-3-

CERAMIC PROCESSING

3.1 Introduction

Despite the great diversity of techniques used in the production of ceramic articles, there are a set of operations and processes that are prac-tically common to all industries. Generally, the manufacture of a ceramic product goes through the following steps: Crushing and grinding of the raw materials, shaping (or forming), followed by drying and firing. Occasionally, some ceramic products are glazed or decorated.

3.2 Preliminary treatment of raw materials

3.2.1 Quarrying and storage of raw materials

Raw materials, particularly clays, are usually quarried from open pits. The composition of clay is usually non – uniform. Figure (3.1) shows an open quarry in Aswan. It can be seen that clay layers are not uniform in nature. That is why; it is preferable to have large amounts of clay stored in the factory sheds so as to have at least a three month reserve to ensure the uniformity of clay batches. Since such batches will tend to have versatile composition, it is customary to have clays removed from storage piles using cranes moving vertically along the stored mass so as to always have a uniform average composition. (Figure 3.2)

Fig 3.1: Clay open pit

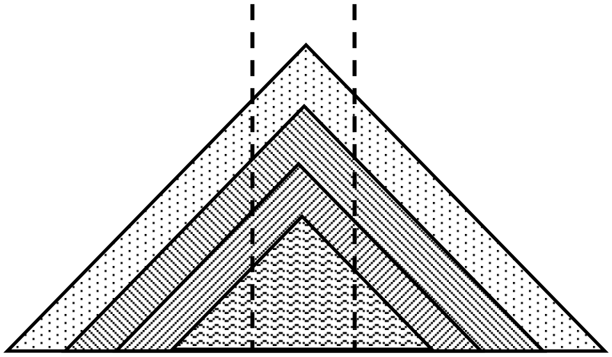


Fig 3.2: Vertical extraction of Clays from piles

3.2.1 Crushing and grinding

Preliminary crushing of raw materials is usually performed in jaw crushers. Because of the difference in hardness, raw materials are generally crushed separately. Crushed products have sizes in the range 20 – 50 mm. Intermediate crushing follows to produce particles in the size range 10^0 mm. Crushing rolls and hammer crushers are commonly used to this aim. The products from this step are then stored prior to grinding.

In general, crushing is accomplished in open areas often at the quarry location. In that case, the factory receives its raw materials in the crushed form.

On the other hand, in traditional ceramic industries, grinding is commonly accomplished in ball or tube mills, although lately Vertical Roller Mill shave also been employed. Because of the difference in hardness, it is advisable to dry grind silica and feldspar separately and wet grind clays in a different mill, although some factories use one or more common ball mill for grinding the whole batch.

In other instances, such as the refractory industry, raw materials are dry ground together, while in the clay brick industry, sand of specific particle size is mixed with ground clay in presence of water.

The internal lining and the type of balls used depend on the hardness of the raw materials. For example, it is common to use porcelain balls in case of grinding soft materials such as clays or talc. In case of a harder material such as bauxite, manganese steel balls or corundum balls (Al_2O_3) are used. When grinding quartz, large silica pebbles are used. Since these are siliceous in nature, no contamination is expected. In case of feed of versatile hardness, vulcanized rubber lining can be used.

3.2.2 Screening

The ground products from the grinding unit are either in a solid form or in the form of slurry, depending on the particular industry. Either way, this product has to be screened to meet specific particle size requirements. For example, **in the refractory industry**, it is common to have three different sizes to achieve maximum compactness. A common ratio is 50% coarse, 20% intermediate and 30% fine. A set of vibrating screens or a Trommel screen are used for this purpose. On the other hand, in the tile industry, wet screening is performed on a horizontal vibrated screen. In all ceramic industries, it is common to have a strong magnet placed prior to the screen to eliminate any metallic inclusion.

3.2.3 Mixing

Next, the ground ingredients have to be mixed together to produce a homogeneous mix. The type of mixer used depends on the particular industry. For example, **in the clay bricks industry**, ribbon, paddle or Muller double roller mixers are used (Figures 3.4 and 3.5) where the water content ranges from 15 to 25%. In the tile, sanitary or porcelain industry, underground paddles are used and a substantial amount of water is added to produce a homogeneous slip (slurry). To this mixture is added scrap recycled from the different process steps prior to firing. This slurry is then processed in different ways depending on the method of shaping.

