould, and lets it cool; it becomes solid again, the same metal with which he started. The glassmaker, using forms of solid matter which are much nearer to their natural state and much less refined than metals, has a different experience. He also heats up his solids (sand, soda, lime, felspar and so on) until they become a liquid. But during the melting and cooling they turn into something entirely different from the materials with which he started – a brittle, transparent, apparently solid substance.

Scientists have agreed to call glass a 'supercooled liquid'. When a material (e.g. water) is heated above its melting point and is then cooled again to the same temperature, it normally freezes (i.e. crystallises). But if it is cooled under special conditions (e.g. under pressure) it can exist in a liquid state below its freezing point. Liquids vary greatly in their viscosity; the complex hydrocarbon liquid known as pitch has such a high viscosity that it seems to be a brittle solid at normal temperature and pressure, and can even be shattered with a hammer; but if left for several months it will begin to flow under its own weight and to take the shape of the vessel in which it is placed. Ordinary glass might do the same, if given time: but long before the flow became measurable, crystallisation would have begun, i.e. it would become a true solid.

The stable condition for a material below its freezing temperature is crystalline, whether the crystals are visible or sub-microscopic. Ancient Roman glasses, and the glazes on early Islamic pottery, often have an iridescence which shows that crystallisation has begun at the surface layers. Lava ejected from a volcano sometimes cools quickly enough to form glassy rocks (e.g. obsidian), but given sufficient time (e.g. a few million years) they would be altered to some crystalline form.[1] All glasses are physically unstable (or rather, metastable), tending to crystallise; but some glasses will last many centuries longer than others.

There are very few glass-forming elements. Two things are necessary: small 'size' (ionic radius) and a high valency.[2] The most important glass-formers are silicon (valency 4, ionic radius 0.4Å), boron (valency 3, ionic radius 0.2Å) and phosphorus (valency 5, ionic radius 0.35Å). We have seen (Ch. 3, p. 59) that the structure of pure silica glass is thought to be a random network of silicon and oxygen continued indefinitely in three dimensions without any regular repetition (i.e. lacking the regular unit cell which is the basis of all crystals). But this random network still consists of tetrahedra of oxygens, with a small silicon in the centre, giving a whole charge to each oxygen. These bonds are very strong, and this glass therefore requires a very high temperature to melt it (i.e. to loosen those bonds).

On the other hand, atoms like potassium (valency 1, ionic radius 1.33Å) and sodium (valency 1, ionic radius 0.98Å), with large radius and low valency, have to surround themselves with eight oxygens (Ch. 4, p. 61) and can only supply one-eighth of a charge to each; their bonding power is therefore weak. If the network is modified by the presence of these atoms, two changes occur: the melting point becomes much lower, and the glass much less stable. In practice glasses containing only potash (or soda) and silica, can be made to melt as low as 780°C (with potash) or 850°C (with soda); but they are soluble in water and therefore useless as glasses or glazes.

Early in the history of glass technology it was found that if limestone replaced some of the potash or soda, the glass would not dissolve in water. This is because the calcium atom, though about the same 'size' as potassium or sodium, is divalent, and can make a stronger bond (a quarter-charge) with the oxygen atoms. This combination soda-lime-silica continues to the present day as the basis of common glass.

A later improvement was to introduce small quantities of alumina into the glass batch, usually in the form of felspar. Aluminium (valency 3, ionic radius 0.57Å) can act either as a network-maker or as a network-modifier. At the centre of a tetrahedron it can give each oxygen three-quarters of a charge (cf. p. 60); at the centre of an octahedron it will give them half a charge (p. 43). In both roles, its presence in moderate amounts will make the melt more viscous, and improve the durability of the glass.

Glassmakers like their melt to be fairly fluid, so that it can be manipulated, and they therefore use only a small quantity of alumina in the batch. But potters need a viscous melt, to prevent the glaze from trickling off the surface of their pots, and they therefore use much more of it. Glazes are simply high alumina glasses.

