CERAMIC PRODUCTS

The term "ceramics" refers to any pottery made from fired high-quality clay, silica and feldspar. The ceramics produced are used for a wide variety of applications, ranging from electronic components to sewer-pipes to fine china. All of these products are made in the same basic four-step process.

Step 1 - Shaping
The ingredients are mixed together and soaked in water. The excess water is squeezed out to make a clay with a moisture content of about 20%, and the mixture is shaped appropriately. This is either done by forcing the clay into a mould or by pressing a mould into the clay while it is spinning on a turn-table.

Step 2 - Drying
The items are dried slowly in an oven, during which stage they lose all of the water except that which is bound up in crystal lattices. This results in a 3 - 7% volume reduction.

Step 3 - Firing
The item is heated to temperatures up to 1170°C, during which time the clay undergoes some chemical changes and the silica and feldspar undergo physical changes. The reactions of the clay can be summarised as follows:

$$\underset{\text{kaolinite}}{6Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{metakaolinite}}{6Al_2Si_2O_7} \rightarrow \underset{\text{silicon spinel}}{3Al_4Si_3O_{12}} \rightarrow \underset{\text{mullite}}{2Al_6Si_2O_{13}}$$

Silica and water (from the crystal lattice) are also expelled during firing, resulting in a further 5 - 7% volume reduction. This silica mixes with the silica already present and melts to form a glass. It is this glass, which also includes metallic ions from the feldspar, that makes the ceramic item non-porous and water-tight.

Step 4 - Glazing
The glaze is either applied before firing or between a first and second firing. Glazes are glassy substances used to provide a smooth surface on the item (which can then be textured if necessary) and to colour the ceramic surface. Glazes are thus mixtures of silica, SiO_2, and boric oxide, B_2O_3 (which form the glass), and various transition metal oxides that give the colours. Other metal oxides are also added to alter various properties of the glaze as desired.

INTRODUCTION

Ceramic articles are solids made mainly from inorganic, non-metallic material. Bricks, tiles, sewer-pipes, pottery and china are familiar examples. In general, pottery is made by shaping and firing a mixture of clay, silica and feldspar. The reactions that occur when this mixture is heated are very complex, and in order to understand the chemistry of firing it is necessary to examine the nature of each of the constituents.

The composition of raw materials, firing times etc. in this article are those used until recently by Crown Lynn Potteries, now closed, and are typical of those used in New Zealand.

The history of ceramics

Dr V Heine, in his Ceramics lectures at Crown Lynn Potteries (unpublished), summarised the history of ceramics as follows:

> *The term "ceramics" is derived from the Greek word "Keramos" which originally meant a drinking vessel, but was later applied by the Greeks to all fired clay products.*
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> *In most languages except English it is pronounced and spelt with a "K" instead of a "C".*
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> *The meaning of the term "ceramics" varies from country to country. Sometimes it includes also glass, cement, enamels on a metal base, and grinding wheels, because these four products are made mainly from the same raw materials as the other ceramic bodies.*
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> *Here, we will use the term "ceramics" with a narrower meaning confined to products which are shaped at room temperature, but must be fired in a kiln in order to become hard and usable. This is not the case with three of the types of products mentioned above.*
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> *Making ceramics is a very ancient craft. It was first developed in Egypt and Mesopotamia about 4,000 to 3,000 years B.C. In the Bible we find already in Genesis II:3, a reference to the fired bricks of which the Tower of Babel was built.*
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> *Products of tremendous perfection and beauty were achieved in ancient times, especially in Babylonia in the 6th Century B.C. and in Crete and Greece about the same time.*
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> *Still unrivalled is the beauty the early Chinese achieved in their pottery during the T'ang Dynasty (618-906 A.D.) and the Sung Dynasty (960-1279A.D.).*
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> *All these great craftsmen had no scientific knowledge. Their work was based on trial and error, on accidental discoveries and on tradition handed down from one generation of potters to the next. Frequently, the stream of tradition was interrupted, and later potters had to experiment afresh and re-invent what had been forgotten. The great French artist and potter, Bernard Palissy (1510-1589) re-discovered many of the forgotten earlier achievements, but did not pass on his knowledge to his successors.*
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> *Fortunately, nowadays, tradition is replaced by text-books and scientific knowledge.*

Ceramics have only a short history in New Zealand, as can be seen in this quote from Gail Lambert in her "Pottery in New Zealand, Commercial and Collectable" (Heinemann):

