The Practice of Ash Glazes

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Behold within the curious chemist’s cell
when he would gain the essential salts of plants
he turns them all to ash, the stuff of soap and
from that death revives a perfect work,
restores to life the secret source of ideas enclosed
within the tomb, lilies and roses,
roots, branches, stalks, leaves and flowers
that reveal to our eyes the brightest hues
having the fire for father, ash for mother:
their resurrection then may teach the fearful
that those who are burned, ashes cast to the winds,
rise up again more lively and more lovely than before.

Agrippa d’Aubigné
Les Tragiques, book 7

Introduction

The art of using ashes in the development of stoneware glazes is full of paradoxes. To start with, it is not difficult to imagine how potters first discovered it in times gone by. Once they had mastered the use of high temperatures, using wood as their fuel, the ash from their kilns must very soon have appeared as a possible component of a glaze, simply by the way it would begin to melt on contact with the bricks of the kiln or the pots themselves. Needless to say, it took a stroke of genius to pass from the observation of that phenomenon to the glazing of a pot, but it certainly looks as though such genius was not lacking in the early days! So ash was made use of, a readily available raw material, and it provided what might be called ‘poor man’s glaze’ because ash is so generous that, with only a minimum of manipulation, it provides useful and pleasant glazes.

As is so often the case in many areas of life, ‘old style’ techniques that used to be very common, widespread in different regions, are nowadays invested with a new prestige; for example, smoked pottery, where the introduction of free carbon into the body of pots as they are cooling makes them more or less watertight, despite their lack of glaze. The same is true of varnished earthenware, waterproofed thanks to the minute size of the particles of the clay slip applied to the raw body. Other examples that might be quoted include salted stoneware and even raku, certainly very different from one another but both involving a minimum of means.

We might wonder if nowadays the creative craftsman does not feel an almost visceral need to go back to the origins of the craft, to repeat the experiences that underlie its basic techniques. This in response to the anonymous nature of industrially produced objects, easily employed on a daily basis by everyone, while remaining totally ignorant of what they are made of or how they are made.

One extreme example we might take could be the television screen, truly a ‘magic lantern’ for everyone, yet people no longer feel any sense of wonder at the production of such an instrument, that works at the simple push of a finger, the magic wand available to all.

Such a return to primitive techniques can sometimes be the result of a nostalgia, staking a claim to the prestige attached to things from the past. Assuming it escapes that danger, however, the effort of documentation and understanding of the phenomena involved often encourages a creative adventure that is firmly turned toward new directions.

The art of ash is part of this return to the sources. For those who engage in it, the result is a renewal that very soon achieves an interest far beyond a simple liking for old-fashioned methods. While the potter is, likewise very soon, going to discover that things that seemed so simple to begin with belong in fact to a universe of immense complexity.

Ash, the remains left after combustion, is composed of a mixture of minerals that have been extracted from the ground by an intermediary, the plant, a living organism. This collection of minerals is by no means the fruit of chance, but represents in its own way the type of vegetable that produced it. As might easily be expected, then, introducing ash into our potters’ glazes involves introducing the very complexity of life itself into our research. That means accepting from the start the need for a constant adaptation to the variations found in our raw materials. It also means accepting from the word go that we shall find no answers to many questions, imposing on us a certain measure of empiricism, in the midst of which we are obliged to try to find the best possible method to avoid losing our way amidst the shifting sands.

Many questions indeed, and many uncertainties caused by a lack of books on a subject that scientific research has taken little interest in. All of which might discourage potters seeking new glazes, those at least who avoid anything that cannot be exactly measured and controlled, always assuming that with our art of fire it is at all possible to claim any mastery over the agents that produce the essential metamorphoses!

In actual fact, it is the abundance of riddles that serves rather to stimulate this kind of specifically small-scale research, potters being in a situation where they can permit themselves to make use of such limited and ever-changing materials as ash.

As we have already said, the potter can obtain good glazes from ash with a minimum of additions, or to be more precise, with varying additions of alumina and silica. The history of ceramics, especially in Asia, gives many examples of this. If now the potter begins to modify the quantities of these additions in order to change the fusion or the appearance of a glaze, or takes ash of a different plant, and if s/he is careful to interpret the resulting test pieces, s/he ends up making a great number of observations that constantly provoke new questions and new experiments. Phenomena may appear in the color or texture of a glaze that a potter tries to find the cause of. In this, analysis of the elements contained in an ash will prove useful, since it will permit the approximate reconstitution of an ash using the workshop's usual minerals. The elements combined in an ash are indissoluble, whereas an artificial reconstitution allows us to vary their proportions and thus better determine the role of each.

At the point we have reached in our research, we see a double originality in vegetable ash: there is the association of different minerals that characterizes each species of plant, and to this we must add the necessary presence of phosphorus, the element responsible for the distribution of the energy captured by each plant's chlorophyll. So it is that we owe to ashes the discovery of 'models' of glazes that without them we would never have been able to imagine. That leaves unanswered the question of how it is that this or that plant, with its personal history linked to its species, terrain, and to meteorological variations, is able by its ash to direct us toward this or that glaze? To put it in other words: what is this strange 'cousining' by which a complex of minerals that in nature yields a pear, a pineapple or a grain of corn, yields in the potter's kiln a green, a blue or a nucleated glaze?

This book is a revised version of a text first published nearly thirty years ago. It does not claim to be a scientific *opus*, or an exhaustive study of its subject; it is simply a report of the research and work of a workshop, to the history of which it is closely linked. Many questions we have asked ourselves remain without a reply and we have refused to generalize on the basis of experiences that are necessarily fragmentary. At times we have preferred to describe step by step certain experiments when their results have seemed significant to us, in particular when dealing with compositions that include phosphorus.

This work often refers to the text of its companion volume, *The Practice of Stoneware Glazes*, whose method it follows and complements.

Part One: Obtaining ashes

“There is no plant or species of grass on this earth that does not contain within it some kind of salt, and moreover I tell you, that there is no tree of whatever kind that does not consequently contain it, some more, some less.”

Bernard Palissy: *Veritable Recipe by which all the men of France may learn how to multiply and augment their treasures.*

Initial approach

An ash obtained from a plant is the residue of that plant after its combustion. Incombustible by definition, that ash has left the vegetal world and henceforth belongs to the mineral realm. Expressed in terms of an analysis of its elements, it presents itself in the form of a collection of oxides that can now be used, like the oxides of many elements, by the ceramic craftsman. That may seem simple and obvious but in reality it is less so.

The first thing that has to be stressed is that the ash obtained by the potter is never the residue of the whole of a plant. For example, we might burn logs hewed from the trunk or main branches of an oak, bundles of the small branches, or the dead leaves of the tree, or the cuttings from a vine after pruning, the bark of pine trees, the straw of a cereal after threshing. No matter what the plant, the roots will almost always be lacking, those essential organs that constitute the doorway by which the minerals composing the ash entered the plant.

Thus an ash derives from one part or several parts of a plant. But those parts too are composite. A single log will contain fragments of the heart, the sapwood, and the bark. In wheat straw we find both the stalk and the ear emptied of its grains, in maize a sort of soft kernel contained in its envelope, and so on.

Moreover, an ash comes from a plant at a particular moment in its growth, cut at a particular season, at the rise or after the fall of the sap, before or after the fruit has ripened.

In addition, one ash may constitute the residue of a mixture of botanic species. The ash of hay is a classic example. You may heat your house with a mixture of species, soft or hard. The fires set to clear a forest that is being exploited supply ashes that are particularly composite. Likewise cutting from hedges, which are very often reservoirs of diverse species.

All of that has its influence on the composition of an ash, as we shall see later. For now, we may simply make do with the following statement: an ash is always an averaging out of the minerals distributed in different proportions in the various parts of the plants. That necessarily imposes limits on our selection. That selection will have to be made within the limits of the possible, allowing us to make manifest the ‘ceramic specificity’ of a particular species or part of a species: wood, leaves, etc. But there is no need to reject anything in this domain, and a selection is by no means an absolute necessity. At most, it is important to avoid mixing ashes of wood with those from straw from grass or bracken, for reasons that will become clear later.

The question remains as to whether the ashes of every kind of plant can be used in stoneware glazes. In principle, we may answer affirmatively, but every rule has its exceptions.

Finally, one result of what has just been said is that each category of ash must be harvested in a quantity sufficient to justify the search for a glaze. The period of experiments will take about a pound of powder, and in order to take full advantage of the initial research it seems reasonable to have a homogeneous stock of between five and ten kilograms, ten to twenty pounds or so. If you dispose of excessively limited quantities of several ashes, you will do better to combine them into a single batch.

Sources of ash

It is much to be preferred that the potter, who is normally present at each stage, should in person select and collect the plants providing ash. But it is easy to imagine that this much-to-be-desired situation is not always so readily come by. The potter whose kiln is fired with wood is obviously privileged, at least in obtaining quantities of a certain kind of ash. The potter living in the city is going to have to get in touch with bakers with wood-fired ovens, with pizzerias, carpenters' and furniture workshops that steam their planks using scrap wood, or burn their scraps and sawdust, or incinerators of cuttings in public parks. It can be an occasion to discover how willingly many people are eager to get involved in this unusual enterprise in which ashes are no longer seen as a return to zero, not simply something to be thrown away. But potters who use kilns heated by gas or electricity are going to have to arrange some outings to the countryside, since it is obviously there that they are going to find the main sources of plant-ash.

As a rough guide, here is a list, obviously limited in scope, of some of the plants that can easily be collected in the rural areas of western Europe. Sometimes they may have been burned to ashes before the potter intervenes. Well, as people say, the occasion makes the thief, and we ourselves have often taken advantage of unexpected supplies of ash, those produced for example from scraps of exotic timber in a door-frame factory.

Waste wood from a commercially expoited woodland (branches cut off before felling, small branches of underwood growth, pine bark, etc.)

Scrap wood from sawmills or carpenters' workshops.

The branches pruned from vines in vineyards, each year increasingly burned on the spot in portable stoves.

The residue left after lavender has been distilled, often later used to heat the stills.

Scraps of cane used to make fences.

Ashes from wood burned in furnaces and fireplaces.

Grass cut back along roadsides, that is often left lying where it falls.

Old hay thrown out when cleaning haylofts; bales of straw or hay spoilt by exposure to prolonged rain.

Ferns and bracken.

Plants from marshlands and river banks: reeds, sedges.

Rice straw.

Various harvested plants: rape seed, maize, so long as they have not been chopped to be plowed back into the ground.

Hedge cuttings.

Dead leaves, collected when very dry.

Every potter will be able to collect a sufficient variety, depending on the geographical situations, and personal initiative. Still, this might be the moment to warn against the dangers of being distracted by accumulating too many kinds. Wisdom suggests limiting oneself, at least in the early stages, to two kinds of ash, one wood ash and one graminous plant (or hay) and pursuing research as far as possible using a single representative of each of these categories, very distinct, as we shall see later.

Whatever the plants you collect, the first precaution is to ensure that they are clean before burning them. Take the example of a tree-trunk with deep fissures in the bark. During transport after felling, those fissures can easily fill with earth and mud, especially in wet weather. When it is burned, that earth is going to mingle with the ashes in proportions that are sometimes considerable. A few hundred grams of earth for one hundred kilograms of wood may not seem much but you have to remember that one hundred kilograms of wood only yield five or six hundred grams of ash! Then all the research for your glaze will be compromised by the presence of that earth. A potter once sent us a specimen of 'hard wood ash' he had purchased somewhere and that he had been unable to get to melt. A simple examination with a magnifying glass showed a considerable quantity of siliceous sand mixed with the ash. Ash should only be bought if the merchant offers certain technical guarantees as to its quality.

Vine-stocks and suchlike that have been uprooted should be washed thoroughly using a strong jet of water before burning.

At the same time, in this domain wanting the best can be the enemy of what is good enough and perfectionism should be avoided. A mineral introduced into an ash from outside can also produce good results. For several years we looked after a flock of sheep put out to pasture in a huge field that had been poorly tended and was partly invaded by a kind of couch grass that the sheep would not touch. It had to be mowed, providing us with large mounds of the plant in question. But moles had been at work there for a long time and the mechanical mower could not help but mix with the grass some of the strongly ferruginous limestone-based earth of the mole-hills. Despite our careful cleaning of the ashes, a significant quantity of baked red clay-dust passed through the sieve. Yet that unavoidable mixture put us on the track, from the very first test firings, of iron-red glazes produced in the presence of phosphorus in an oxidized firing.