The analysis of an ordinary 'container glass' is:[3]

	per cent
SiO_2	72.1
Al_2O_3	1.8
CaO	5.6
MgO	4.2
BaO	0.3
Na_2O	15.6

It is instructive to convert this into a Seger Formula, in order to compare it with a normal stoneware glaze. In this form it becomes:

$$\left.\begin{array}{l} 0.55\ Na_2O \\ 0.22\ CaO \\ 0.22\ MgO \\ 0.01\ BaO \end{array}\right] \quad 0.04\ Al_2O_3,\ 2.655\ SiO_2$$

If this glass were to be ground and used on a pottery body, it would probably be too fluid, running down into 'pools', because the alumina content is not sufficient. It would also be likely to craze on a normal body, because it has too much soda and not enough silica. (Crazing is a trouble which the glassmaker does not meet, since he is not using his glass as a 'coat' on another material, clay.)

To obtain a conventional stoneware glaze, with a suitably high viscosity and low thermal expansion, the potter would work to a formula more like:

$$\left.\begin{array}{l} 0.3\ Na_2O + K_2O \\ 0.7\ CaO + MgO \end{array}\right] \quad 0.5\ Al_2O_3,\ 4.5\ SiO_2$$

using felspar (for the alkali and for some of the alumina), a little clay (for additional alumina), limestone to balance the alkali, and enough quartz to balance the alumina. (For bright glazes the best ratio of alumina to silica lies between 1:7 and 1:10.)

We owe this system of expressing glazes as formulas to Hermann Seger (1839–94). The formula takes the same shape as that of felspar (1.0 K_2O, 1.0 Al_2O_3, 6.0 SiO_2), but it was found that for glazes the best ratio for the alkali and alkali-earth oxides (CaO, MgO, etc.) was 0.3 K_2O, 0.7 CaO (or in general terms, 0.3 R_2O, 0.7 RO). Seger's cones are expressed in this form, the 'R_2O plus RO group' (usually written simply as the 'RO group') being kept constant at unity, the Al_2O_3 and SiO_2 being in the ratio of 1:10, and both increasing by definite steps of 0.1 and 1.0, so that the batches become gradually less fusible and more refractory. His system was based on chemical concepts, the alkali and alkali-earth oxides being the bases, the silica the acid, the alumina the amphoteric oxide; but it harmonises well with the random-network theory of glass, the silica being the network-former, and the RO group the network-modifiers, while the alumina is still in an 'amphoteric' position, a sort of honest broker acting either as a network-former or modifier according to the proportions of the other oxides.

The formulas for some of Seger's cones have been modified since he first produced them, especially in the lower temperature range. But in the stoneware and porcelain range they remain unchanged; thus cone 7 is RO, Al_2O_3 0.7, SiO_2 7.0; cone 8 is RO, Al_2O_3 0.8, SiO_2 8.0, and so on. His system is thus particularly useful for stoneware and porcelain glazes.[4]

It is sometimes held by artist potters, especially in England, that it is a waste of time to calculate glazes according to the Seger Formula; that the method does not help in producing glazes of an interesting aesthetic quality; that better glazes were being made for centuries before this method was introduced; that stoneware glazes in particular allow a wide variation in composition, so that provided you have a sound point of departure, such as the '4–3–2–1 Rule',[5] there is no need for formulas and formula weights; that calculations involving abstract quantities like atomic weights, which must be looked up in reference books, are meaningless to an artist's temperament; that in any case the foundation of the method is unscientific, since silicate crystals are not made up of the 'molecules' of conventional chemistry;[6] finally, that such calculations are useless unless they are accurate, and that they cannot be accurate unless one has a complete chemical analysis of each and all of one's materials, and that the cost of this would be prohibitive.

In spite of these objections, the pioneer potter would be unwise to deprive himself of this useful tool which is still the standard practice in industry, and which only involves quite simple arithmetic. The pioneer in a strange country may often find he has to use unknown materials. Even if they have not been analysed, an approximate calculation based on intelligent guesswork is better than random experimentation. The 'back-yard' pioneer will often wish to try out unusual raw materials, and here again, even approximate calculations will help him. There are so many possible causes of failure in a potter's life that it would be a mistake for him to reject a method which will save valuable time, which is certainly capable of enhancing both the technical and the artistic merits of his glazes, and which in the process may possibly also enlarge the confines of his wits.