> *The history of the clay industry in New Zealand is only as old as that of European colonisation. The Polynesian ancestry of the Maori lost the art of pottery-making several hundred years before New Zealand was settled, and no pottery was made by the prehistoric Maori. Pakeha settlers, bringing knowledge of the craft with them, were quick to realise the value of the clay deposits which were to be found in most*

> *areas of the colony. Early use of these was confined to the making of drainage pipes and bricks. As the demand for building materials grew, more and more machines were imported, the quantity and range of clay products increased, and techniques improved. However, it was during the troubled years of the social and industrial revolution in Great Britain that the greatest growth of the pottery industry in nineteenth century New Zealand occurred.*
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> *The 1870s and 1880s saw the closure of the many small potteries in Britain and the opportunities offering in the New Zealand clay industries were grasped eagerly. Tentative moves had been made towards the production of utility and ornamental pottery during the 1860s. By the 1870s there was employment offering not only for clay workers, but also for craftsmen skilled in the finer aspects of the trade.*

INGREDIENTS

Ceramics are made from three basic ingredients: clay, silica and feldspar. However, these do not necessarily occur in nature in pure or separated form. The naturally occurring raw materials typically used in New Zealand potteries, their relative amounts and, where appropriate, their composition are given in **Table 1**.

Table 1 - The raw materials used in clay production

Ingredient	**Proportion / %**	**Source**	**Composition**
Halloysite clay	30	Kerikeri, Northland	½ quartz, ½ kaolinite
Sunnydale clay	9	Mt. Somers, North Canterbury	35% quartz, 65% kaolinite
Fire clay*	31	Waikato	kaolinite and quartz
English ball clay	5	England	
Quartz sinter	10	sand north of Kerikeri	
Naphtheline syenite	10	Norway	feldspar
Talc	2		

* This is a ball clay. A ball clay (so-called because it was originally mined using hand-tools, and was extracted in ball-like lumps) is a sedimentary clay, i.e. it has been transported from elsewhere and deposited over a long period of time, usually by water, but some deposits have built up from airborne deposition. It is normally very fine in particle size and plastic, and thus is used to improve the plasticity of the clay mix.

The iron content of the materials must be low, otherwise the typical red-brown colour of bricks etc., which are made from cheaper raw materials, would be produced.

The nature and function of the three ingredients obtained from these raw materials are given below.

Clay

Clay consists of tiny crystals often in flat, plate-like forms with a diameter of 1 m to 10 m. When mixed with water the crystals can easily slide over each other (like a pack of cards), and this phenomenon gives rise to the plasticity of clays. Clays are formed from rocks which have been weathered by physical and chemical action, e.g. orthoclase, a mineral found in granite, reacts with H_2O and CO_2 from the atmosphere as follows:

$$\underset{\text{orthoclase}}{K_2O\cdot Al_2O_3\cdot 6SiO_2} + 2H_2O + CO_2 \rightarrow \underset{\text{kaolin clay}}{Al_2O_3\cdot 2SiO_2\cdot 2H_2O} + 4SiO_2 + K_2CO_3$$

Kaolin clay is the clay most commonly used for pottery-making and, in common with all clays, the clay particles or crystals have a special layer structure.

The silicon ions are in fourfold coordination with oxygen, and the vertices of all the SiO_4 tetrahedra point in one direction. These apical oxygens link the tetrahedral layer to another sub-layer, called the octahedral layer, which is formed by Al ions in six-fold coordination with O and OH. The oxygens form a hexagonal ring of approximately the same size as the SiO rings. A kaolinite crystal consists of a stack of many layer with adjacent units linked by hydrogen bonds. This structure is broken down when the clay body is fired.

Silica

Silica, SiO_2, is mixed with clay to reduce shrinkage of the ware while it is being fired, and thus prevent cracking, and to increase the rigidity of the ware so that it will not collapse at the high temperatures required for firing. Silica is useful for this purpose becasue it is hard, chemically stable, has a high melting point and can readily be obtained in a pure state in the form of quartz. However, in the ceramic industry, silica is often obtained from sandstone (see **Table 1**), which consists of lightly bonded quartz grains.