In conclusion, let us say that the potter should be contented with what can be found, when it is found, in the best possible state. At the moment we are studying an ash produced from olive pits from Fès in Morocco where potters use the residue from olive oil presses to heat their kilns. A potter living not far from us takes advantage of the bales of straw used as safety barriers on a motorcycle racetrack . . .

Burning the plants

First, it will be as well to draw attention to a number of precautions to be taken in order, once again, to avoid mixing undesirable minerals with the ash. All traces of rust (iron hydrate) or black iron oxide must be carefully removed from stoves, furnaces or metal drums used for burning. The coloring effects characterizing many ashes could easily be affected by the presence of iron. Likewise, the space where bonfires of wood or straw are to be lit must be suitably prepared. Firmly packed earth or a layer of earthenware tiles simply placed on the ground will be enough. However, a layer of ordinary cement, not refractory, is to be avoided at all costs. Likewise fibrocement, which absorbs moisture, and then explodes when exposed to sudden heat.

When burning plants in the open air, a windless day will be best, otherwise the ashes will be scattered. They are also inclined to drift away in the rising column of hot air that results if the fire is allowed to blaze freely.

Both these points are especially important when burning plants as finely textured as straw or hay. But in these two cases there is another risk, specific to graminous stalks and bracken. In addition to the alkalis, sodium and potassium, that all ashes contain, these two species are rich in silica. In the heat of the fire, the alkalis and the silica tend to be transformed into silicates. If a wind is blowing, it may serve as the bellows, provoking a blowtorch-effect, that completes the transformation and produces liquid glass that mingles with the less burned embers and is difficult to use.

We can now turn to the actual process of burning. When it comes to logs of wood, it is hardly possible to imagine any other method than to burn them in a stove from which a portion of the ashes is cleared each day. It is advisable to place these ashes in a clean metal container including among them a small amount of still burning embers. Ash has powerful isolating qualities, and this will slow down the transformation of the embers. Their heat will spread and complete the burning of the small fragments of charcoal still present in the ashes. The same method should be used when burning wood in the open. The recipient should be filled with ashes before the fire is completely out. This will considerably diminish the ‘loss in firing’ of the resulting glaze, a great help in later stages.

Now let us consider the burning of straw, hay and stalks of maize. Here we are dealing with a real ‘flash in the pan’! the slender stalks of such plants have scarcely begun to burn before they lose their heat, yielding black filaments still rich in carbon. The following method will be found advantageous here. A large metal barrel open at the top and with the bottom pierced with small holes is placed beside the space where the burning is to be done. Fire is set to an initial batch of the straw. As soon as the smoke diminishes, the glowing straw is transferred to the barrel with an iron fork. This is repeated until all the straw has been burned. The glowing embers in the barrel must be pressed down, as a smoker tamps down his pipe. A circular disk of wood nailed to the bottom of a broomstick will do for this. Once the initial burning is finished, the tamping down must be repeated regularly until the fire is completely out. Depending on the quantity of straw, the cooling period may last several days, a week even, such is the isolating quality of ash. Obviously, the barrel should be covered with a sheet of galvanized iron in case it rains.

Other situations may also be encountered. Dead leaves, collected when they are very dry, should be burned handful by handful directly in the barrel. The husks of cereals, difficult to handle, can only be burned in a pile, kindled with the help of some paraffin. The fire burns slowly inward and the ashes should be gradually ‘creamed off’ as they form.

Ferns are burned while still green, the fire in this case too being lit with paraffin. They are burned after mowing, usually in July. These used to play a major role in glass-making, before sodium was extracted from sea-water, on account of their rich alkali content. Again, too fierce a fire presents the danger of making these silica-rich ashes melt. In the old days, ferns were burned in a smothered fire, a new layer of green plants being placed on top of the flames before combustion had advanced too far.

In all this, experience will help the potter invent the methods best adapted to each situation.

Sieving and washing

Once you have your ashes, your next task is to ensure the homogeneity of your stock, This is done by sieving, done over a large sheet of plastic. Since ash is corrosive, a well-fitting mask is a necessary protection. For all types of ash, a mason’s sieve for finely grained mortar (3 meshes per centimeter) will do. The act of sieving, repeated two or three times, will separate out most of the imperfectly burned embers, if any remain. From now on, the work will vary, depending on whether you are dealing with wood ash or straw ash. Wood ash does not need to be washed. It only has to be passed once through a finer sieve (13 mesh). Although in actual fact, each potter should feel free to decide the most suitable mesh for the sieving, it may be finer or coarser than that indicated here.

The choice depends on an examination of the ash through the most powerful available magnifying glass (a thread-counter). If you can see a significant quantity of grains that are clearly foreign to the ash, you may want to try using a finer mesh while recognizing that it is virtually impossible to obtain an ash free of all ‘impurities.’ Once the operation is complete, the ashes, which are highly absorbent, must be stored in airtight containers tightly closed and placed away from humidity. Each container must be labeled in an indelible ink that does not fade in daylight.

For reasons which will be explained later, the ashes of cereal straw and grasses need to be washed. This will most conveniently be done by milling the ash in water. This is perhaps the moment to insist that for all work using ashes, the use of a ball-mill is strongly recommended. This saves a lot of time otherwise wasted in grinding everything by hand in a mortar, to say nothing of the resulting waste of raw materials, which can be considerable. Straw ash, after a first sieving (mesh 3) is milled for one hour. Since the mill will not be able to contain all the ash at once, the milling will be repeated as many times as is necessary. The contents of each succeeding milling are poured into the same tub, thus achieving the homogeneity of the batch by a thorough mixing. Even if the straw was well burned, the resulting slurry will almost always be black, probably on account of the presence of graphite, that only disappears at high temperatures. After the slurry has settled, the surface layer of water is siphoned off; it is extremely alkaline and soapy after this first washing (ashes were used in times past for washing linen). It should be noted that containers made of aluminum must be rigorously excluded since they are dissolved by alkalis. Fresh water is then added, the mixture stirred and allowed to settle, then the water removed again, an operation repeated several times, depending on the quantity of ashes and the size of the tub. Four or five washings are usually needed before the water loses its high alkaline content, verified by simple touch. Finally, as much water as is possible is siphoned off and the milled ash is allowed to dry completely on planks of wood (never plaster). It is also possible to employ filtering bags made of nylon. The storage follows the same rules as above.

It may happen that a wood ash has been moistened or soaked by rain or need washing for some other cause, ashes from a forest fire for example. Such ashes must then be completely washed for the following reason. As the ashes dry out, evaporation will bring to the surface partly dissolved alkalis. These then tend to form a crystalline film that may be more or less thick and hard, that will make the remaining operations difficult. This surface deposit also occurs whenever a clay body contains salts, which are soluble by definition. This is the phenomenon governing the production of clays known as ‘Egyptian.’ It can equally be observed with clays that contain iron salts. If you apply an adhesive strip of any kind to a plate of such a clay, preventing evaporation from the portion covered, there will be a clear contrast between the masked portion and the rest of the plate.

At this point, a remark about lavender ash must be made. Once it has been distilled, the residue of this plant is used to heat the stills. The resulting ashes are then thrown out by the distillers, and form a deposit in the open air that may be of considerable thickness. When rain falls, the alkalis, which are here very abundant, dissolve and filter down toward the bottom of the pile where they crystallize out. One day we were given a batch of such ash collected at the bottom of the pile, that looked like coarse salt. Once washed, almost nothing remained. As a result we learned that lavender ash must be collected directly from the hearths of the stills.

Part Two: The composition of ashes

The first question facing potters is what contribution an ash is going to make to the creation of a glaze. But they may also be interested in the journey those minerals have made from underground to the glaze, by way of a plant and its ashes. We have asked ourselves many questions about it, and have asked many every time we met, often by chance, some ‘specialist.’ We have thus obtained a certain number of answers, but also a lot more questions, since the questions have not always been studied, or even asked, at least not in the way the potter asks them. In what follows, we will only indicate a few essentials points, those likely to shed some light on the potter’s undertaking.

From the soil to the plant

Of the 106 elements composing the earth’s crust, 99 are put to use by the vegetal realm. In order to be admitted into a plant, the molecules in question have first to be dissociated into negatively charged ions. That first operation is done by the micro-organisms in the soil, bacteria and fungoids. After that, by means of osmosis, those ions are able to pass through the membrane of the roots. They then go on to fulfill their specific function in the plant’s physiology, a function that is at present only known for 32 elements.

Each vegetal species draws in this way from the ground the minerals that characterize it. Just as, in the animal realm, we find herbivores, carnivores and omnivores, plants too do not necessarily all ‘feed’ in the same way. More precisely, while most of the elements absorbed can be found in every plant, the proportions vary to an often considerable extent.

The mineral selection proper to each plant is therefore not dictated by the nature of the ground, as people often think. It is not because the soil in one place is rich in a certain element that the plants growing there will absorb more of it. We have confirmed this by comparing analyses of ashes of the same species gathered from a limestone region and from a granitic one.

Naturally, if a certain mineral required by a species is too rare or absent from the soil, the plant will suffer certain consequences. We have heard reports of oats deprived of manganese and therefore unable to grow more than ten centimeters high.

It is, then, the capacity of selective absorption of every species (and to a far lesser extent of each individual plant) that is decisive and here great disparities can be found.

Many species will grow anywhere. Pines, oaks, hazels etc. all manage to choose the necessary ions in any type of soil. Thanks to their remarkable power of concentration, such plants are capable of absorbing from an acid soil the small amount of calcium available, which then forms the dominant constituent of their ashes.

Whereas for other species, the nature of the soil conditions entirely their existence. Every walker knows that you do not find bracken on limestone or boxwood on granite. Broom grows on an acid soil, yet its concentrating power is such that it is able to provide itself with reserves of calcium in the form of small concretions of carbonate attached to its roots. The chestnut tree definitely prefers acid soil, yet that does not prevent it from making do on limestone. While the analysis of the two kinds of wood shows only minimal differences.

Certain plants are amazing in their ability to adapt to unusual soil conditions. People familiar with commercially exploited woodlands will have noticed circular carpets, pale green in springtime and rust-colored in autumn, composed of moss. That moss seems to be the only plant capable of growing on the mounds of ash left over from the fires set by the woodcutters to burn waste wood, and it will grow nowhere else. That only goes to show, if it was needed, to what extent nature has learned to adapt to every situation, developing ways of living that constantly amaze us.

The elements in the ashes

The elements gain entry into plants in the form of compounds, oxides, carbonates, sulfates, nitrates, phosphates, silicates. Some are destined to become an integral part of the plant. Whereas the sodium and potassium are only ‘lent’ to the plant until it is fully grown, then returned to the soil. That explains why the alkaline level of an ash depends on what stage of growth the plant had reached when it was harvested, before or after full maturity. If sodium and potassium are present in the ash, that is because when the plant was being burned, the silica present combined with part of the alkalis, the remaining part remaining soluble, ready to be removed by washing.

What is important for the potter is that the analysis of an ash, whatever the method used (spectrograph, X-ray fluorescence), must always be expressed in terms of the oxides of the various elements present. In that way, the analysis harmonizes with the conventional notation of the oxides in a glaze, and it is that form that we will from now on indicate the contents of an ash.

First, here are two examples:

	Oak	Horsetail (*Esquisetum arvense*)
Lost in firing (LF)	31.61	16.58
SiO_2 Silica	5.45	40.96
Al_2O_3 Alumina	1.09	1.97
Fe_2O_3 Ferric iron oxide	0.3	0.4
P_2O_5 Phosphorus oxide	4.38	3.34
TiO_2 Titanium oxide	0.07	0.08
CaO Calcium oxide or lime	37.97	18.79
MgO Magnesium oxide	2.79	6.43
MnO Manganese oxide	3	0.02
K_2O Potassium oxide	10.56	10.58
Na_2O Sodium oxide	0.26	0.19

A comparison of the compositions of these two ashes leads us to make several additional observations and comments.

For the practical needs of the analysis, the ashes had first to be subjected to a temperature of about 1000 ° for several hours. That served to reduce the volume of unburned particles and the carbonates included in the ash, making up the total of what is ‘lost in firing’ (LF). An analysis after this serves to indicate what will remain of the ash in the fired glaze. It is essential that this LF quantity be indicated in each analysis, in order to find the molar mass of the ash.