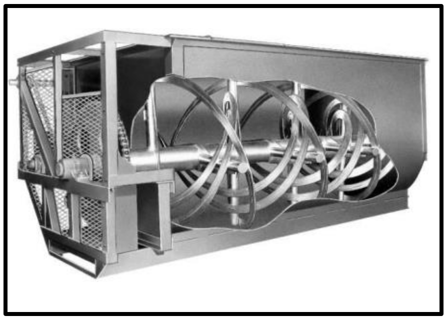


Fig 3.3: Ribbon mixer

Fig 3.4: Muller mixer

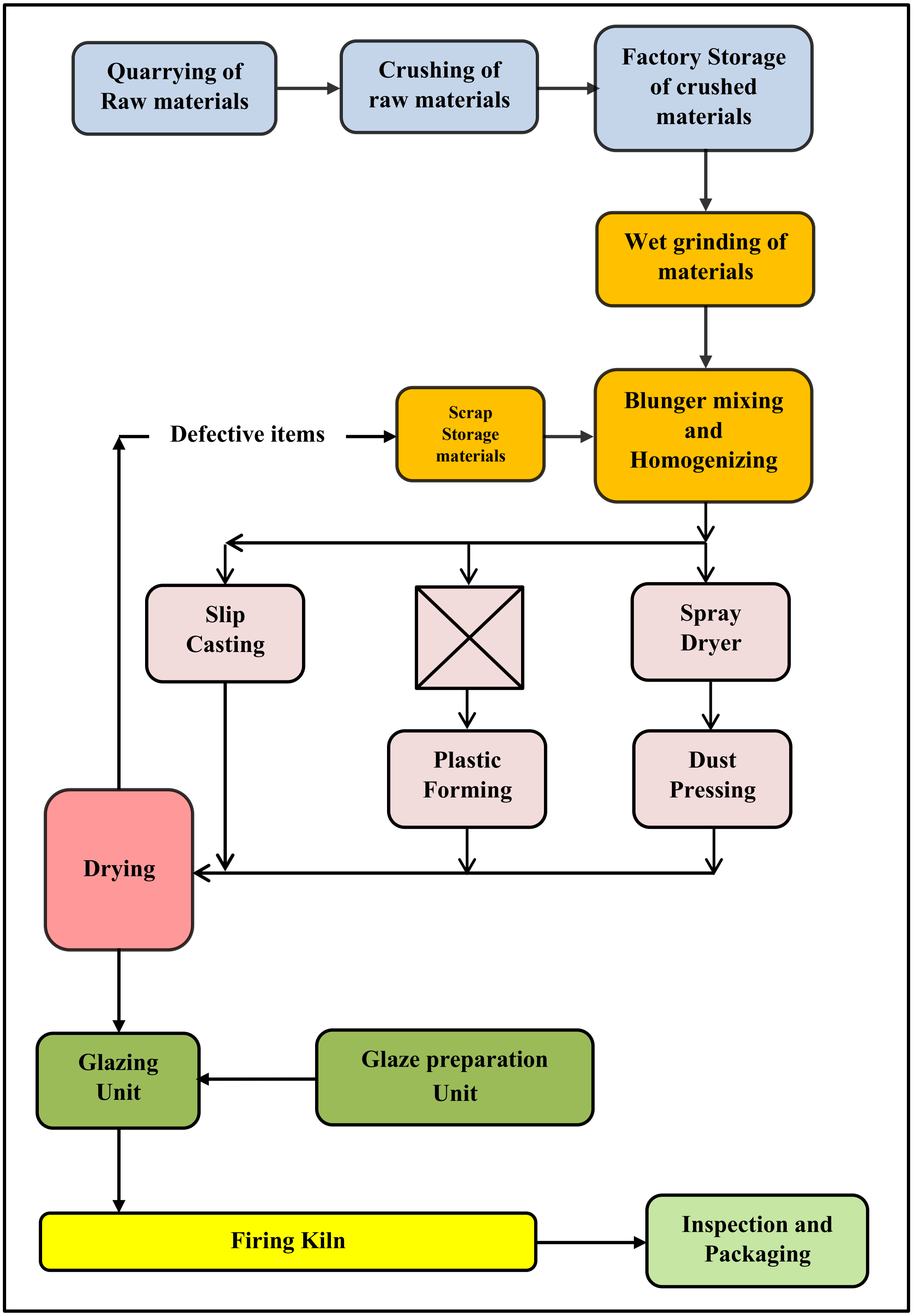


Fig 3.5: Collective flow diagram for production of traditional ceramics

If the **slip casting** shaping technique is used, then this slurry is used as such after some additions. If shaping is done using the **plastic forming** technique, then it is customary to first filter off a large amount of water in a filter press. The wet cake from the press is then admitted to a homogenizing extruding machine known as the pug mill (or vacuum auger) that produces a wet column consisting of a homogeneous mix. Further shaping may be required as will be explained later. In case of using the **dust pressing** forming technique, a spray dryer is used to deliver a powder of extremely narrow particle size distribution before pressing. A collective flow diagram for the manufacture of traditional ceramic products is shown in Figure (3.5). In this diagram, it has been assumed that the raw materials are first crushed separately and then mixed together with adding water to form the slip.