The so-called 'molecular' or 'formula' weights of potters' materials are a stumbling-block to the non-scientific temperament because they have no apparent connection with sensible weight or lightness. When the scientist tells us that the specific gravity of galena (lead sulphide, PbS) is 7.5, and of felspar 2.6, we feel in our bodies a common ground of instinctive agreement, but when we are told that the 'formula weight' of galena is 239, while that of potash felspar is 556, our senses naturally rebel. The formula weight is simply the sum of the atomic weights in a formula; the more complicated the formula becomes, the 'higher' the formula weight: thus sugar, the formula for which is ($C_{12}H_{22}O_{11}$), has a formula weight of 342, but it is not so heavy as sand (formula weight 60). Atomic weights, on the other hand, like specific gravity, express the sensible lightness or heaviness of a material; e.g. metallic lead, specific gravity 11.34, has also a high atomic weight (207).[7] The difficulty with atomic weights is that since atoms are far too small to be weighed, an indirect standard has to be used. The atomic weight of oxygen (16) means that 16 g (or 16 lb) of oxygen *contain the same number of atoms* as 1 g (or 1 lb) of hydrogen. Similarly with 27 g of aluminium, 28 g of silicon, or 56 g of iron; they contain the same number of atoms as 1 g of hydrogen or 16 of oxygen.

In glaze-making we are not using elements, but mixing compounds – combinations of elements – which can be expressed as chemical formulae. Our object is to mix the materials – ultimately the atoms – in the right proportions. If the material is sufficiently pure we can use its theoretical or 'ideal' formula and formula weight.[8] If it is not pure (e.g. a natural rock or clay) the formula and formula weight can be found, provided we have sufficient data about the atoms it contains – that is, provided we have an analysis. The calculation can then be done in exactly the same way as for pure materials.

The formula and formula weight are arrived at from the ultimate analysis as follows:

Granite analysis[9]

SiO_2	71.86	MgO	0.66
TiO_2	0.50	MnO	0.06
Al_2O_3	14.63	K_2O	5.32
Fe_2O_3	0.15	Na_2O	2.92
FeO	1.26	P_2O_5	0.42
CaO	0.87	FeS_3	0.31
BaO	0.03		

Each oxide is first divided by its formula weight (SiO_2 by 60, TiO_2 by 80, etc.) the atomic weights being obtained from a reference book. The equivalents are now arranged as a formula collected into their groups thus:

Delank granite	75 per cent
Limestone	17.5 per cent
Fusible clay F	7.5 per cent

This mixture has about 1.7 per cent iron oxide, and is a good medium celadon at 1260°–1270°C.

The Seger Formula in fact enables us to make, in a few hours, a transition which in the evolution of ceramics took about a thousand years. This does not mean that we make better pots than the ancient Chinese: it merely shows that we have better tools at our disposal.

The main use of the Seger Formula is that it provides a simple means for controlling the balance of the three groups (RO, Al_2O_3 and SiO_2) and the composition within the RO group. These play the chief part in determining the character of a glaze; for example, (1) its fusibility; (2) the length of the temperature range over which a glaze can be used without overfiring; (3) crazing; (4) viscosity; (5) the colour and stability of in-glaze pigments (especially iron pigment); (6) surface quality (whether 'bright' or 'matt').

All these factors are closely interconnected, but before stoneware glazes are considered in detail it is useful to have a general picture of glaze compositions. Various classifications have been proposed; e.g. by the maturing temperature, as 'soft' (800°–1050°C), 'intermediate' (1050°–1250°C) and 'hard' (above 1250°C); or as fritted[12] and raw, a 'raw' glaze in industrial terms meaning one which contains no fritted material.[13] The most useful classification is that based on chemical composition, e.g. lead, alkaline, borosilicate, zinc, felspathic, etc. Typical formulas of standard industrial glazes over a wide range of temperatures are well illustrated by a chart published in 1931 (see Fig. 8.1, p. 158). The upper part of the diagram shows the equivalents for the alumina and silica through the range 800° to 1400°C; the lower part, the distribution of the $R_2O + RO$ group among the various bases. Borosilicate glazes cannot conveniently be shown on the chart, since the presence of B_2O_3 reguires changes in the proportions of the alumina and silica. B_2O_3 is a usual ingredient in the 'fritted range' (960°–1200°C), starting at about 1.5 equivalents at the lower end (960°C) and decreasing to about 0.25 at the upper end (1200°C). But in boron-free glazes the diagram enables us to read off the approximate formula of a typical glaze at any maturing temperature; e.g. a glaze for cone 8 (1250°C) has the formula RO, 0.5 Al_2O_3, 4.55 SiO_2; and the RO group consists of about 0.3 'KNaO', the balance of 0.7 equivalents being made up chiefly of CaO, with small and optional amounts of MgO and ZnO. But the chart is only a general guide to the standard glazes used in industry; there are many good glazes which depart widely, for one reason or another, from the proportions given.