The ashes of two organisms as different as an oak tree and a little horsetail plant turn out to be made of the same oxides. Only the percentages vary, as with every plant. A number of trace elements (oligo-elements) have not been included in the analysis on account of the minute quantities involved (copper, boron, fluorine, cobalt, cesium, strontium, etc.), though they are essential for the metabolism of the cells. That does not mean that the potter’s fire will not make anything of them (!) but it is impossible to indicate to what extent each is chosen by different species of plant.

Lime predominates strongly in the oak ash. That will prove true of all kinds of wood, calcium “being employed especially for the pectins that ensure the rigidity of the plant” (C. Bourguignon, *Nature et Progrès* numbers 110-111). By contrast, in the horsetail ash it is silica that dominates. The role played by silica in the life of plants is not yet clearly known, although it is clear that without it almost nothing will grow.

But it is especially striking that the oxides composing these ashes are precisely those that give their basic structure to stoneware glazes. What the table above gives us is nothing less than the detailed technical description (technical card) of each ash, it is perfectly possible to transcribe the percentages of oxides given by the analysis into the molecular formulation we commonly employ for every product we use in glazes.

This will have the following layout:

_.__CaO	_.__Al_2O_3	_.___.__SiO_2
_.__MgO		
_.__K_2O		
_.__Na_2O		

For simplicity's sake, we have not included the formulae for the oxides of iron, titanium or manganese. The first two may sometimes have a slight influence on the coloring of a glaze. As for manganese oxide, we know that in a reducing kiln atmosphere, MnO_2 becomes MnO which has no coloring effect, the lost oxygen being captured by iron oxide, that thus passes from FeO to Fe_2O_3. This phenomenon of oxidoreduction earned manganese the name of 'glaziers' soap' since it allows the passage from blue to yellow, the latter being much preferred for window-glass.

We may now transform our two model analyses into formulae (for the method of calculation see *The Practice of Stoneware Glazes*). That give the following results:

Oak:

0.78 CaO	0.012Al_2O_3	0.105 SiO_2
0.08 MgO		
0.13 K_2O		0.035 P_2O_5
0.005 Na_2O		

Horsetail:

0.55 CaO	0.02 Al_2O_3	_.1.12_SiO_2
0.26 MgO		
0.18 K_2O		0.04 P_2O_5
0.005 Na_2O		

This method of notation allows us to more easily compare different ashes and attempt a possible classification.

The families of ashes

Glazes being silicates, what first interests us in ashes is the proportion between their basic oxides (totaling one mole) and their silica. That is therefore the angle from which we intend to classify our ashes, always remembering that in a glaze, the quantity of silica must never be less than 1.5 moles. We have seen in the example given above that the proportion is variable, being 1 to 0.1

of a mole for oak and 1 to 1.12 moles for horsetail. Observing the ashes of which we possessed an analysis, we have found ourselves led to set up, *grosso modo*, three categories of ashes: basic, acid, and mixed. But at the same time, we have observed that each individual botanic family could ever only be included in one of these categories.

We can affirm without fear of error that every wood yields a basic ash from which silica is virtually absent. But that is not enough, since one and the same family may include trees and plants used for fodder, such being the case of the false-acacia or locust tree and lucerne or alfalfa, both belonging to the family of *Leguminosae*:

	False acacia	Lucerne
CaO	0.88	0.81
MgO	0.05	0.13
K_2O	0.07	0.04
Na_2O	--	0.02
Al_2O_3	0.01	0.03
SiO_2	0.06	0.03

Seeing this, it is clearly better to say to which of the three categories each botanic family belongs. We have of course only worked with a limited number of ashes and the information given below is inevitably based on limited research.

The basic ashes

Here are a number of examples of wood ashes. The values for P_2O_5 have not always been communicated to us.

	CaO	MgO	K_2O	Na_2O	Al_2O_3	SiO_2	P_2O_5
Green oak	0.88	0.08	0.02	0.01	0.05	0.07	0.02
Hornbeam	0.86	0.06	0.07		0.01	0.05	0.03
Elm	0.85	0.08	0.05		0.01	0.27	0.04
Hawthorn	0.85	0.08	0.01	0.07	0.02	0.09	0.03
Okoume	0.7	0.29	0.01			0.03	0.02
Maple	0.83	0.08		0.09	0.02	0.18	0.03
Boxwood	0.85	0.8		0.06	0.01	0.06	0.02
Apple	0.81	0.09	0.09		0.02	0.18	0.03
Hazel	0.81	0.13	0.03	0.01	0.08	0.03	
False acacia (bark)	0.7	0.19	0.11		0.05	0.09	
Spruce (on limestone)	0.91	0.02	0.03	0.03	0.03	0.09	
Spruce (on granite)	0.8	0.11	0.03	0.03	0.11	0.1	
Oak (on granite)	0.7	0.18	0.04	0.02	0.04	0.03	
Oak (on limestone)	0.82	0.07	0.06	0.03	0.04	0.05	
Juniper	0.86	0.07	0.03	0.02	0.03	0.05	

Among basic ashes are included those of the vine. We will mention them separately on account of the high level of alumina that characterizes them. We will see later what the result of this is. We should add that vine cuttings often contain copper oxide from the copper sulphate sprays they receive. Here are the compositions of four ashes of vine cuttings.

	1	2	3	4
CaO	0.646	0.75	0.765	0.792
MgO	0.189	0.129	0.099	0.14
Na_2O	0.084	0.052	0.066	0.016
K_2O	0.066	0.051	0.057	0.03
Al_2O_3	0.182	0.136	0.279	0.157
SiO_2	0.032	0.132	0.026	0.393

The labiate family gives us lavender ash, that is especially rich in magnesia. Here are three examples.

	CaO	MgO	K_2O	Al_2O_3	SiO_2	P_2O_5
Lavender 1	0.72	0.22	0.05	0.03	0.34	0.06
Lavender 2	0.71	0.24	0.05	0.01	0.19	0.08
Lavender 3	0.77	0.2	0.02	0.12	0.24	0.01

It should be noted that these three lavender ashes were all washed before analysis. They represent an exception to the rule that basic ashes do not need to be washed, on account of the large quantities of soluble alkalis they contain, that would provoke serious problems in any glaze made with them.

There is also the family of the *Cruciferae*, here represented by ashes of rape seed plants:

0.7 CaO
0.06 MgO 0.01Al_2O_3 0.11 SiO_2
0.18 Na_2O
0.06 K_2O

The ashes of the family of the *Asteraceae* (which used to be termed C*ompositae*) ought in theory to be mentioned here, too. However, our experience leads us to say that these ashes represent an exception. The large quantities of sulfur and chlorine they contain render them unsuitable for glazes, which these elements cause to blister, a problem to which, so far as we know, no solution has been found. It is well-known that chlorine has no place in the formation of glass. In the technique of salt-glazed stoneware (using sodium chloride), while the sodium oxidizes and unites with the outer layer of the clay body, the chlorine separated from the sodium by hydrolysis leaves the kiln in the form of hydrochloric acid. Still, here are the compositions of two of the *Asteraceae*:

	CaO	MgO	K_2O	Al_2O_3	SiO_2	P_2O_5
Yarrow	0.31	0.09	0.58	-	0.12	0.05
Sunflower	0.38	0.09	0.51	-	0.04	0.03

Analysis shows percentages of 2.41 SO_3 and 4.96 Cl for yarrow and 2.9 SO_3 and 5.64 Cl for the sunflower.

Acid ashes

So far as we know, four botanic families are particularly notable for their high levels of silica, the grasses (*Graminaceae*), horsetails (*Equisetaceae*), sedges (*Cyperaceae*), and ferns (*Polypodiaceae*). Among the *Graminaceae*, rice furnishes the ash with the highest levels of silica. Here is the analysis made using some rice chaff:

LF	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5
0.89	91.5	0.43	0.25	0.01	1.18	0.89	0.18	2.92	0.84

Transcribed in the usual formula style, this would give:

0.272 CaO
0.288 MgO 0.054 Al_2O_3 19.7 SiO_2
0.037 Na_2O 0.019 Fe_2O_3 0.076 P_2O_5
0.402 K_2O

Obviously, with such an ash it would be impossible to compose a glaze requiring the same basic oxides, on account of the excessive quantity of silica. For that reason, we have brought the silica, and not the basic oxides, to unity. This gives;

0.01 CaO
0.01 MgO 0.002 Al_2O_3 SiO_2
0.001 Na_2O 0.0009 Fe_2O_3 0.0004 P_2O_5
0.002 K_2O

Given the low levels of basic and mixed oxides, we have decided, without subsequent inconvenience, to consider rice ash as a simple silica with a molar mass of 60.

Now here are the compositions of some of the other *Graminaceae:*

	CaO	MgO	K_2O	Na_2O	Al_2O_3	SiO_2	P_2O_5
Wheat straw 1	0.28	0.25	0.43	0.02	0.08	3.13	0.03
Wheat straw 2	0.45	0.32	0.19	0.04	0.07	1.55	0.19
Rye straw	0.35	0.25	0.4	-	0.16	4.40	0.09
Maize straw 1	0.44	0.27	0.27	0.02	0.15	5.13	0.08
Maize straw 2	0.37	0.23	0.38	0.01	0.08	2.33	0.05
Outer envelope of corncobs	0.31	0.19	0.47	0.03	0.18	3.25	0.08
Millet	0.33	0.27	0.4	-	0.09	3.88	-
Reed	0.53	0.15	0.23	0.12	0.04	5.4	-

It must be remembered that all the acid ashes were washed before analysis.

Horsetails (*Equisetaceae*) generally grow on damp or marshy soils. The horsetail found in meadows and on banks is an exception. Here is a formula of the ash:

0.56 CaO
0.26 MgO 0.03 Al_2O_3 1.13 SiO_2
0.18 K_2O 0.04 P_2O_5

Sedges of various kinds are plentiful along the banks of river and ponds. They yield excellent siliceous ashes:

Sedge 1 0.51 CaO
0.22 MgO 0.34 Al_2O_3 4.04 SiO_2
0.14 K_2O
0.25 Na_2O

Sedge 2 0.64 CaO
0.19 MgO 0.11 Al_2O_3 1.81 SiO_2
0.14 K_2O 0.06 P_2O_5

Bracken grows in large colonies, which makes it easy to harvest. Here are three formulae of bracken ashes, the third being that of ashes that melted in an over-ventilated brazier.

	CaO	MgO	K_2O	Na_2O	Al_2O_3	SiO_2	P_2O_5
Bracken 1	0.42	0.28	0.07	0.22	-	1.03	-
Bracken 2	0.41	0.16	0.06	0.36	0.03	1.01	-
Molten ash	0.3	0.21	0.08	0.4	0.01	1.2	-

Whereas in the vast majority of ashes potassium predominates over sodium, the opposite is true of bracken.

Certain ashes are especially rich in phosphorus (P_2O_5). You can be almost certain that they come from seeds. It has been observed that when plants mature, the phosphorus migrates toward the seeds, where it concentrates.

Here is the formula of an olive pit ash:

0.73 CaO
0.21 MgO 0.2 Al_2O_3 0.24 SiO_2
0.06 K_2O 0.14 P_2O_5

Since the olive is a tree, this is necessarily a basic ash! The following ash, from the heart of corn-cobs, is naturally acid:

0.28 CaO
0.43 MgO 0.13 Al_2O_3 2.13 SiO_2
0.29 K_2O 0.16 P_2O_5

Finally, let us see the formula of the ash of the debris after grain has been threshed, taken from the hopper of a combine harvester:

0.64 CaO
0.23 MgO 0.02 Al_2O_3 0.2 SiO_2
0.13 K_2O 0.23 P_2O_5

Mixed ashes

Every classification of ashes is bound to be arbitrary, especially when we remember that they vary from one portion of a plant to another, as can be seen from the following components of the beech tree:

	CaO	MgO	K_2O	Na_2O	SiO_2	P_2O_5
Trunk	0.664	0.180	0.115	0.038	0.059	0.026
Branches	0.659	0.193	0.113	0.03	0.125	0.066
Leaves	0.8	0.147	0.055	0.011	0.563	0.033

As can be seen, the silica increases when we pass from trunk to leaves. Indeed, the gradual acidification of the soil is due to the accumulation of fallen leaves.