3.3 Forming techniques

3.3.1 Slip casting

In this method, slurry consisting of a mixture of raw materials (Slip) is poured through hoses to a mold, usually made of porous gypsum. Water flows off the mold leaving behind a solid cake that deposes on the internal surface of the mold, in a filtration – like process. If the body to be shaped is hollow, as in the case of sanitary ware or some tableware, then enough time is allowed for the required wall thickness to build up and excess slip is drained from the mold. This process is known as **Drain (or hollow) casting.**

If, on the other hand, the body to be shaped is plain, like for instance a dinner tray, then enough time must be allowed to fill the mold. This is known as **Solid (or plain) casting.** Figure (3.6) shows its steps while Figure (3.7) shows casting molds

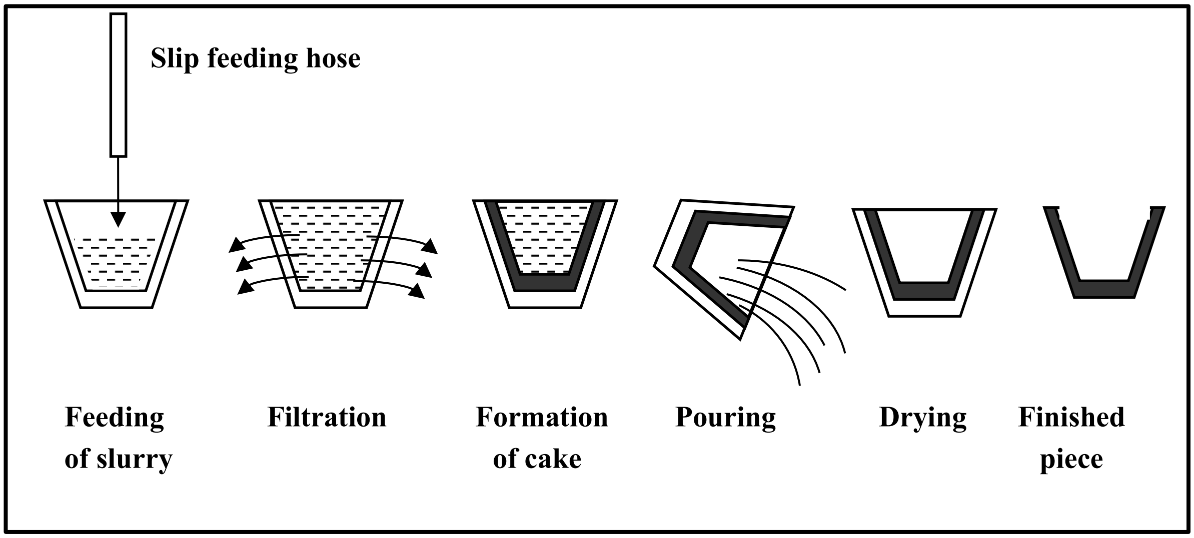


Fig 3.6: Steps of drain casting

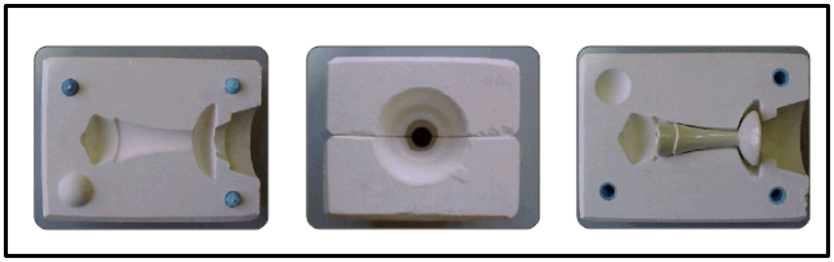


Fig 3.7: Slip casting molds

(a) Theory

As previously stated, the flow of water through pores in the gypsum mold is a filtration process, controlled by the rate of diffusion of water through the cake layer built on the wall and the pores of the mold. The main resistance to water flow resides in the solid cake. This means that one can write down the following equation relating the time of filtration t (s) to the volume of collected filtrate V (m^3):

$$t = \frac{\alpha\mu c}{A^2 \Delta p} V^2 \tag{3.1}$$

Where,

α is the average specific cake resistance ($m.kg^{-1}$)