To return now to the six factors listed on p. 149:

1. *Fusibility* is obtained in the cone 8 region by keeping the alumina and silica fairly low without departing far from the 1 :10 ratio, e.g. the porcelain glaze quoted on p. 148, in which the alumina and silica are much lower than the chart lays down as normal. It makes a bright, transparent, simple and 'truthful' glaze which is good for displaying the colour and quality of body and slip, and of inlay or sgraffito decoration. It takes blue pigment well, provided it is used on a porcelain or white stoneware body, but it reacts quickly with iron pigment, making it run.

2. This glaze has a rather narrow *maturing range*. Above cone 9 it becomes watery in quality and sometimes develops blisters. This can be cured by increasing the 'KNaO' at the expense of the CaO, and increasing the alumina and silica up to and even beyond the norm given by the diagram, so that the formula becomes:

$$\left.\begin{matrix} \text{KNaO} & 0.424 \\ \text{CaO} & 0.576 \end{matrix}\right] Al_2O_3\ 0.61;\ SiO_2\ 4.00\ \text{(Glaze 'HF')}$$

with the batch recipe potash felspar 60, quartz 6.25, limestone 13.75, SG plastic clay 20. This has a range from about cone 7 to cone 10. In spite of the low Al_2O_3/SiO_2 ratio (1:6.6) it is still a bright glaze, almost as clear as the first, but with more body; the surface though not at all matt has more texture. This is because of the high ratio of alkali in the RO group (or the high percentage of felspar in the batch); the composition has moved some way towards the formula of ideal felspar (in which the alkali occupies the whole of the RO and the Al_2O_3/SiO_2 ratio is 1:6) and away from that of the $CaO - Al_2O_3 - SiO_2$ eutectic (page 67), in which the Al_2O_3/SiO_2 ratio is 1:8.1.

3. *Crazing*. Both this glaze and the first will have a tendency to craze on some bodies, the first because the silica is low, the second because the alkali is high (cf. Appendix 12). This is cured by increasing the silica to more than four equivalents, keeping the Al_2O_3/SiO_2, ratio of about 1:9; and in the case of the second glaze (HF) by increasing the CaO at the expense of the alkali (that is, by using less felspar). This new formula (NC):

$$\left.\begin{matrix} 0.28\ \text{KNaO} \\ 0.72\ \text{CaO} \end{matrix}\right]\ 0.49\ Al_2O_3,\ 4.39\ SiO_2$$

with recipe K felspar 35.0, SG clay 27.5, quartz 21.25, limestone 16.25, brings us almost back to the proportions indicated by Fig. 8.1. This is a reliable, hard, rich glaze, but it begins to mature at a slightly higher temperature than HF.

4. Both these glazes will have more *viscosity* than the first, but above cone 8, HF will be better in this respect because of the high proportion of felspar, a felspar melt being always very viscous.[14] When CaO is added it becomes more fluid, unless the silica is again increased. But a glaze with more than 4.5 equivalents of silica might be underdone at cone 8. Viscosity is desirable in a glaze because it gives body, and prevents pigments from running; but a glaze which is too viscous will tend to *crawl* (p. 168).

5. The stability of in-glaze pigments depends on the viscosity, since a viscous glaze will not carry away the painting, and will not react so quickly with it. The colours produced by pigments, especially iron pigments, are much affected by the relative proportions of the oxides in the RO group (see p. 163).

6. True matt glazes (as distinct from the somewhat similar effect caused by underfiring), are due to crystallisation, the crystals being so small that they do not interfere with the smoothness of the surface. They are encouraged by moderately slow cooling down to about 1000°C, though if the cooling is too slow they may become large enough to produce roughness. There are many types of matt glaze, but in the most usual kind the crystals are thought to be anorthite; glazes tend therefore to be matt if they are high in lime and alumina, and low in the glass-forming silica. e.g.:

$$\left.\begin{array}{l}02\ \mathrm{KNaO}\\ 0.8\ \mathrm{CaO}\end{array}\right]\ 0.7\ \mathrm{Al_2O_3},\ 3.0\ \mathrm{SiO_2}$$

with a recipe felspar 33, limestone 22, china clay 35, quartz 10. Glazes containing 5 to 10 per cent of iron oxide normally give a matt or semi-matt surface (due presumably to haematite crystals) unless the cooling is especially quick.