However, we have decided to term ‘mixed ashes’ those in which silica, although not plentiful, nonetheless has to be taken into account. This includes the leaves of trees, including those of this maple:

0.838 CaO
0.078 MgO 0.026 Al_2O_3 0.353 SiO_2
0.081 K_2O

Also included among the mixed ashes are those of heather. Here is an example:

0.436 CaO
0.269 MgO 0.763 SiO_2
0.183 K_2O
0.110 Na_2O

As documentation, here is the ash of comfrey (*Symphytum officinale*) of the *Boraginaceae* family, that is plentiful in certain damp meadows:

0.38 CaO
0.06 MgO 0.06 Al_2O_3 0.4 SiO_2
0.01 Na_2O
0.54 K_2O

Ashes from hay

A number of different botanic families come together in a meadow. Even the least informed walker notices that it contains both flowering plants and grasses with an ‘ear’ of seeds at the tip of a stalk. A combination of this sort is not due to chance. Whereas certain types of plant prefer to grow alone, and are even able to create an empty space around themselves, others prefer to grow in close proximity with a few different species, and some seek out the greatest possible diversity. It is as if there were a sociology of plants as well. For the potter, that counts. There is every reason to suppose that the hay from a variety of such meadows will provide a whole series of ashes more or less rich in silica, to mention just one oxide.

We have often been able to gather hay in natural meadows, that have not been plowed, fertilized, or treated in any artificial way. The ashes from such meadows have always provided glazes with a balanced acid-basic ratio, meaning that no additions were needed. Ashes of this kind were the first to provide us with examples of nucleations. Here are three samples:

	CaO	MgO	K_2O	Na_2O	Al_2O_3	SiO_2	P_2O_5
Hay 1	0.67	0.2	0.13	-	0.08	1.72	0.05
Hay 2	0.53	0.26	0.13	0.08	0.06	1.61	0.06
Hay 3	0.6	0.16	0.21	0.03	0.18	1.85	0.08

And here are two specimens with less silica:

	CaO	MgO	K_2O	Na_2O	Al_2O_3	SiO_2	P_2O_5
Hay 4	0.73	0.18	0.09	-	0.02	0.63	0.08
Hay 5	0.61	0.18	0.21	-	0.01	0.78	0.12

If a hay ash is rich in phosphorus, that is a sign that the hay was harvested when the seeds had ripened.

The position of ashes among stoneware glazes

The classification into families has so far depended on the quantity of silica found in the different ashes. Another classification is possible, that only takes account of the basic oxides, CaO, MgO, and KNaO.

Here we take the general ‘Table of Contents’ diagram for all stoneware glazes, and calculate the position on it of the basic mole of the ashes listed below. The number is that of the corresponding intersection in the diagram.

Basic ashes			Acid or mixed ashes	
Oak (trunk)	10		Rye	35
Acacia	9		Rye	36
Acacia	10		Maize	27
Hazel	9		Maize	28
Oak (branches)	10		Rice	36
Evergreen oak	2		Maize (heart of cobs)	44
Rape	2		Sedge	27
Pine (branches)	10		Sedge	11
Vine	10		Hay	19

Juniper	9		Hay	11
Acacia (bark)	11		Hay	20
Hornbeam	18		Hay	11
Hawthorn	10		Horsetail	20
Maple (wood)	10		Wheat	20
Maple (leaves)	10		Bracken	28
Lavender	10		Bracken	35
Elm	10		Thresher scraps	11
Madder	18			10

(For the purposes of the diagram, fractions have been rounded off to the nearest tenth)

This diagram allows the following remarks:

a) The basic ashes occupy a tiny portion of the diagram, in the CaO corner.
b) The acid and mixed ashes occupy a narrow zone moving across the diagram.
c) Ash glazes therefore represent a special case among stoneware glazes. We can take advantage of this fact when it comes to reconstituting ashes using our usual minerals.

[Diagram p.41]

Methods for identifying ashes in practice

So far we have been describing the various ashes using the analysis of their elements, which yields the most precise indication of their composition. But it is rare to find a laboratory that will undertake such a task, which moreover costs a lot. So here we want to provide some hints that will allow potters with only limited means available to deduce the main characteristics of their ashes.

Percentage of ash

The higher the proportion of silica in a plant, the more ash it will yield. So by weighing the ashes provided by a known weight of dry materials, it will be possible to situate that plant in one of the families. Provided it is carefully done, this experiment can be performed using quite small quantities of dried plants. Here are some examples of the resulting percentages:

1.				
Beech (branches)	1.23		Bracken	5.89
Beech (leaves)	3.05		Reed	4.56
Beech (trunk)	0.55		Bulrush	3.85
Oak	0.51		Heather	3.61
Apple	1.1		Barley straw	4.39
Mulberry	1.37		Maize (heart of cobs)	44
2.				
Birch	0.85		Beech	1.12
Aspen	2.11		Pine	1.15
Oak	1.66		Fir	1.29
3.				

Hornbeam	1		Beech	1.12
Wheat straw	4 - 8		Sedge (Carex)	8
Horsetail	17			

1. From P. Piganiol, *Le verre, son histoire, sa technique*. Hachette. 196
2. From M. Larcheveque. *Fabrication industrielle de porcelaine*. Paris. 1929.
3. Our own measurements.

This allows the following classification:

Basic ashes : less than 2%
Mixed ashes : from 2% to 4%
Acid ashes : more than 4%

Identification by calcining the plant

When it comes to grasses (*Graminaceae*) and horsetails (*Equisetaceae*), botany text-books tell us: “At the end of these plants’ growth, the external membranes of the cells are impregnated with calcium and silica. As a result, the edges of the leaves may become sharp as knives. Certain kinds of sedge, so rich in silica that it makes them abrasive, are still used to polish precious woods.” (From *Atlas de Biologie*. Stock, p.57.)

The same holds true for most members of the great family of sedges (*Cyperaceae*).

One way of experiencing fully this fact is by placing some fully dried specimens of these plants in a biscuiting kiln laid flat on a kiln shelf. After the firing, it will be seen that the ash of these plants with high silica content retains exactly the original morphology of the plant. A piece of wood treated in the same way yields an ash of quite different structure.

In Japan, some potters have taken advantage of this phenomenon to decorate their pots, fixing rice straw for example directly to the raw clay. This straw is first soaked in salt water (to ensure the production of an alkaline silicate) containing iron oxide (to bring out the form more clearly.

Identification by calcining ash specimens

This method involves the preparation of small blocks of compressed ash using a little wooden mould that is easily made. These blocks are then calcined in a biscuiting kiln at 900-950 degrees.

[Photos p44 - 6:

1. Maize leaf calcined at 950° (magnified 40x). It is still possible to distinguish the mineral outer envelope composed of linked cells.
2. Sedge branch calcined at 950° (magnified 20x). The natural mineralization of the cells by silica and chalk enable the plant to preserve its exact form even after burning.
3. Tools used to produce pellets of compressed ash.
4. Four blocks of ash calcined at 950°. Above, left: oak Above, right: bracken. Below, left: hay. Below, right: rowan

Upper photo taken directly after firing.
Lower photo taken 2 weeks later. The oak is less powdered than the rowan on

account of its 0.10 of SiO_2.

Once the blocks emerge from the kiln, a number of observations can be made. First, the color will have changed, mainly because the carbonized debris found in the raw ash has disappeared. We will see a little later what can be deduced from that.

The second observation has to do with the hardness of the blocks. Some are more difficult to scratch with a knife than others. That indicates that they are richer in both alkalis and silica. But the clearest observations are those made after exposing the blocks to the air. After ten days or so, depending on the humidity, those composed of basic ashes begin to lose their form and return to a powder while the blocks of acid ashes remain unchanged. The explanation seems to be the following: the alkalis in the acid ashes react when heated to red heat with silica, forming a silicate that is stabilized by the calcium oxide. In the basic ashes, those same alkalis are unable to react with magnesium oxide or with the quicklime that is formed. On the contrary, the quicklime recomposes quickly into slaked lime on contact with the moisture in the air. That recomposition and the expansion that accompanies it begin on the surface and progress inward, provoking a return to a powdery state.

It should also be noted that calcining causes the blocks of basic ashes to shrink in volume. This shrinkage is caused by a more or less developed vitrification. It should be added that blocks that are easily scratched but keep their form are found to contain a particularly high level of silica.

The blocks of mixed ashes may react differently. The quantity of silica present is sometimes sufficient to combine with the alkalis, preventing the quicklime CaO, even when it is plentiful, from recomposing. These blocks remain soft and unchanged in form.

If the blocks produced by your mould are small enough, the experiment can be speeded up by simply using a blowtorch to bring them to red heat. With a welder’s torch, there will be no difficulty in reaching the fusion point of acid ashes.

This method of testing by blocks often produces surprises. Certain ashes, probably rich in silica and in alkalis but lacking in chalk, may soften and even melt after calcination, because the alkaline silicates, not being stabilized by CaO, are soluble. We have noticed this phenomenon with ashes of millet and ashes of banana skins.

[Color photos of tests p48 – 9

Acacia	Maize	Beech	Hazel
Boxwood	Fir	Hay	Pine
Oak	Bracken	Seaweed	Salicorn

Identifying the coloring oxides in ashes

When you burn a variety of plants, you soon notice a difference in the color of the ashes. That does not mean that the ashes that are darker in hue are necessarily richer in coloring oxides. For example, if straw generally yields black ashes, it is because it does not burn well. That is why the method of test blocks is needed. The following observations are made using calcined ashes.

Here, approximately, is what can be deduced from the color of the calcined specimens:

White ash: these will be poor in coloring oxides but necessarily contain traces of iron oxide since that, with magnesium, is needed in the formation of chlorophyll.

Gray ash: indicates the presence of iron oxide.

Brown ash: in addition to iron this will contain manganese. Very high levels of manganese produce the black color found, for example, in birch ash.

Violet ash: indicates the presence of manganese in siliceous-alkaline ash, such as that of heather.

Other phenomena linked to the color of ashes leave us baffled, such as an ash of comfrey that was royal blue on emerging from the kiln, and emerald green the next day!

Ashes and nepheline-syenite

Here is a different kind of experiment, involving both the fusion and the color of a mixture of ash with nepheline-syenite (or of another mixed or sodic feldspar).

The two components (the ash being first ground in a mill and passed through a 100-mesh sieve) are weighed out in equal quantities, mixed together, and enough water is added to form a slip. A thick layer of this is applied as a coating to the inside surface of a small biscuited bowl. This is then fired to 1280 degrees, preferably in reduction.

The result will demonstrate clearly the nature of the ash. If the glaze has run to form a pool at the bottom of the cup, the ash was basic. The little lake of glass may reveal a variety of colors (green, blue, turquoise or brown) and show different types of crystallization.

Acid ashes give a glaze that does not run, light in color, already useable with more research if needed. If you wish to take advantage of the mixture containing basic ashes, silica should be added to ensure a good proportion between base and acid in the composition. This would produce the following recipe:

Ash	100
Nepheline-syenite	100
Silica	60

Discovery of eutexy

It is the kiln, fired to stoneware temperatures, that will teach the potter most about ashes, and all the raw materials of a glaze. A specimen of each ash available, fired separately in a number of little bowls, will provide ample information about their degree of vitrification and even fusion, as well as about the bond that each has established with the clay body. Sometimes it will be found that a thin layer of vitrification has formed where ash and clay meet, even though the upper layer of the ash remains powdery. This phenomenon is most obvious when the bowl is filled with chalk.

We know that chalk ($CaCO_3$) decomposes at 900 degrees to give quicklime, that melts at 2580 degrees. We also know that if silica (melts at 1700 degrees) and alumina (melts at 2020 degrees) are added to chalk, the melting point of the mixture is considerably lower. That is an example of a natural phenomenon known as eutexy, without which pottery would never get past the stage of earthenware, since such high temperatures are impossible in a potter’s kiln. In our bowl, fusion occurs when the chalk comes in contact with the silica and alumina of the clay body.

But chalk is not alone in provoking eutexy with silica and alumina. Magnesia (MgO), potassium oxide (K_2O) and sodium oxide (Na_2O) have the same effect, and those are the oxides, together with lime, that make up the basic mole of ashes. A layer of ashes, therefore, is very likely to form a vitrified interface with a clay body.