Feldspar

Feldspars are alumino-silicate minerals found in nearly all igneous rocks; they have very similar chemical compositions, e.g.

potash feldspar or orthoclase	$K_2O\cdot Al_2O_3\cdot 6SiO_2$
soda feldspar or albite	$Na_2O\cdot Al_2O_3\cdot 6SiO_2$
lime feldspar or anorthite	$CaO\cdot Al_2O_3\cdot 2SiO_2$

Feldspars are widespread in nature and most commercial supplies are recovered from pegmatites, which are coarsely crystalline rocks formed in the later stages of crystallisation of a magma.

Feldspars are used as a flux in the firing of ceramic ware. When a body is fired, the feldspar melts at a lower temperature than clay or silica, due to the presence of Na^+, K^+ or Ca^{2+} ions, and forms a molten glass which causes solid particles of clay to cling together: when the glass solidifies it gives strength and hardness to the body. The molten glass also reacts with the silica and clay particles.

THE MANUFACTURING PROCESS

This consists of four basic stages: shaping, drying, firing and glazing. Sometimes the glaze is applied before firing (once-firing), and sometimes the item is fired, then the glaze is applied and then the item is refired (twice-firing). Both methods are used in New Zealand and their chemistry is very similar.

Step 1 - Shaping

The materials are thoroughly mixed with water and the excess squeezed out to give a workable clay mix. The material is either shaped by casting in enclosed moulds which open in half to release the formed article, or shaped by "jiggering". This involves laying a sheet of mix onto an open mould, which spins, and then pressing a profile into the sheet to give the article the required shape.

All the equipment is fully or partly automatic. Operations like putting handles on cups are done by hand.

Step 2 - Drying

Before the ware can be fired to high temperatures it must first be dried to remove water. Water is added to increase the plasticity of the clay; this water is still present in the body after it has been formed, and can be removed only slowly as it must migrate through the spaces between the particles of clay, silica and feldspar to evaporate from the surface. During the drying period the body will shrink by a significant amount. Shrinkage stops when the particles come into contact. However, if drying is not uniform, stresses can build to the extent that the body warps or possibly cracks.

Castware is in the mould for 0.5 - 1 hour, where some drying occurs, and then air-dried for 1 - 4 days. Jiggered-ware is dried at a little above ambient temperature for a little over an hour in a "mangle drier" and then air-dried for 1 - 5 days.

Step 3 - Firing

Once drying is complete the body is ready for firing. All unglazed articles and many glazed ones are fired using the "once-firing" method. However, a small number of articles are fired twice in a method whereby the glaze is applied after the first, biscuit, firing and is fixed on by a second, glost, firing. In this method the dried articles pass through the first, biscuit (or "bisque"), firing at a slow rate. For hollow-ware, such as cups, the total time from cold through the kiln and back to cold is about 26 hours, while for other articles it is 44 hours, although modern kiln design is able to significantly decrease both these times. After this the glaze is applied and the ware is fired again. The maximum temperature in both kilns is 1170°C.

To understand this process it it necessary to consider what happens to the individual components of the body when they are heated to high temperatures.

Chemical reactions of clay

When heated to 1100°C, kaolinite decomposes by first order kinetics[1] according to the following sequence of steps:

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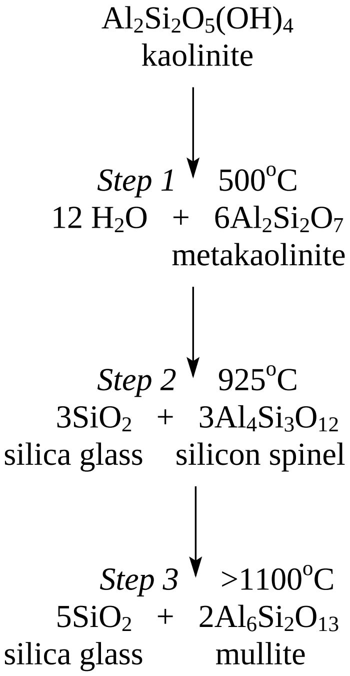
[1] This means that the reaction rate is proportional to the concentration of the substances reacting.



Step 1 is a very important step, and the temperature must be carefully controlled as the clay decomposes. The water given off by this reaction is not water remaining between the particles, but water bound into the mineral lattice. The loss of this water causes the lattice and hence the clay particles and therefore the clay body to shrink. If this step is not carefully controlled, the body can be destroyed by thermal stresses and by the rapidly escaping steam. The weight loss during *Step 1* is about 14%, which means that the volume of steam evolved at 550^{o}C from a 3 kg lump of clay would be approximately 2 m^3 at S. T. P. Large masses of clayware being fired in a kiln must be well ventilated.