A glaze which matures at a temperature considerably lower than cone 8 is sometimes needed, e.g. for a kiln which has cool places, or for a second chamber. But though many formulations have been proposed, it is hardly possible, using only the conventional materials of raw leadless glazes, to make a good glaze which matures at cone 5 (1180°C). Hanna[15] reported a low-melting felspathic glaze with the formula:

$$\left.\begin{array}{l}0.6\ \mathrm{K_2O}\\ 0.4\ \mathrm{CaO}\end{array}\right]\ 0.739\ \mathrm{Al_2O_3},\ 4.829\ \mathrm{SiO_2}$$

(felspar 75, plastic clay 16.25, limestone 8.75).

Like other high-felspar glazes it has a long maturing-range, beginning at about cone 6, but the quality is not interesting until cone is 8 reached, and it is liable to craze on some bodies.

Iron glazes to melt at or below cone 6 can be made by using intermediate or basic rocks of the alkali series (p. 22); thus the ferruginous nepheline syenite from Ghana (analysis and formula, p. 71) makes a good dark glaze at cone 5, when used alone, with no additions. (Cf. p. 66.) Raw glazes containing zinc oxide, which mature at about cone 4–5, are well known in industry; the following is quoted as the most fusible mixture:

$$\left.\begin{array}{l}0.4\ \mathrm{KNaO}\\ 0.3\ \mathrm{CaO}\\ 0.3\ \mathrm{ZnO}\end{array}\right]\ 0.6\ \mathrm{Al_2O_3},\ 3.55\ \mathrm{SiO_2}$$ [16]

But these glazes require an oxidising atmosphere.

In theory, the melting point of any glaze can be brought lower by diversifying the RO group, adding small quantities of Li_2O (in the form of petalite or spodumene, p. 72), and of strontium and barium carbonate; but in practice their effect is small unless they are first made into a frit. The most satisfactory solution is perhaps to introduce a small quantity of boric oxide into the formula, either as a frit or as colemanite (p. 73). The composition of this mineral varies, but a typical analysis is:

Boric oxide	(B_2O_3)	47.00[17]
Lime	(CaO)	31.00
Magnesia	(MgO)	0.70
Water		18.55
Alumina	(Al_2O_3)	0.3
Iron	(Fe_2O_3)	0.15
Silica	(SiO_2)	1.00
Sulphur trioxide	(SO_3)	1.30

The formula would be:
$$\left.\begin{array}{l}\mathrm{CaO}\\ \mathrm{MgO}\end{array}\right]\ 0.843;\ \mathrm{B_2O_3}\ 1.0;\ \mathrm{SiO_2}\ 0.024;\ \mathrm{H_2O}\ 1.55$$

and the formula weight 149.27.

Not more than 8 or 9 per cent of colemanite should be used in a batch, since it tends to cause crawling in larger amounts. Less than 10 per cent, however, is usually enough to bring the maturing temperature down to about cone 4 or 5. The following rather complicated formula develops a good quality in this range:

Formula:

$$\left.\begin{array}{l}0.25\ \mathrm{KNaO}\\ 0.07\ \mathrm{Li_2O}\\ 0.43\ \mathrm{CaO}\\ 0.20\ \mathrm{SrO}\\ 0.05\ \mathrm{MgO}\end{array}\right]\ \left.\begin{array}{l}0.45\ \mathrm{Al_2O_3}\\ \\ 0.20\ \mathrm{B_2O_3}\end{array}\right]\ 3.08\ \mathrm{SiO_2}$$

Batch:	Potash felspar	17.5	Basic slag[18]	6.25
	Soda felspar	15.0	Quartz	6.25
	Petalite	15.0	Vitrifiable ball clay CC	7.50
	Borocalcite	8.75	Fusible clay F	15.0
	Strontium carbonate ($SrCO_3$)	8.75		

The iron oxide content of this glaze is about 2.5 per cent which gives it a fairly dark celadon colour in reduction. There is a perceptible tendency to opalescence, which may be due to the basic slag, but is just as likely to come from the colemanite.[19] The melting point of this glaze might be brought lower by a small addition of lead oxide or lead frit; but since lead oxide is easily reduced to the metal, it is not usually successful if the kiln has a reducing atmosphere, as little PbO as 0.1 equivalent in the RO group producing dirty-grey opaque patches.