μ is the viscosity of the filtrate (Pa.s)

c is the solid concentration per unit volume of filtrate = m/V ($kg.m^{-3}$)

A is the filtration area (m^2)

Δp is the pressure drop across the cake deposited on the inner walls (Pa)

Now, $V = m/c$, where m is the mass of deposited solid
And $m = \rho.A.x$, where: ρ is the cake density and x its thickness.
This way, equation (3.1) can be written in the following form:

$$t = \frac{\alpha\mu\rho^2}{c.\Delta p} x^2 \tag{3.2}$$

This means that during the casting process, the time of casting is directly proportional to the square of the thickness of the built solid layer. One can use this relation to predict the time required to build a certain wall thickness, as shown in the next example.

Example 3.1

During slip casting of solid cylinders 100 mm in diameter; it was found that it took 10 minutes to build the first 20 mm of wall. How long should the solid casting process last?

Solution:

Since $t = k.x^2$, then $\frac{t_2}{t_1} = \left(\frac{x_2}{x_1}\right)^2$

Now, $x_1 = 20$ mm and $x_2 = 100/2 = 50$mm, hence we get:

t_2 = **62.5 min**

(b) The slip

Due to extremely slow ion exchange over eons, some aluminum (III) ions in clays have been substituted by divalent ions, like Mg^{++}, resulting in a deficiency in positive charge, a process known as isomorphous substitution. This results in negative charges that concentrate on the external surface of the clay sheet. Second, the valences of oxygen ions at crystal edges are not satisfied and consequently, have to bind to some positive ion.

These surface negative charges are neutralized by positive cations present in the vicinity of the surface. (Figure3.8). Common such cations are Mg^{++}, Ca^{++} and H^{+}. As can be seen from Figure (3.9) forces of attraction between cations and negative charges are competitive with forces of repulsion between like charges.

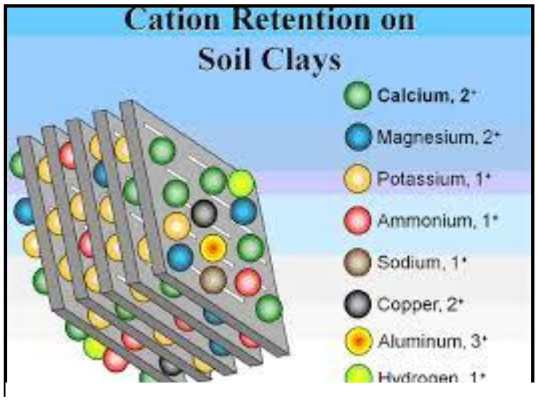


Fig 3.8: Adsorption of cations on clay surface

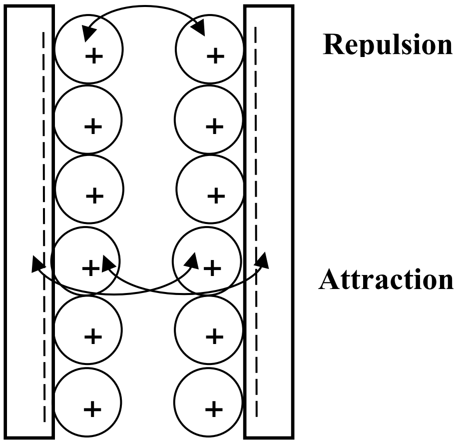


Fig 3.9: Attractive and repulsive forces

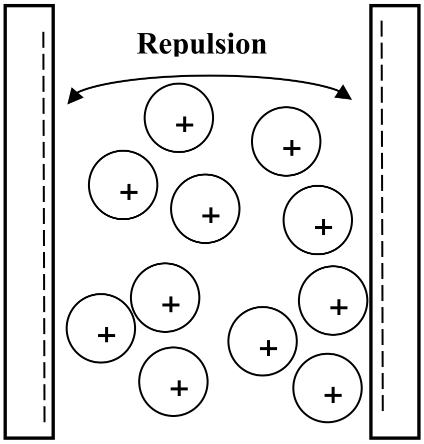


Fig 3.10: Alkali ions go into solution

In general, attractive forces overcome repulsive ones so that clay particles tend to attract each other forming bigger agglomerations that readily settle down in clay – water suspensions. This phenomenon known as **flocculation** causes severe problems in many ceramic manufacturing processes, particularly the slip casting technique.