This phenomenon of eutexy is going to bring us to a test that is especially important, not only for the knowledge of an ash it brings but as an indication of the way in which to develop a glaze.

This test may be carried out as follows. On a disk of biscuited clay some 10 cm in diameter, three concentric zones are defined. The outer zone is coated with liquid wax (we use the following recipe: 2/3 paraffin wax, 1/3 liquid paraffin, to which is added a little refined kerosene to control the fluidity. This is heated in a *bain-marie*. This mixture is used in decorations by wax-reserve.). The disk is then coated with a regular layer of ash (using a slurry of ash and water) about 1 mm thick. In the center is placed a block of that ash 1 cm thick.

[Diagram p.52]

1. block
2. Glazed zone
3. Waxed zone

[Photo p.53: Apple-tree ash, alone. 1280°, reduction]

After firing, the following observations can be made;

a) If the surface of the glazed zone and the block are both still powdery, you have used an ash that is very rich in chalk but from which silica and alumina are virtually absent.
b) If a glaze has formed but the block has the consistency of a hardened crust, the ash contains some silica but the alumina needed to form the glaze has been drawn from the clay body.
c) If the glaze has formed and the block has melted, both silica and alumina were present in the ash.

With acid ashes:

a) If the ash has not vitrified but remains powdery, it is poor in chalk, very rich in silica but with no alumina (rice straw, for example).
b) If the glaze has formed properly but the block is not fully melted, there is insufficient alumina in the ash.
c) If everything has melted, all the elements are present in the ash.

These observations are necessarily rather schematic, and in practice all kinds of intermediate stages are possible. It should be noted that the outer zone, left unglazed thanks to the wax coating, may be more or less covered with a shiny halo. This is the result of alkalis evaporating from the ash and being captured by the silica and alumina in the clay body.

Part Three: Glaze research in practice

Basic oxides as a constant

As we have just seen, fusion is the result of a proper ratio between the ash, alumina, and silica. Now the question arises as to how to determine the quantity of each mineral that must be added to any given ash, with as little left to chance as possible. Of course, an analysis of an ash and a precise indication of its molar mass would provide the answer. But that is rarely possible and, inevitably, other methods must be found.

Fortunately, nature comes to the help of the potter. Adding together the masses of the four basic oxides found in many ashes (CaO, MgO, K_2O, Na_2O) we have discovered that the result, no matter what proportion of each individual oxide is present in a given ash, is close to being a constant. This is probably a sign of the balance that the mineral salts in a plant establish by antagonism or interdependence.

Here are two examples of such a calculation, one on a basic ash, one on an acid one:

False acacia

0.822 CaO	(x 56 = 46.032)	0.006 Al_2O_3	0.062 SiO_2
0.124 MgO	(x 40 = 4.96)		
0.036 K_2O	(x 94 = 3.384)	0.005 P_2O_5	
0.015 Na_2O	(x 62 = 0.93)		
	55.306g		

Sedge

0.643 CaO	(x 56 = 36.008)	0.106 Al_2O_3	0.181 SiO_2
0.192 MgO	(x 40 = 7.68)	0.057 P_2O_5	
0.137 K_2O	(x 94 = 12.878)		
0.009 Na_2O	(x 62 = 0.558)		
	57.124g		

Another equation, based this time on an elemental analysis, gives the same result:

$$\frac{A + B + C + D}{a + b + c + d} = \text{constant}$$

in which A = % CaO, B = % MgO, C = % K_2O, D = % Na_2O

while a = A/56, b = B/40, c = C/94, d = D/62

Here is an example of this second method of calculation:

SiO_2	9.5%	Na_2O	0.5%
Al_2O_3	5.7%	K_2O	4.55%
CaO	35.6%	P_2O_5	1.1%
MgO	5.5%		

$$\frac{35.6 + 5.5 + 4.55 + 0.5}{35.6/56 + 5.5/40 + 4.55/94 + 0.5/62} = 55.8$$

Different ashes have yielded the following results:

Vine 1	55.3		Maize	56.55
Vine 2	56.13		Bracken	57.32
Vine 3	56.25		Hay 1	55.98
Vine 4	53.76		Hay 2	57.12
Acacia 1	55.53		Poplar	55.28
Acacia 2	55.3		Elm	57.3
Oak 1	56.19		Wheat straw	62.84
Oak 2	56.39			

All these results, taken together, show something that can be formulated in the following manner (on the basis of the second method of calculation): in the ash of any plant, the percentages of CaO, MgO, K_2O, Na_2O may vary, like their total, but we find that the ratio of those percentages to the total of the corresponding molecular equivalents seems to be a constant, in the region of 56.

However, we have noticed that certain acid ashes tend to exceed that figure.

Of course, to the figure 56 must be added the mass of the other, non-basic oxides in the ash, as well as the overall loss in firing, since all the preceding calculations have been made using calcined ashes.

The mass of non-basic oxides

Here, it is not possible to establish a single, average figure because there are considerable variations in the levels of silica. That means we will have to come back to our families of ashes and establish for each of them a mass, not an average but a minimum, adding together the alumina, the silica and the phosphoric acid. We shall see later why a minimum mass is preferable to an average mass.

It would be tedious to report here all the lists of figures and calculations, so we will simply provide a list of rounded off conclusions in a table that can provide a basis for the creation of glazes.

Family of ash	Mass of basic oxides	Mass of Al_2O_3 + SiO_2 + P_2O_5	Total mass without LF
Acid	56	134	190
Basic	56	10	66
Mixed	56	64	120

Calculating the Loss in Firing (LF)

This is a simple calculation. First, 100 g of a representative sample of a harvested ash are calcined in a biscuit kiln (900° - 950°). The weight of the calcined ash allows us to calculate the following ratio:

$$\frac{\text{Mass of non-calcined ash}}{\text{Mass of calcined ash}} = \frac{100}{100 - LF}$$

which means:

$$\text{Mass of non calcined ash} = \frac{100 \times \text{mass of calcined ash}}{100 - LF}$$

So if, for example, 100 g of an oak ash lose 20 g when calcined, the mass of the ash will be:

$$\text{Mass} = \frac{100 \times 66}{100 - 20} = 82.5$$

For a wheat ash that loses 40 g we have:

$$\text{Mass} = \frac{100 \times 190}{100 - 40} = 316.6$$

Conclusion: The whole first part of this study serves to establish the following double task in the development of a glaze:

1) Find out which family any particular ash belongs to, then choose which mass, 66 or 120 or 190 to assign to it .
2) Establish the LF that has to be added to the chosen mass to obtain the approximate molar mass of the ash.

Once this last figure has been found, it is possible to tackle the problems involved in making glazes.

Eutectics and ash glazes

We have seen that the fusion of an ash depends on the phenomenon known as eutexy, which manifests itself to a greater or lesser degree, but to some extent at least, no matter what the proportions of a glaze – ash, alumina, silica. But there exist a range of optimal proportions that bring the melting point of the mixture down to the lowest possible point. This is known as the eutectic point. The following list indicates the points of greatest interest for ash glazes:

Number	Composition			Melting point
1.	CaO	$0.35\ Al_2O_3$	$2.48\ SiO_2$	1170°
2.	MgO	$0.39\ Al_2O_3$	$2\ SiO_2$	1330°
3.	K_2O	Al_2O_3	$6\ SiO_2$	1220°
4.	Na_2O	Al_2O_3	$6\ SiO_2$	1200°

Potters need to correct somewhat the notion of ‘melting agent’ that is commonly found in workshops. People tend to say, for example, that an ash or a feldspar serve to make a glaze melt, and that is not entirely false. In reality, what makes a glaze melt at a given temperature is rather the happy combination of various oxides in a particular proportion.

The eutectic points on the figure above were established using chemically pure oxides. Such a situation is never of course encountered using the ashes and minerals available to the potter. As a consequence, the temperatures reached in a workshop will never be as low as those indicated. The four basic oxides being represented in the ashes, it is possible to speak of eutectic mixtures always favoring fusion.

[Photo p.61: ‘CHALK’ written using chalk! The eutectic has formed on contact with the silica and alumina in the clay body.]

You may wonder now what is the lowest temperature at which ash glazes can be realized. It is hard to give an exact answer but experience has shown us that with certain ashes, rich in alkalis and chalk, fusion can be reached as low as 1230°. But it is clear that the richest array of glazes is found once you reach about 1280°.

The method of progressions

Now it is possible to start experiments in which progressively greater quantities of alumina and silica are added to a fixed quantity of ash (molar mass + loss in firing). This method is used without variation with every kind of ash with the exception of certain kinds of acid ash, rich in silica, where it is the basic mole that has to be modified.

The chart below contains all the fusion zones of ash-based glazes. It indicates, for each experiment, the molecular quantities of alumina and silica. At the bottom, the first line of tests (from 1 to 0.2 Al_2O_3) in which no silica is added, will be made using finely powdered alumina, except for the first test, where the ash stands alone. The following tests (0.5, 1, 1.5 SiO_2 etc.) are made using kaolin and silica following the usual method.

[Figure p.62]

It is clear that we can only speak of stable silicates once we have at least 1.5 moles of silica. But in order to know one’s ashes better it is interesting to see what happens below that point.

Accelerated method of progressions

To test an ash quickly, if it is basic, the following chart may be used. The weight of ash used in each test is fixed at 100 g, the average molar mass for the basic family.

[Figure p.63]

In every case, the weight of kaolin is written above that of the silica. We have used the mass of kaolinite, 258, (2 SiO_2 Al_2O_3 2 H_2O). The commercially available kaolins usually contain more silica, each potter will make the necessary adjustments.

[Photo p.64-5: Complete series of tests using an apple-tree ash]

In order to avoid waste, only one tenth of the quantities indicated will be weighed out for the tests.

Interpretation of a series of tests made using a basic ash

Clearly all the rest of the development of a glaze will depend on this initial interpretation. Each ash here reveals its particular features and its nuances, that the potter must be able to spot. Below we will try to indicate what seem to us to be features common to all the basic ashes we have been able to study.

a) The chart shows a central zone of fusion, triangular in shape, wider below and narrowing near the top. In the lower par of this zone, the glaze runs.

b) Fusion may appear from the very first line of tests at the bottom of the chart, where the ash is first alone then receives increasing quantities of alumina. In such a case we are in the presence of a basic ash that contains a little silica. If the ash melts on its own, that means that a small quantity of alumina is also present in it. Once again, until we reach the fourth line (1.5 SiO_2) these fusible mixtures cannot be assimilated to stable silicates.

c) At the start and end of each line, fusion diminishes. To the right, on account of excess alumina; to the left, of excess silica.

d) A test that does not melt on account of excess alumina begins to melt when more silica is added. Likewise, where excess silica prevents fusion, melting comes with additional alumina. Whence the way the zone of fusion expands toward the right.

e) Reduction of fusion is paralleled by a reduction of brilliance and transparency, as well as a shift from color to white. (To the left and right of each line of tests, it will be noticed that an addition or diminution of only 0.05 Al_2O_3 is enough to provoke a shift from opaque to transparent, and the reverse; likewise for the passage form color to white.)

f) If this series is made using another basic ash, the zone of fusion may be smaller or larger, but always following the same basic schema.

So for any given temperature, there will be a number of different proportions of SiO_2 and Al_2O_3 permitting an identical fusion. The overall picture of these proportions can be represented in a graph where the course of the line will vary depending on the composition of the basic mole.

Starting with this method of progressions applied to ashes, and basing our work on the studies of many researchers, our workshop has been able to establish fusion diagrams for a wide variety of stoneware glazes. As regards the basic mole in all these diagrams, we have always limited ourselves to the main basic oxides found in ashes, CaO, MgO, K_2O, Na_2O.

Fusion of acid ashes

Sometimes acid ashes melt badly or not at all on account of an excessive quantity of silica. In the absence of a detailed analysis, this is how to proceed:

a) The lack of fusion is often due to a lack of alumina. To a given weight of ash, corresponding to 190 g to which is added the figure determined for the LF, alumina is added, 0.05 moles at a time, by way of kaolin, which will also increase slightly the silica.

b) If fusion does not appear with the addition of alumina, we vary the composition of the basic mole to reduce the ratio between base and acid. That offers the choice of modifying alternatively the proportions of CaO and KNaO, experience having shown that it is inexpedient to modify MgO.

c) We have often found that insufficient quantities of both CaO and Al_2O_3 were responsible for the lack of fusion. In such a case, kaolin and chalk need to be increased together, in percentages. This will generally happen in the case of an ash with a high level of silica. In the extreme case of a rice ash, assimilated to pure silica, we quickly reached fusion by adding chalk and kaolin corresponding to the eutectic CaO, 0.35 Al_2O_3, 2.48 SiO_2.