Stoneware glazes give so much variety in colour, texture and quality, and in the interaction of glaze and body, of glaze and slip, of pigment on (and in) glaze and even of glaze on glaze, that there is no real need to work with more than about four standard glazes. But this good rule, which would simplify the work of the dipping-shop, is always under attack from the temptations of special materials, the lure of new experiments, and the need arising from time to time to make new adjustments and to strike a balance between properties which call for some compromise solution (e.g. transparency and viscosity). The types of glazes which a stoneware potter is likely to use may be summarised as follows:

Celadons
Iron glazes
Slip glazes
Opaque white glaze
Coloured glazes (including the special case of opalescent or chün colours).

The complaint that stoneware lacks colour is rather like the complaint that there are no ‘tunes’ in the music of classical composers. The tunes are there, sometimes (though not always) better ones than those of popular music. But they are more complex and are given, so to speak, new dimensions by counterpoint, development and modulation. To enjoy and appreciate them is usually the result of a long and gradual process of cultivation, punctuated by moments of sudden enlightenment. ‘Good taste’ is a thing which has suffered by keeping bad company. Taste is rather like education: just as true education makes a man better able to realise how little he knows and increases his capacity and appetite for more knowledge, so good taste means not merely taste which has been cultivated and refined, but one which recognises its own limitations, and is capable of developing in new directions. The maxim that 'there can be no disputing about tastes' does not mean that they cannot be cultivated. Sooner or later, by cultivation or by intuition, the stage is reached where the sober colours of stoneware appear, as philosophy did to the young Milton,

a perpetual feast of nectar'd sweets,
Where no crude surfeit reigns.

The colours of glazes, unlike those of glasses, which can be seen either by reflected or by transmitted light, are normally seen only by reflected light. There are three main kinds of colour in glass: solution, colloidal and optical colours. In the first, the colouring oxide dissolves in the liquid and stains it in the same way that, for instance, potassium permanganate dissolves in and colours water. These colours are the same by transmitted and by reflected light. In the second kind, the colouring material (e.g. copper or gold) is precipitated as a suspension of solids in liquid, the suspended material being of colloidal size.[20] In the third kind, the colour is also due to a suspension, but the suspended material is not itself coloured; it exists within a particular size range (between 0.7 and 0.4m) which corresponds with the wavelength of light rays. If the suspended matter is of the size to intercept and reflect blue light, the glaze will be blue, all the other colours being absorbed.

Celadon

Celadon is a solution colour. If a glaze containing 1.5 to 3 per cent Fe_2O_3 is fired in an oxidising atmosphere, the oxide dissolves in the melt and makes a yellowish or brownish colour. The range of celadon colours, from a pale grey blue through the typical bluish-green to grey or grey green, will vary according as the firing atmosphere is fully or incompletely reducing. The colours, which are essentially the same as those of ordinary glass wine bottles, are produced by a blend of the blue of ferrous oxide with the yellow or brown of ferric oxide.[21] If the body also contains iron oxide, this will be reduced too, and will modify or deepen the colour; a glaze which would be almost colourless on a white body can give celadon colours over a dark body.

Celadon is not merely a colour; its essential quality depends also on its thickness, and on a particular kind of semi-opacity which is due to tiny bubbles of air suspended in the glaze. As the temperature rises these bubbles gradually increase in size and coalesce with each other, so that an overfired glaze, though it still has the celadon colour, will become transparent and lose its true character. A celadon glaze should therefore have high viscosity and a long firing range (e.g. the glaze HF, p. 151). The composition of the RO group is also important. The colour develops well over a range from 0.25 to 0.45 KNaO, 0.75 to 0.55 CaO; but MgO in excess tends to make brown colours even in reduction, and should if possible be kept below 0.1 equivalent. Since the analyses of some wood ashes are rather high in MgO, [22] it is probably safer, for celadons, to use the normal porcelain glaze materials.