If now, alkali ions such as Na^{+}, are added to the suspension an exchange takes place between the adsorbed ions and sodium ions. This can be simplified into the following equation:

$$\text{Clay.Ca}^{++} + 2\ \text{Na}^{++} = \text{Clay.Na}_2^{+} + \text{Ca}^{++}$$

Sodium ions, however, do not remain on the clay surface, but rather go into solution leaving bare surfaces with residual negative charges. The resulting repulsion causes deflocculation of the particles that imparts stability to the suspension. (Figure 3.10). This phenomenon is also of use in the tile industry to guarantee stability of the mix suspension prior to introduction to the spray dryer.

If a plot is made between the viscosity of the slip and the amount of deflocculating solution added, the curve passes through a minimum value after which the viscosity rises once more due to the decrease of the repulsive forces present between adjacent sheets (Figure 3.11). The optimum amount of deflocculating addition should correspond to the minimum value of viscosity.

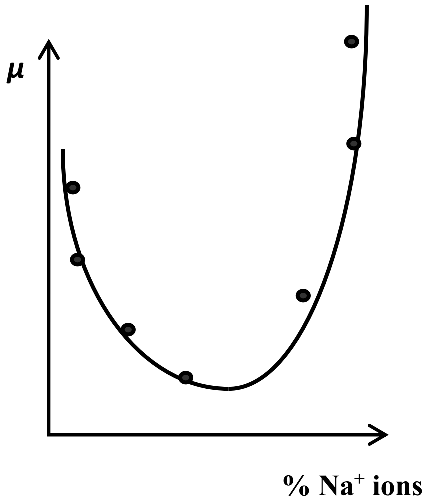


Fig 3.11: Deflocculation

This state is known as **totally deflocculated slip**. In practice, it is common to have only partial deflocculation, in order not to have too many fine particles. Typical deflocculants are sodium silicate or polyphosphate. The slip should fulfill many conflicting requirements:

a) It should have a low enough viscosity to flow readily.
b) It should have the ability to drain slowly or give sound solid casting.
c) The rate of settling should be low.
d) The cast body should have a low drying shrinkage.
e) The cast body should have a reasonable green strength.
f) The slip should be free from air bubbles.

Actually, too low a particle size will increase both the drying shrinkage and the green strength and will cause little settling. On the other hand, the presence of non - plastic material will decrease both drying shrinkage and green strength. Typical products are cast in a few hours.

(c) The mold

As previously stated, plaster molds are used in slip casting practice. The reason is that plaster is cheap, available and can be readily molded in the form of a porous body. Actually, if water is added to plaster (Hemihydrate), about 18% water is needed for the transformation of plaster to gypsum (Dihydrate) according to the reaction:

$CaSO_4.\frac{1}{2}H_2O + \frac{3}{2}H_2O = CaSO_4.2H_2O$

In practice, however, from 40% to 80% water may be needed to perform full hydration. As the mold is dried, excess water vaporizes off and pores are left into the gypsum mold. Gypsum molds are prepared using a standard master mold made from a polymeric material or a pure brand of gypsum. The lifetime of a mold is typically a few weeks since gypsum is slightly soluble in water (0.23% at room temperature). The dissolved sulfate will tend to depose on the external surface of the mold and it is said that the mold has "salted".

(d) Products shaped by slip casting

Slip casting is used in forming complex shapes that cannot be formed by other methods. Typical products are sanitary ware, dinnerware, porcelain products and complex refractory shapes. Slip cast products generally have a high porosity and hence suffer from low green strength. That is why they are usually left to dry into the mold after shaping. After some time, they are removed from the molds and left to dry on shelves into a hot environment before final drying in ovens. Non-plastic products can be shaped by slip casting using a suitable deflocculating solution. For example, alumina refractory blocks are slip cast using HCl at pH =4 as a deflocculant. In case the solid might react with water, such as in case of magnesia powders, a liquid vehicle other than water, such as alcohol, is used.

3.3.2 Plastic forming by the stiff mud process

(a) Plasticity of ceramic muds

By plasticity is meant the workability of the mud. This is a property that combines two conflicting requirements: First, a paste should not be stiff to the point that it cannot be worked. Second, it should not be too fluid since it should withstand handling. The plasticity of ceramic muds depends on the following factors:

(i) **Amount of water used:** To fulfill the two above requirements, the optimum amount of water to be added to the solid powder should be determined experimentally.