Steps 2 and *3* illustrate that the mineral undergoes further solid state reactions where the parent crystal is rearranged and silica is rejected in the form of a glass. Finally, at about 1250^{o}C, mullite and silica glass remain.

Step 1 is a first order reaction, the rate being proportional to the amount of unreacted kaolinite remaining. The activation energy for the reaction is about 468 kJ mol^{-1}, which is very high, but typical of solid state reactions which only occur at elevated temperatures.

Chemical reactions of silica
Silica will not decompose at the temperature encountered in firing kilns and melts at 1725^{o}C.

Chemical reactions of feldspar
Pure feldspar grains begin to melt at about 1140^{o}C to form a solid and a viscous liquid; as the temperaure is raised the solid decomposes to form more liquid.

Combined chemical reaction
When a clay body consisting of the above components (clay, silica and feldspar) is heated sufficiently, all of the above reactions occur as well as several others. These other reactions are between the components themselves.

When a dry clay body is heated, the first reaction is the loss of water by the clay particles, illustrated in *Step 1* in the decomposition of kaolinite reaction. This is then followed by *Step 2*, the decomposition of metakaolinite to form silicon spinel, and then between 1000 - 1100°C mullite crystals form and SiO_2 glass begins to form (*Step 3*). The mullite crystals remain in the vicinity of the clay particles. At 1140°C, feldspar grains smaller than about 10 μm have completely disappeared by reaction with the surrounding clay. The alkali metal ions diffuse out of the feldspar and the remaining solid decomposes to form mullite and a silica-rich liquid. If the body is fired to about 1250°C the alkali metal ions, Na^+ and K^+ dissolve on to the outer layers of the quartz particles in a silica glass containing alkali metal ions. This glass cements the whole structure together and makes it non-porous and water-tight.

Step 4 - Glazing

Glaze is a thin layer of glass or glass and crystals that adheres to the surface of the clay body. It provides a smooth, non-absorbent surface that can be coloured and textured in a manner not possible on the clay body itself. Glazes are composed of various oxides combined in proportions that will yield the desired properties. Silica, SiO_2, and boric oxide, B_2O_3, are the glass formers, but oxides such as Na_2O, K_2O, CaO, PbO and Al_2O_3 must be present in the stoichiometric sense to give the desired properties. These include, for example, lowering the viscosity of the molten glass so that the glaze will flow smoothly over the surface of the clay body at the temperature at which the glaze is fired.

Glaze application

If a plain coloured article is being produced, the glaze is either applied by dipping or spraying. For patterns, the pattern is printed on, on a special machine, one colour at a time, with a maximum of three colours. Some patterns are hand painted. When the glaze is applied the articles go through a second glazing kiln, taking up to twelve hours cold to cold to go through and reaching a maximum temperature of 1050°C. Some patterns are put on after glazing by a transfer process, and these articles then go through another oven at a temperature of 720°C.

Colours of glazes

Some of the substances commonly used in forming glazes are listed below in **Table 2**.

The chemistry of glazes

Early glazes had a high lead content. Lead silicate glazes have a number of advantages. They give high brilliancy of colour due to the high refractive index, dissolve most colouring oxides, lower the surface tension of the glaze to give a smooth surface, and lower its coefficient of expansion. However, legislation in industrial countries for many years has required the use of lead free glazes, and these are now in wide use.

Some articles are glazed after the main firing so that the glazing temperature can be lower than that required to fire the clay body.

A glaze is usually formulated by mixing together the appropriate amounts of finely-ground potter's flint (SiO_2), boric acid, feldspar (a source of K_2O, Na_2O, CaO and Al_2O_3) and whiting ($CaCO_3$) plus, if required, a colouring agent. An appropriate mixture of these components, when made into a slurry with water, can be painted onto the clay body and fired. The