Iron glazes

Stoneware glazes can hold only a rather small amount of iron oxide in solution, when they have solidified; the limit seems to be between 3.0 and about 4.5 per cent. But while the glaze is liquid it can dissolve much more than this, just as hot water can dissolve more salt or sugar than can cold, and it will even attack and dissolve the iron oxide from a black slip or a ferruginous body. If it is now cooled at a normal rate (e.g. six hours from top temperature down to about 800°C), the surplus oxide is precipitated as crystals of Fe_2O_3. The resulting glaze will be opaque, with a semi-matt or microcrystalline surface, and usually a reddish brown relieved with flashes, streaks or flecks of other colours, green, yellow and sometimes blue. The higher the content of iron oxide, the more opaque and metallic the glaze becomes. But if it is cooled quickly down to about 800°C, at which temperature, though still plastic, it is so viscous that crystallisation becomes difficult, as much as 5 per cent iron oxide can be kept in solution, and the glaze will be a clear bright black. Tenmoku glaze is a supersaturated solution, containing about 5 per cent iron oxide.

Two other factors have an overriding effect in deciding the character of iron glazes: the Fe_2O_3 content of the body or slip and the thickness of the glaze. Where the glaze is thin (e.g. on rims) a clear black tenmoku will become opaque brown or red, with the normal microcrystalline surface. In the critical range, between 3.5 and 4.5 per cent oxide, the glaze even if cooled normally will be a clear dark brown or dark green, with only a slight tendency to crystallisation; but if the body also contains much iron oxide (e.g. 4 per cent) the character may change quite suddenly from clear to opaque, according to the thickness of the glaze and the firing conditions. Iron glazes have an enormous range of colour and quality. Though they are affected much less than celadons by variations in the kiln atmosphere, they can be profoundly changed by alterations in the time-temperature curve of the kiln.

Opaque white glazes

Opacity in glazes is caused by suspended matter, whether gas (air bubbles), liquid (emulsion glazes) or solid. A fine mist of air bubbles will only make a glaze semi-opaque. Emulsion whites can be obtained from certain glaze compositions [23] which on melting separate into two immiscible liquids. Each liquid would be transparent alone, but if the globules of one are suspended as fine particles in the other, the glaze will be a perfect opaque white. The firing conditions for emulsion glazes must be carefully controlled because the whiteness depends on the size range of the suspended globules.[24]

The most usual opaques, and the easiest to control, are made by adding to a normal glaze a small quantity (generally about 10 per cent) of some material which will not dissolve too much in the melt; which has a sufficiently fine particle size; and which has a *refractive index* different from (usually higher than) that of the glaze itself (which is usually between 1.4 and 1.7), so that the suspended particles will scatter the incident light. Two materials satisfy these conditions: tin oxide (SnO_2 R.1. 2.0) and zircon ($ZrSiO_4$, R.1. 1.94). The chief advantage of zircon over tin oxide is that it is much cheaper. Both dissolve to some extent in the melt, and in doing so, improve the crazing resistance. Dissolved zircon also increases the hardness and durability of the glaze.

Where materials are not obtainable from potter's merchants in a milled and processed state, the tin oxide or zircon must be finely ground, since the opacifying effect is greatest if the particles are very small, approaching in size the wavelength of light (i.e. around 1μ). Natural zircon comes in the form of sand, and since its hardness is 7.5 on Moh's Scale, it has to be ground for much longer than usual, for example thirty-two hours (instead of the eight hours which is normal for felspar and quartz), with rather severe wear of the porcelain cylinder and grinding balls. (See Appendix 7, p. 297.) Even after this, the smallest size fractions must be separated by diluting the slop with excess water and carefully decanting the finest suspended particles, leaving the coarser part to be reground. In this way a very fine grade can be obtained.[25]

Zircon is a more refractory material than silica (p. 176) and an addition of 10 per cent might be expected to raise the maturing temperature of a glaze, but if this is so, the effect is too small to be noticeable in an ordinary stoneware kiln. For the cone 8–9 range, a glaze of normal composition such as NC (p. 151) produces a handsome opaque white, e.g.:

K felspar	43.75
Limestone	16.25
Quartz	17.50
SG clay	11.25
Kaolin	11.25
Zircon	10.00 (water-ground and decanted)

Formula:
$$\left.\begin{array}{ll} \mathrm{KNaO} & 0.31 \\ \mathrm{CaO} & 0.69 \end{array}\right] \mathrm{Al_2O_3},\ 0.58;\ \mathrm{SiO_2},\ 4.44;\ \mathrm{ZrO_2},\ 0.32$$

If used too thick, this glaze is liable to crawl in firing, because opaque glazes are more viscous than others.