It is easy to imagine that in this domain it is hardly possible to establish precise rules, and that a step-by-step research method allows the best progress. Here, ‘the best’ means determining the lowest amounts of additional oxides allowing the best qualities of an ash to appear.

The fusion of hay ash

[Photo p.68: Hay ash alone with formation of nucleations]

The proportions of the components of hay ashes can vary greatly, depending on the different kinds of botanic species that are represented. If *Graminaceae* are predominant, the ash will be high in silica. At the opposite extreme, the more clover or other *Leguminosae* are present the more the ash will be basic. Actual observation of the field yielding the ash will be helpful here. Either of these extremes is possible, together with all the intermediate mixtures.

Ashes rich in *Graminaceae* will be dealt with in the way described in the previous paragraph. Ashes that are more basic or at least mixed will require additional alumina and silica, following the method of progressions.

As already indicated, the ash from a natural meadow usually melts without any addition, forming a stable silicate. That does not mean that we need take that as the only solution, far from it. As you add progressively more alumina and silica, you will be amazed to see the great size of the fusion zone. If we take as an example a hay ash already mentioned above:

$0.67\ CaO$ $0.08\ Al_2O_3$ $1.72\ SiO_2$
$0.2\ MgO$ $0.02\ Fe_2O_3$ $0.05\ P_2O_5$
$0.01\ Na_2O$
$0.13\ K_2O$

On adding progressively more alumina and silica, the fusion zone was found to extend as high as $0.75\ Al_2O_3$ and $5\ SiO_2$.

At the time when that experiment was made, we had not established our set of diagrams, number 11 of which corresponds to this ash. If we had had it, it would have allowed us to anticipate such an extensive fusion zone, without any need for experiments.

In addition to the large fusion zone, the complete set of tests for this ash fired in reduction allowed us to discover two other things. The first concerns the color of glazes. As far up as $0.15\ Al_2O_3$ and $2.5\ SiO_2$, the tests show an orange color, probably caused by an iron phosphate. Above those values, the orange quickly gives way to varieties of greenish-blue.

The second phenomenon is hard to describe, we term it ‘nucleation’ on the advice of a glass specialist. These nucleations are circular in form, microcrystalline spots spreading from a central seed, the nature of which has not yet been determined. We will discuss this more a little later. Here we will simply note that the appearance of nucleations is very localized, and does not occur above $2\ SiO_2$ and $0.1\ Al_2O_3$.

Exercises

Now we would like to propose a few lines of research that emerge in the course of work centered on ashes.

Ashes and varieties of clay

If a sufficient supply of alumina is one of the fundamental conditions for the fusion of most ashes, that means that there are as many possible corrective possibilities as there are varieties of clay.

By using a simple kaolin, we allow the ash full rein, so to speak, in characterizing the appearance of the glaze. But if the alumina is introduced using some other kind of clay, obviously the appearance will be influenced by the other oxides present in addition to alumina and silica. This is one possible field for research.

The results will be very different, depending on whether a stoneware clay or a faience clay is used. The former contain few basic oxides while silica may vary between 4 and 8 moles for one mole of alumina. Oxides of iron and titanium will be present in strongly varying proportions.

In contrast, the clays used in faience contain a sometimes considerable proportion of chalk, either naturally or added artificially. They can therefore be classed among the marls which often provide ‘naturally occurring’ glazes when fired at stoneware temperatures. These can be used to introduce extra alumina, not into basic ashes of course, but into acid ashes that are not sufficiently fusible.

Making a glaze from the clay of the pot

It is also possible to reverse what was seen in the previous exercise, exploring ways of making a glaze from a stoneware clay. The exercise will be that much easier if the composition of the clay is known. Failing that, we can take an average type of stoneware clay. Here is an example:

LF	1.31		MgO	0.4
SiO_2	72.07		CaO	traces
Al_2O_3	19.29		Na_2O	0.15
Fe_2O_3	1.95		K_2O	2.07
MnO	0.02		TiO_2	1.18

These figures are in % and for additional information here are the parts per million of trace elements offered by the same analysis:

Ba	329		Ni	61
Cr	111		Sr	72
Cu	13		Va	143

With the alumina as unity, we then calculate the simplified molecular formula of this clay, which gives:

Al_2O_3 6.34 SiO_2 with a molar mass of 520

We then follow the method of progressions, adding to a basic ash the appropriate quantities of this clay and silica.

If you wish to find the shortest route to make your stoneware clay melt, you will recall that the figure 56, corresponding to the constant of the basic oxides in an ash, is also that for the mass of CaO. You may then take as your starting point the eutectic CaO 0.35 Al_2O_3 2.48 SiO_2 which can be composed by mixing chalk, stoneware clay and silica, giving:

Chalk	100
Clay	182
Silica	133

After which it may be necessary to modify the levels of alumina and silica to regulate the fusion or appearance of the resulting glaze.

A glaze modified by an ash

Even though our principal intention is to limit as far as possible the addition of external materials in order to bring out to the maximum the ‘ceramic specificity’ of each plant’s ash, it also happens that a discerning addition of a certain ash can bring a welcome modification to a previously used glaze composed entirely of minerals.

Obviously, substitution is far easier when we have the analysis of the ash as well as the formula of the glaze. Even without that, it is possible, for example, to replace the chalk in a glaze with the same weight of a basic ash. Or, on the contrary, replace the silica by a rice ash. This offers infinite varieties of experiment, so long as care is taken not to distort the base-acid proportions of the glaze.

Mixing ashes

Here what is meant is mixing basic ashes with acid ones. A less than fully fusible hay ash can be corrected by an addition of a hard wood ash, a sedge being matched with a beech, a reed with a fir! This is valid for fusible mixtures that work with little alumina. With the exception of the few plants that supply more alumina, such as the vine, kaolin will have to be used to attain fusion.

Recuperating the soluble alkalis

We know that alkalis react with silica as soon as they reach red heat. This fact can be exploited in order to preserve the alkalis in a basic ash, a portion of which would otherwise be eliminated by washing. That is especially advantageous in the case of an ash that is particularly rich in soluble salts of sodium and potassium, lavender for instance.

This is done by calcining in a biscuit kiln (950 degrees) the unwashed ash mixed with a quantity of silica. By first measuring the amount lost in washing, it is possible to evaluate very roughly the quantity of silica to be added. In practice, it will be best to mix 1.5 or 2 moles of silica with 100 grams of ash. That will make later calculations easier and avoid an excessive vitrification of the mixture. After calcining, the result is ground and tests are made following the method of progressions. It is worth noting that this process, employed with ashes rich in K_2O, favors the development of iron blues.

Reconstitution of ashes

[Photos p.73: Reconstituted hay ash. (Diagram 18)   Reconstitution of a wood ash. (Diagram 3)]

The reconstitution of an ash using the usual minerals is of double interest. An ash is an indissoluble entity, and it is not possible at the outset to determine the precise role of each of its component oxides in the structure and appearance of a glaze. However, so long as a precise analysis is available, a *sine qua non* for this exercise, it becomes possible in the course of the reconstitution to suppress or experiment with variations in the quantity of a given element, allowing us to determine its function. Second, if an ash has given good results but then the supply runs out, this method permits the reconstitution of the glaze it helped produce.

If the ash in question was a basic ash, there will be no great difficulty. Chalk, talc, feldspar allow the reconstitution of the basic mole. The minimal amount of alumina will be introduced by the feldspar and kaolin will make up the rest. Phosphorus can be introduced using bone ash.

It is with the reconstitution of acid ashes that a whole new chapter of stoneware glazes opens. It becomes impossible to employ feldspar once the amount of alumina in the glaze is less than that of the alkalis. Here we find ourselves in the same situation as that indicated in more than half the diagrams for the fusion of stoneware glazes. This means that we are obliged to employ an alkaline frit with a minimal level of alumina (such as 0.3 CaO, 0.7 KNaO, 0.03 to 0.05 Al_2O_3, 2.5 SiO_2). Frits of this kind are not always easy to find on the market, where such products are usually conceived for faience glazes and therefore include derivatives of boron, which must be avoided here.

In this work of reconstitution, we recommend composing the same glaze formula in a number of different ways. In this manner, the alkaline minerals will vary, with magnesia now introduced by talc, now by dolomite, etc. For sometimes it is a matter of playing with very fine margins in order to find the best reconstituted equivalent for an ash glaze, in particular when it comes to the color, where the proportions of iron and phosphorus seem to play a decisive role.

Part Four: The presence of phosphorus

Once chlorophyll has captured solar energy, it is phosphorus that has the job of distributing that energy to the places where the plant needs it. The soil, both humus and minerals, has therefore to contain considerable stocks of that element, between 800 kilograms and 15 tonnes per hectare. Once inside a plant, phosphorus constitutes between 0.1 and 0.9% of the vegetal matter when it is dried.

What then is the role of phosphorus in a glaze? We know that P_2O_5 like silica produces glass. But what is its influence on fusion and color, in relation with the other oxides in the silicate?

Making use of the exercises proposed earlier, and other methods of research, the following descriptions are an attempt to reply, at least in a fragmentary way, to such questions.

Iron red glaze in reduction

One of our first encounters with phosphorus dates from the years when a disease killed almost all the elms. That provided us with an ash of elm that, with the addition of kaolin, silica and iron oxide, at the end of a series of experiments gave us in a reducing atmosphere a matt-surfaced red glaze with micro-crystals of hematite.

Waiting to receive the analysis of the ash, we were curious to discover the causes of that very special red hue. To start with, we decided to employ the least number of oxides possible. Knowing that CaO dominates in wood ashes, we took as our initial formula:

CaO	0.7 Al_2O_3	3.5 SiO_2
	0.3 Fe_2O_3	

That meant an implied interplay of the two eutectics 0.35 Al_2O_3 2.48 SiO_2 and CaO, 4 FeO, 5 SiO_2 with additional kaolin to avoid excessive fusion. The first test produced a black matt glaze that was slightly ‘tight’.

After that, the iron oxide was progressively diminished, down to 0.15 Fe_2O_3. The color gradually changed from black to dark brown. The alumina was brought down to 0.3 Al_2O_3 with a constant level of 0.25 Fe_2O_3. At 0.5 Al_2O_3 a brick red hue suddenly appeared, but without the other qualities we were looking for. This glaze ran, forming a black pool containing crystals arranged in a rosette. The red disappeared with 0.4 Al_2O_3.

We then decided to vary the silica, maintaining CaO, 0.5 Al_2O_3, 0.25 Fe_2O_3. Once below 3.5 of silica, the tests produced glazes that were too fluid, red in color with streaks of green then black. Below 3.5 SiO_2, the red disappeared in favor of an olive green, then an irregular brown.

The search had to head in new directions. Remembering the presence of magnesia in ashes, we introduced MgO into the formula, reducing the CaO. The red hue reappeared up to 0.1 MgO then disappeared.

We tried one last experiment, introducing alkalis into the basic mole. The color seemed to improve until we reached the following formula:

0.85 CaO	0.5 Al_2O_3	3.5 SiO_2
0.1 MgO	0.25 Fe_2O_3	
0.05 KNaO		

At that moment, we received the analysis of the elm ash, which allowed us to establish the formula of our initial glaze:

0.85 CaO	0.45 Al_2O_3	3.3 SiO_2
0.08 MgO	0.28 Fe_2O_3	0.04 P_2O_5
0.05 KNaO		

We composed that formula, introducing phosphorus by a bone ash; immediately we could see that this reconstitution corresponded to the glaze made using the ash. Subsequently, we diminished slightly the amount of iron oxide to reduce the size of the hematite crystals.

Thus the presence of phosphorus proved essential for both the quality and the color of the glaze. Once again, we need to insist that a final result is always the result of a relationship between all the oxides expressed in the formula, interpreted by minerals that differ from one workshop to another. What we have proposed here is a possible method of research, and not a list of figures to be taken literally.