Table 2 - Glaze colours

Colour	Chemical(s)
Blue	Cobalt. When Co^{2+} ions are in a tetrahedral environment a blue colour results. In Matte blue, cobalt is present as a cobalt aluminate. Royal blue, mazarine and willow are Co^{2+} in tetrahedral environments in silica glazes.
Green	Many green glazes contain Cr_2O_3, with Cr^{3+} in an octahedral environment. As Cr_2O_3 is not soluble in most glazes, the glazes are opaque. Virtually all complexes and compounds of Cu^{2+} are blue or green. CuO (green) dissolves in boric oxide (B_2O_3) glaze, giving transparent green shades. If SnO_2 is added to this glaze it becomes opaque and if alkalis, e.g. Na_2O or K_2O, are added, a blue colour may be produced.
Red	Many red coloured glazes contain the red oxide Fe_2O_3 where the ferric ion, Fe^{3+}, is held in an octahedral environment. This is achieved by dissolving Fe_2O_3 in Al_2O_3 to form a solid solution, particles of this solid being suspended in the glaze. If Fe_2O_3 is dissolved directly into a silica-containing glaze, the red colour is lost because the two components react to give an iron silicate that is brown.
Black	A combination of CoO (blue), Cr_2O_3 (green) and MnO (black).
Yellow	Lead chromate, $PbCrO_4$

components will react together to form a viscous liquid which, when cooled, becomes a coloured glass.

The colouring agent (ceramic stain) is usually a transition metal oxide. Transition metals are well known for the great variety of coloured compounds they produce. This is a result of the splitting of the 3d energy levels in the the first row transition elements, and the 4d and 5d for the second and third rows respectively. It is the transition of electrons between these two levels that absorbs energy. The frequency of radiation absorbed depends on the ion, the oxidation state of the ion, and the environment in which the ion is situated. If the ion absorbs light in one region of the spectrum only, the complementary colour is observed.

THE ROLE OF THE LABORATORY

The laboratory is responsible for initially designing a ceramic formulation to produce the required product under given production restraints of the equipment available for raw materials processing and drying and firing conditions.

Incoming raw materials are tested on arrival to ensure compliance with specifications, and where such raw materials are received in "as-mined" condition, the testing will include sampling of the deposit prior to extraction of the raw material. Testing will include chemical analysis, moisture content, sieve analysis as a minimum, and may also include mineralogy, XRD and other tests. Clays may be tested for green and fired strength. Once cleared for use, and any minor compensating adjustments made in the formulation, the materials are processed together, using crushing and grinding, to give the ceramic body. The laboratory runs control tests on this body to ensure that its properties are correct for further use. Plasticity, green and fired strength, shrinkage wet to dry and dry to fired, pyroplastic index (the amount by which the body sags under its own weight at red-hot temperatures) are all tested. Other tests such as thermal expansion, dispersibility, dispersant demand, speed of casting, fired colour, and others, may also be done at this stage.

The batch of body, once tested and approved, is released for production, and control functions largely pass to production personnel at this point, with the laboratory overviewing and spot checking such items as machine settings, kiln and dryer conditions and the like.

In the preparation of glazes, the laboratory will also test incoming raw materials and will perform appropriate tests on the glaze preparation and the glaze properties. Preparation parameters such as density, particle size, fluidity are measured and control steps are taken. Glaze properties such as translucency, colour, maturing temperature, molten viscosity and flow, hardness, brilliance, thermal expansion are also measured to ensure compliance with specifications.

Once glazed, various parameters such as glaze fit (the critical difference in thermal expansion between glaze and body) and chip resistance are measured.

Grading and reject rates are studied by the laboratory once the ware has been fired, to determine causes of faults and to recommend appropriate action.

ENVIRONMENTAL IMPLICATIONS

Ceramics is essentially a "clean" industry, using naturally occurring materials such as clay, sand, feldspar and talc. For use in fine ceramics, these materials generally arrive in refined form, and mining or quarrying is not necessary. Where quarries are operated, stringent controls regarding drainage, benching, and operational safety are in force. Run-off of muddy storm water from quarries is normally directed to ponds, where the particles can settle out, and the discharge from the property is of clean stormwater only. Most mining licences now include provision for reinstatement of the area once extraction has finished, and this usually involves leaving natural drainage, gentle contours and the initiation of appropriate revegetation.

In most countries, clean air legislation is also in force, and exhaust gases are required to comply. With modern energy-efficient kilns this is usually no problem, and the black smoke of coal fired kilns is a thing of the past. Conversion of a raw ceramic body to a fired article does not release toxic gases of its own, so the industry is fortunate in not having to make special provision for this.

This article is an edited version of a lecture "The Chemistry of the Firing and Glazing of Pottery" by Dr. S. I. Smedley (Victoria University) with additional information from an essay by Miss O. M. Sullivan (Chemistry 100 student) and supplied by Mr. T. Clark Jnr. of Crown Lynn. Updated by Heather Wansbrough with reference to notes by Mr. J. M. Clark (New Zealand China Clays).