Opaque tin glaze was used by the Delft potters to cover a porous buff-coloured earthenware body, in order to imitate Chinese porcelain. A stoneware potter may need a white opaque glaze for a similar reason; not indeed to imitate porcelain, but in order to cover a dark body and provide a white ground so that he can exploit the possibilities of painting. A good zircon opaque has the same milk-white character as a good tin glaze, and at stoneware temperature offers almost as wide a field of decorative possibilities, with the added advantage that the ware is much stronger than faience and maiolica.

Chün glazes

Since the opalescent colours of chün glazes are not of great industrial importance, they have apparently never been studied scientifically, and their causes remain a matter of conjecture. It is, however, generally agreed that they are optical colours; and the most likely hypothesis is that they are produced by a suspension of liquid in liquid (or rather glass in glass), like the emulsion glazes mentioned on p. 155. If the majority of the suspended globules are between 0.45 and 0.5μ in size, the colour will be blue.[26] If their sizes are mixed, the glaze will be a white, grey or greenish opaque.

Since the theory of these colours is still uncertain, any rules on how to produce them must be purely empirical, based on observation and on evidence which is inevitably partial and incomplete. The factors which seem to favour chün colours may be listed as follows:

1. Chemical composition of the glaze. The Seger Formula of a chün glaze is not strikingly different from the normal, e.g. 'V2' (Abuja), a fairly reliable chün glaze:

$$\left.\begin{array}{ll} \mathrm{KNaO}, & 0.34 \\ \mathrm{CaO}, & 0.47 \\ \mathrm{MgO}, & 0.19 \end{array}\right] \quad Al_2O_3\ 0.357,\ SiO_2\ 3.54$$

with about 1.8 per cent Fe_2O_3 and 0.7 per cent P_2O_5.

The MgO is slightly higher than usual, and the Al_2O_3/SiO_2 ratio is fairly high at 1:9.9. Possibly this glaze could be improved by increasing the MgO still further, and reducing the Al_2O_3 to about 0.25 equivalents.

2. The materials used. Certain materials, especially wood ash, talc, and some sort of frit, are thought by many potters to favour chün colours. The batch for the glaze quoted above is:

Albite felspar	35 per cent
Quartz	15 per cent
Plastic clay	10 per cent
Talc schist	5 per cent
VF slag	35 per cent

The last ingredient could be described as a kind of 'accidental' frit. In kilns fired with wood, the ash (if it contains enough silica) will, in the hottest places, melt to a clinker, not unlike the clinker formed in furnaces by the much more fusible ashes of coal, but of an opaque whitish colour. The analysis of this material is:[27]

SiO_2	52.05	CaO	23.05	SO_3	0.07
TiO_2	0.41	MgO	2.57	Cl	0.04
Al_2O_3	4.04	K_2O	6.68	CO_2	3.28
Fe_2O_3	2.68	Na_2O	0.96	H_2O+	1.19
MnO	0.11	P_2O_5	1.96	H_2O-	1.46

which indicates that it consists of about 86 per cent glass, of composition:

$$\left.\begin{array}{ll} \mathrm{KNaO} & 0.20 \\ \mathrm{CaO} & 0.66 \\ \mathrm{MgO} & 0.14 \end{array}\right] \left.\begin{array}{l} Al_2O_3\ 0.09 \\ Fe_2O_3\ 0.04 \end{array}\right] \quad SiO_2\ \ 1.95$$

the remainder being mostly calcium carbonate (7.5 per cent) and calcium phosphate (4.3 per cent), though it is quite possible that the latter is also in the form of glass.

The formation of a small quantity of a second liquid in the glaze (V2 above) is probably promoted by (a) the fact that part of the batch was already in the form of a low-alumina glass before firing; (b) the presence of a small quantity of calcium phosphate; and perhaps also (c) by the fairly high MgO content. The chün colours were obtained more often after the composition had been modified by the addition of the talc.

3. The thickness of the glaze. It is well known that chün glazes must be applied thick. Opalescence does not appear where the glaze is thin.

Figure 8.1. Seger formulas of glazes (from F. H. Norton, *Elements of Ceramics*) p. 12