Iron blues in oxidation

Part of the additional alumina needed to make an ash melt can be added by using feldspar. Experience shows that this is a good solution for those using an electric kiln, that is to say, under conditions in which no reduction is possible. Using an oxidizing atmosphere in a gas-fired kiln, this addition of alkalis to an ash led us toward the blues that are specific to iron.

While we added feldspar to all the basic ashes at our disposition, only two yielded such blues. Those were ashes of hawthorn and maple, of the following compositions:

Hawthorn:	0.85 CaO	0.007 Al_2O_3	0.087 SiO_2
	0.075 MgO	0.002 Fe_2O_3	0.028 P_2O_5
	0.07 Na_2O		
	0.004 K_2O		
Maple:	0.833 CaO	0.018 Al_2O_3	0.187 SiO_2
	0.075 MgO	0.005 Fe_2O_3	0.028 P_2O_5
	0.087 Na_2O		
	0.003 K_2O		

It will be noted that the basic moles of these two ashes are very similar, and that they contain identical levels of phosphorus. Adding feldspar, kaolin and iron oxide results in the following reconstituted formula:

0.7 CaO	0.3 Al_2O_3	3.5 SiO_2
0.05 MgO	0.04 Fe_2O_3	0.03 P_2O_5
0.25 $KNaO$		

With this reconstitution, suppressing the phosphorus brought about the disappearance of the blue, giving a pale bottle-green, while increasing the phosphorus preserved the color while intensifying the opacity of the glaze. Here the phosphorus was introduced by means of a bicalcic phosphate. In a reducing atmosphere, all tests yielded a pale greenish-yellow.

It should be noted that the blue attains its maximum intensity when the glaze is added as an overglaze to an iron-rich glaze, particularly one producing ‘oil-spots’. This serves to confirm that this technique is limited to an oxidizing atmosphere. Iron blues produced in a reducing atmosphere (diagrams 40, 46, and 51 for example) must contain no phosphorus and prefer potassium to sodium, this latter rather favoring green hues.

[Photos p.80: Iron blue, hawthorn ash over oil-spot. Oxidation.   Iron red in oxidation.]

Iron reds in oxidation (kaki)

We mentioned previously a hay ash mixed with iron-rich clay on account of the many mole-hills harvested with it. This is its composition:

0.58 CaO	0.308 Al_2O_3	4.53 SiO_2

0.185 MgO	0.074 Fe_2O_3	0.088 P_2O_5
0.022 Na_2O		
0.211 K_2O		

In a wood-fired kiln at 1280 degrees, the test shows a dark green vitrified covering.

Added kaolin, feldspar and iron oxide allow satisfactory fusion and spread, corresponding to the following:

0.54 CaO	0.3 Al_2O_3	5 SiO_2
0.17 MgO	0.27 Fe_2O_3	0.08 P_2O_5
0.28 $KNaO$		

The color shifts to red, while the same test in a gas kiln with a reducing atmosphere yields a brown.

If we reconstitute this formula using the usual minerals, P_2O_5 being introduced by a bone ash, the result is just the same.

The amount of phosphorus is raised twice and fired in a wood-kiln. 0.13 P_2O_5 give an intense crimson, while 0.18 P_2O_5 (an addition representing the total amount of CaO) shows green spots embedded in the red. The same tests, fired in a gas kiln in reduction give spangles of hematite in a dark bordeaux-red glaze. This confirms that the family of ‘kaki’ glazes (‘kaki’ is the Japanese word for ‘persimmon’), rich in iron and phosphorus, requires an oxidizing atmosphere. A controlled oxidation in the gas kiln serves to give an additional confirmation.

The following tests allow us to make new checks.

First, the complete withdrawal of P_2O_5 from the reconstituted glaze makes the red disappear, giving a brown.

Next, we introduce the phosphorus (0.088 P_2O_5) using a wheat ash of the following composition:

0.45 CaO	0.072 Al_2O_3	1.55 SiO_2
0.316 MgO	0.034 Fe_2O_3	0.194 P_2O_5
0.043 Na_2O		
0.190 K_2O		

The red returns and grows more intense when we pass from 0.088 to 0.113 P_2O_5 using the same wheat ash.

Another harvesting of hay, from the same field but this time without the mole-hills, allows to us to reproduce our initial tests. The composition of this ash is:

0.531 CaO	0.06 Al_2O_3	1.61 SiO_2
0.26 MgO	0.011 Fe_2O_3	0.063 P_2O_5
0.081 Na_2O		
0.128 K_2O		

The quantity of magnesia present, much higher than in the first ash, prevents the appearance of a red. This teaches us to make 0.17 MgO the upper limit for a kaki.

Further variations in the quantity of phosphorus in the initial formula allow us to situate the appearance of a red between 0.1 and 0.2 P_2O_5.

We still have to verify the optimal levels of the other oxides in the formula, with phosphorus at a constant 0.18 P_2O_5. Briefly, we can indicate the following: if the alkalis are increased at the expense of the CaO, that provokes a progressive invasion of the red by green spots. In the reverse direction, increasing the CaO at the expense of the alkalis makes the red disappear. When alumina is diminished, the color veers toward olive green, when it is increased, a metallic red results. Finally, an increase of silica provokes a mixture of red and green.

In conclusion, we might reasonably place the formula for a kaki between the following values:

0.5 – 0.6 CaO	0.45 – 0.55 Al_2O_3	4.5 - 5 SiO_2
0.15 – 0.2 MgO	0.25 – 0.3 Fe_2O_3	0.1 – 0.2 P_2O_5

0.25 – 0.3 KNaO

That is not to exclude the possibility that there may exist other zones allowing the formation of a kaki glaze. We shall see later that similar results can appear with other values for the oxides. But here we need to mention one other property of phosphorus.

It remains true that an oxidizing atmosphere is required to obtain these reds, so that this set of glazes can be fired together with oil-spot glazes. We are even tempted to say that there is a kind of relationship between these two glazes, that a kaki is a variant of the oil-spot that includes phosphorus. The ‘spot’ phenomenon, caused by the decomposition of hematite into magnetite with oxygen being liberated, sometimes occurs in a kaki glaze when it is applied sufficiently thickly. The red color is clearly a surface effect on top of a black glaze.

Phosphorus and fusion

In seeking to bring out to best advantage the role of phosphorus in a glaze, we always select the solution that seems to us *a priori* the most explicit: phosphorus is introduced into a formula permitting the use of the highest quantities possible. Since phosphates of lime are the main suppliers of this oxide, we quite naturally select the first of our diagrams in which CaO constitutes the whole of the basic mole. We equally select a bicalcic phosphate giving us 0.5 P_2O_5 in the formula. (Monocalcic phosphate is soluble in water, while phosphorus on its own burns in it!).

To make the comparison possible, we select a formula from the first diagram, giving us the basis for a well-melted celadon:

CaO	0.55 Al_2O_3	3 SiO_2

This composition with an additional 0.5 P_2O_5 gives a less that fully melted result. It then seems expedient to go directly to the eutectic point of the diagram, which is, including the phosphorus:

CaO	0.35 Al_2O_3	2.48 SiO_2
		0.5 P_2O_5

This second test turns out to be even less well melted than the first. Then, contrary to what might be expected, logic makes us look for fusion on the right side of the diagram, not the left, that is, by increasing the alumina, not decreasing it.

For a constant level of 2.5 SiO_2 and 0.5 P_2O_5, we progressively increase the Al_2O_3. Fusion is then obtained between 0.8 and 1.2 Al_2O_3.

This result encourages us to discover the whole fusion zone by also varying the amounts of silica. The following figure illustrates the results. a and b are the two initial, unmelted tests. The circled points of intersection cover the whole fusion zone.

[figure p 84]

The displacement of the fusion zone can be clearly seen. But it should be noted that it is alumina, in its relation with lime and phosphorus, that is mainly responsible, not the silica. Points b and c that correspond to the eutectic points of the two zones, are located at the same level of silica.

[photo p 85: Ashes of olive pits and hazelnut shells, rich in phosphorus, bring out the incised design.]

Later we were able to obtain the phase diagram in which there is interplay between alumina, silica and a tricalcic phosphate.

[Diagram p.86]

By the same kind of calculation used to establish our sixty diagrams, it is possible to transpose the 1300 zone of the diagram into a new frame, yielding the following comparative table that confirms the results of our step-by-step research.

[Tables p.87]

Glazes with nucleations

[Photo p.88: Nucleations by maize ash. Taizé workshop.]

An ash glaze is the outcome of a combination of two complex realities: that of a mineral structure produced by vegetal life, and the phenomena occurring in firing, that is, a metamorphosis of that structure. There is one field of research, particularly appealing, in which that combination attains a high degree of complexity: glazes with nucleations.

It may not seem opportune to deal with this theme in a chapter dedicated to phosphorus. Can we really say for sure that phosphorus plays a decisive role in the formation of these circular sets of micro-crystals, in the emergence of these ‘isles in the glaze sea’? It would be a delicate matter to be categorical here, in the affirmative or the negative. In order to discover more, it would take a quantity of analyses and observations far exceeding the possibilities and qualifications of a potter. All that can be said here is that, as far as we are concerned, these nucleations have always appeared in ash glazes or their reconstitutions, that is, in compositions that included phosphorus.

It seem that a nucleation must necessarily form around a seed. But for the moment, it has not yet been possible to determine the nature of this ‘seed,’ that may or may not be present in an ash or a glaze. One particular hay ash we had always produced glazes rich in nucleations, a true blessing!

But our supply of that ash is running low. Another hay, from the same field, was employed, producing a ‘sea without islands.’ Since there was a small quantity of the original glaze in the bottom of a bucket, we sprayed a very thin veil of it over the second, and the phenomenon at once materialized.

We have also noted that an ash-based glaze capable of producing nucleations may lose its ‘power’ if it stays mixed with water for too long before being used. That would seem to suggest that the seeds may lie in the soluble elements of the ash. We have never observed this kind of spoiling in reconstituted glazes. Nonetheless, we tend to avoid preparing more glaze than is needed for one firing, or at least siphon off part of the water from a mixture that is too liquid. In this last case, it would be better to allow evaporation to occur.

It was a hay ash that gave us the surprise of our first glaze with nucleations. It was composed as follows:

0.66 CaO	0.08 Al_2O_3	1.7 SiO_2
0.19 MgO	0.02 Fe_2O_3	0.05 P_2O_5
0.001 Na_2O		
0.13 K_2O		

To make the glaze, we went up to 2 SiO_2. Here we noted the formation of little rosettes expanding from a central point, opaque and of a rusty color. They were scattered across a transparent, pale green glaze, influenced probably by the iron in the clay body. The firing was done in a reducing atmosphere, without any particular attempt to slow down the cooling.

On the basis of this result, we feel able to make the following initial comments:

a) Nucleations can form in a glaze low in silica and alumina. This is confirmed by tests using higher levels of both oxides, which eliminate the effect.

b) Unlike classic glazes containing crystals, this formation occurs at various moments in the final phase of the temperature rise. It is possible to observe larger nucleations spreading above or beneath constellations of smaller rosettes.

c) The oxides in the ash are distributed in the glaze in a preferential order, with iron concentrated in the nucleations, especially around their outer edges.

These are bound to be fragmentary and approximative remarks. A variety of experiments have been made in laboratories. A microsounder analysis of a fired glaze reveals a mixture of four 'phases,' four different kinds of glass in each of which CaO and SiO_2 are present in different proportions. Moreover, a prolonged second firing of the glaze at 1250 degrees makes the nucleations disappear. That shows that the phenomenon is a temporary one, occurring at a moment that does not necessarily correspond to the final phase of a firing. This the potter knows, sometimes finding, on opening the kiln, a glaze swamped by an accumulation of nucleations and sometimes a glaze completely homogeneous and transparent, while every possible variation is possible between the two extremes.

All we can do is work by various approaches, depending on our intuition. Now we will mention some steps that have often proved opportune.

An ash that has soaked too long in water, as we saw, is likely to compromise the formation of nucleations. We have found that a cereal ash, even well washed, continues to lose alkalis in water. We have therefore tried correcting a 'sick' ash with a small amount of feldspar, successfully. This prompted us to use the ash glaze as an overglaze to an alkaline, calcic slip with no magnesia (e.g. diagrams 25 or 33).

By this underglaze too we have introduced coloring oxides (copper, cobalt, iron, nickel, etc.) that are generally absorbed by the underlying glaze rather than by the nucleations. Obviously the relative thickness of the two glazes, that needs to be found by experience, plays a major role. Whereas the firing atmosphere seems not to play a decisive role. At most, we have observed that in oxidation the colors, especially iron orange, are sometimes less pronounced. It is noteworthy that copper oxide never produces a red in reduction, at least not in the formulae practiced in our workshop.

This left us with one remaining difficulty, that of an excessive fluidity in the ash glaze. Unable to increase the levels of alumina and silica without compromising the formation of the nucleations, we decided to increase the phosphorus introduced by the ash using bicalcic phosphate, by successive additions of 0.01 P_2O_5. As we passed from 0.05 to 0.08 P_2O_5 the glaze stopped running and the nucleations stayed put on the sides of the pots, instead of gathering on the kiln shelves as before. At 0.01 P_2O_5 the glaze was less than fully melted and the nucleations had vanished. The reasons for this result became apparent later, when we discovered the displacement of the fusion zone that occurs when an increase of alumina accompanies that of phosphorus. By increasing the P_2O_5, we made the glaze harder. By adding Al_2O_3 we could have regained our fusion, but at the expense of our nucleations!

There remain the possibilities offered by reconstitution. Here we will give the formulae of four ash-based glazes that have given good results:

	CaO	MgO	Na_2O	K_2O	Al_2O_3	Fe_2O_3	SiO_2	P_2O_5
Hay	0.67	0.2	0.01	0.12	0.08	0.02	2	0.05
Hay	0.67	0.19	0.01	0.16	0.12	0.02	1.84	0.05
Sedge	0.65	0.19	0.01	0.14	0.11	0.01	1.84	0.06
Maize	0.59	0.15	0.01	0.24	0.11	0.01	1.95	0.08

For the reconstitutions, the choice of formulae will have to observe the following limits:

0.6 – 0.7 CaO		
0.1 – 0.2 MgO	0.05 – 0.12 Al_2O_3	1.8 – 2.1 SiO_2
0.1 – 0.3 KNaO	0.01 – 0.02 Fe_2O_3	0.05 – 0.08 P_2O_5

The feeble quantity of alumina in these formulae shows that these reconstitutions will almost always need the use of frits. Equally significant is the way potassium dominates considerably in the ashes used, and this will determine the choice of frits employed.

[photos p92-3
Four glazes with nucleations produced by the potter Colette Houtmann using ashes of hay and straw. The coloring oxides are incorporated in the underglaze.

Left page: Copper (above) – Titanium, cobalt, copper (below)
Right page; Cobalt, titanium, nickel (above) – Cobalt, nickel (below)

Part Five: Ash glazes and electric kilns

For reasons difficult to establish, firing in an electric kiln is not very favorable for ash glazes. That is especially the case with basic ashes where fusion is obtained by additions of alumina and silica. The high level of lime in such compositions, and the small quantity of iron introduced by the plants, would need a reducing atmosphere to bring out all the qualities of the glaze. Nowadays, a considerable number of ceramists, amateurs and professionals, are unable to use a gas kiln and have to ‘make do’ with electricity.

Introduced to stoneware glazes by Bernard Leach, Mrs. Klug da Silva has striven to overcome this difficulty. Teaching these glazes to students who are for the greater part city-dwellers, without access to combustion kilns, she has established that a ‘reinforcement’ of certain of the oxides constituting the ashes provided a good corrective. In this case, it involved interventions on the alkalis, titanium, phosphorus and iron.

Intervening on the alkalis

[Photos p98-99: Kaki, diagram 20 With increase of 0.25 Fe_2O_3 and 0.15 P_2O_5
Above: Iron blue based on Diagram 25
Explanatory key to opposite page
In one of the glazes above
Variations of P_2O_5
Variations of Fe_2O_3]

We recommend beginning with a basic ash, for it offers a wider range of possibilities. The whole set of tests should be performed, not the simplified set, introducing part of the alumina (0.05 – 0.1 Al_2O_3) by a feldspar, the rest (up to 0.5 Al_2O_3) being provided by a kaolin. Too much feldspar would ‘drown’ the specific possibilities of the ash. We have discovered that the best zone lies between 0.1 - 0.3 Al_2O_3 and 1.5 – 3.5 SiO_2. This can be explained by the fact that an oxidized firing increases the viscosity of glazes. A higher level of alumina, in itself an agent of viscosity, would provoke less than fully matured and poorly spread glazes. In the zone containing 1.5 SiO_2, heterogeneous phenomena (nucleations) may occur. The field with 3.5 SiO_2 yields good utilitarian glazes.

Now the method can be changed, chalk being replaced by a basic ash in an alkaline glaze of which the formula is available. Doing this means diminishing the proportion between base and acid, that must never fall below 1.5 SiO_2. This kind of intervention may confer new qualities on the glaze, both in color and in texture.

As with all glazes, it is recommended to avoid preparing too large a quantity at a time. The prolonged immersion of an ash makes the alkalis dissolve, and may modify the glaze.

Additional titanium

We have seen that this oxide is present in significant quantities in every ash. Although its role in the physiology of plants is not yet known, its action in a glaze is very obvious. We can increase it, knowing that it belongs, like silica and phosphorus, in the column of the acids. The results are interesting above 0.1 TiO_2 and spectacular above 0.17 TiO_2.

Variations of titanium have been made in reconstitutions of ash glazes and have allowed the following observations. The level of titanium can be increased from 0.03 (a level frequently found in ashes) to 0.3 TiO_2. But it is possible to go up as far as 0.45 when the alkalis are in the neighborhood of 0.4 KNaO, with alumina varying between 0.45 - 0.55 Al_2O_3 and silica between 4 – 5 SiO_2.

It is also possible to introduce TiO_2 using rutile, which may also sometimes introduce a little phosphorus. In this latter case, changes in color and texture will be noticed.

While opacifying a glaze to a greater or lesser extent, titanium gives it a particular quality. When it is combined with iron oxide, an interesting range of colors is obtained. With 0.03 Fe_2O_3, we obtain greens and blues if the magnesia in the glaze is below 0.3 MgO, browns with 0.4 or more of MgO. Once above 0.03 Fe_2O_3 there is a risk of excess fusion.

Needless to say, the range of colors grows wider with the introduction of other oxides (CuO, Cr_2O_3, etc.), We should state that this research with titanium has been performed on a large number of diagrams, but with silica and alumina never reaching very high levels.

Additional phosphorus and iron oxide

These two oxides are present in ashes, with the iron always at low levels, those needed for a celadon, for example. The levels of phosphorus, on the other hand, are very variable. But no matter what the values of Fe_2O_3 and P_2O_5, it is essentially in the area of color that the interaction of these two oxides offers the widest range (blues, reds, rusts, grays, greens, etc.). Here we will only mention two categories, the blues and the reds (kaki) obtained by reconstitution and localized in certain of the diagrams.

The blues were obtained using diagram 25 (Basic mole: 0.7 CaO, 0.3 KNaO). We made P_2O_5 vary from 0.01 to 0.04, iron remaining fixed at 0.15 Fe_2O_3. Needless to say, if the clay body contains any iron, that will have to be taken into account. All the alumina is introduced by feldspar (about 0.33 Al_2O_3) and the proportion between alumina and silica varies between 10 and 12 (3.3 – 4 SiO_2). It is equally possible to vary the proportion between CaO and KNaO (diagrams 9, 17, 26), but then it will be necessary to play with the alumina and the silica.

Kakis are more easily obtained in an electric kiln than blues. They differ by the indispensable presence of magnesia. Diagrams 20 (0.5 CaO, 0.3 MgO, 0.2 KNaO) and 27 (0.5 CaO, 0.2 MgO, 0.3 KNaO) have been found most favorable. 0.1 MgO is too weak and 0.5 darkens the red.

We have taken the level of phosphorus from 0.08 to 0.15 P_2O_5 while the iron remains at 0.25 Fe_2O_3. If the P_2O_5 is diminished as far as 0.08, the iron will also need to be diminished (0.2 Fe_2O_3). The proportion of alumina and silica remains obviously essential (cf. color plates).

It is hardly necessary to add that in all this research, noting is gained in advance, that the people in each workshop will have to play very delicately with materials, methods, and the patience at their disposal.

A final note: the iron blue glazes must not be fired above 1280° unlike kakis which can be fired at very high temperatures without any ill effect.

A kind of conclusion

Just as we were completing these notes on ash glazes, we obtained, using a wheat straw ash, a glaze that invites all kinds of questions. This is its formula:

0.45 CaO		
0.32 MgO	0.07 Al_2O_3	1.55 SiO_2
0.04 Na_2O	0.03 Fe_2O_3	0.19 P_2O_5
0.19 K_2O		

Like all the ashes used in our workshop, this too has its own little story. A local farming co-operative practices free stabling. That means that the cattle move freely between the pasture and the stable. This latter is composed of a simple roof and the walls are composed of bales of straw piled up to protect the animals from the prevailing winds. Every year, after the harvest is over, the bales are replaced, but at ground level there remains a layer of straw more or less damp and rotten, that is ‘generously’ offered to us.

We have on many occasions made good use of wheat straw ashes with very varying compositions, some very sodic, other very potassic, with the silica varying between 1.5 and more than 3 moles. But we have never seen an ash so rich in phosphorus. With increased levels of alumina (0.5 Al_2O_3), iron oxide (0.25 Fe_2O_3) and silica (5 SiO_2), an oxidizing atmosphere yields the red already obtained at other times. But it is when we remain as close as possible to the original formula that the questions start.

The ash melts on its own, as can be assumed at sight. The result is very heterogeneous, with craters that will have to be eliminated. So we intervene successively on each term in the basic mole, touching the alumina and silica as little as possible, after a series of negative experiences. Finally, it is a slight increase of the alkalis by a nepheline-syenite (= 0.05 KNaO) and iron oxide (+ 0,01 Fe_2O_3) that gives a positive result. Thus the formula becomes:

0.42 CaO	0.13 Al_2O_3	1.7 SiO_2
0.3 MgO	0.03 Fe_2O_3	0.17 P_2O_5
0.28 KNaO		

Perhaps it is necessary to repeat once more what these symbols are worth, that sketch in their own manner the ‘portrait’ of a mineral, an ash or a glaze. An analysis or a formula in numbers are obviously only a kind of ‘stirrup,’ useful as a foothold, but knowing all the while that the race is far from won. The results of the examination of an ash, for example, may vary enormously from one laboratory to the next, depending on the method of analysis and the degree of precision. The lists of percentages of components may not give any account of the oxides only present as traces. Whereas the fire takes account of everything. If we use another image, we might say that the numerical formula of a glaze is an approximate score, while the fire interprets, without a single wrong note, *the exact score, that it alone knows*. That is the situation in which the glaze-maker is, the challenge that has to be accepted. We have to establish the relationship of cause and effect between what goes into the kiln and what comes out, making step by step, from one firing to the next, the corrections that seem necessary, partly in order to correct technical faults, but also in the hope of achieving that glaze where the potter’s sensitivity finds itself in harmony with the work of the fire.

Finally, we must come back to our ash glaze. Here, harmony is mingled with amazement. What happened during the fusion of this mixture, containing more than 85% of ash? The essential characteristic of this glaze is its heterogeneity. ‘Islands’ slightly in relief emerge from a transparent sea, in which they form opaque specks. They are neither crystals not nucleations. Their curved outlines rather remind you of the pieces of a jigsaw spread on a table before being put together. They tend to soak up the iron oxide until, with their ‘frosty’ structure they have the iridescent rainbow hues of a chandelier. Two variations using traces of copper or cobalt show that in those cases it is the ‘sea’ that absorbs the oxides. Butterfly wings? Lizard skins? We are tempted to look to nature to supply the right comparisons.

But nothing of all that explains the origins of the phenomenon. It is possible to imagine that the heterogeneity comes form the simultaneous formation of two distinct types of glass, a silicate and a phosphate, since phosphorus too forms a glass. But why would each of these two glasses have an affinity, as Palissy would say, for this or that colorant? Why the irregular, sinuous forms of the islands? Why the iridescence? Why? Why? . . . Perhaps to remind us that the more we know, the further away lies the threshold of knowledge, and no doubt, surely, that the adventure of ash glazes, with such very ancient origins, is very far from having reached its end.

[Photo p.107: Wheat ash (85%) and nepheline-syenite. Decorated with the same glaze with cobalt added.’