(ii) **Type of clay:** some metamorphic clays like kaolin are usually of low plasticity, while sedimentary clays, like ball clays tend to be much more plastic. Three-layered clays like bentonite are extremely plastic.

(iii) **Particle size:** in general, plasticity will increase with decreasing particle size.

(iv) **Presence of organic impurities:** The presence of organic impurities, particularly in sedimentary clays, results in the formation of humic and fluvic acids of oily consistency, which facilitates the gliding of clay sheets, thus increasing their plasticity.

(v) **Presence of non-plastic impurities:** The presence of sand, in particular, has a strong negative effect on plasticity.

(vi) **Aging:** Aging the clays for long periods of time enables the growth of anerobic bacteria which accelerate the decay of organic matter to oily substances, thus increasing plasticity.

(b) The extrusion process

In this forming method, the slurry consisting of a suspension of ground raw materials in water is first filter pressed. The filter cake obtained contains 20 – 30% water. This is admitted into an extruding machine known as the **pug mill (or vacuum auger)** shown in

Figure (3.12). It consists of two compartments. In the first compartment, a series of augers (or paddles) mix the feed material and force it to the second compartment through orifices. This compartment is maintained under vacuum and an extrusion auger (consisting of a screw) forces the homogenized air free material through the shaping die. The extruded column is then sectioned to reach its final dimensions or for further shaping.

The application of vacuum is necessary to remove air from the paste. The presence of air bubbles is responsible for many defects encountered in extruded bodies. Table (3.1) shows some of these defects. The mechanical pressure exerted ranges from 4 MPa to 15 MPa. The speed of the extruded column is directly proportional to the applied pressure since paste flow can be approximated in most cases to a Bingham fluid behavior. This speed is in the range of 1 m/min. Common capacities range from 10 – 50 ton.h^{-1}, rarely reaching 100 ton.h^{-1}. They are run by two motors reaching 100 hp. Figure (3.13).

(c) Products shaped by the stiff mud technique

Stiff mud extrusion is used to form articles of **regular cross section** such as building bricks, clay pipes, electrical porcelain products, refractory products… Extruded products tend to have a relatively low porosity and a consequently reasonable green strength owing to the mechanical pressure applied on their forming.

Stiff mud extrusion has also been used to shape non-plastic ceramics such as alumina refractory products. In this case a higher pressure has to be applied and a **piston extruder** is used. It is common to assist the process of extrusion by adding lubricants such as stearate salts and binders such as hydroxymethyl cellulose.

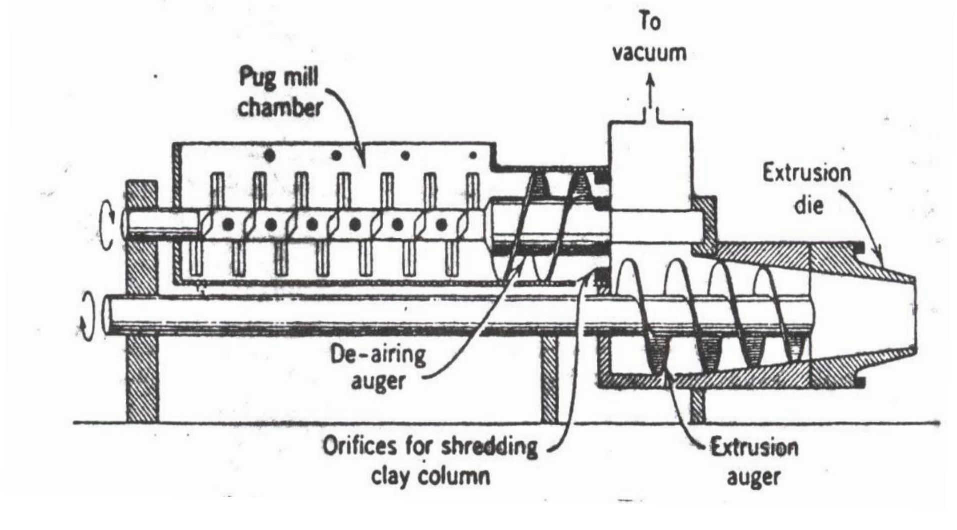


Fig 3.12: Cross-section in Pug mill (vacuum auger)

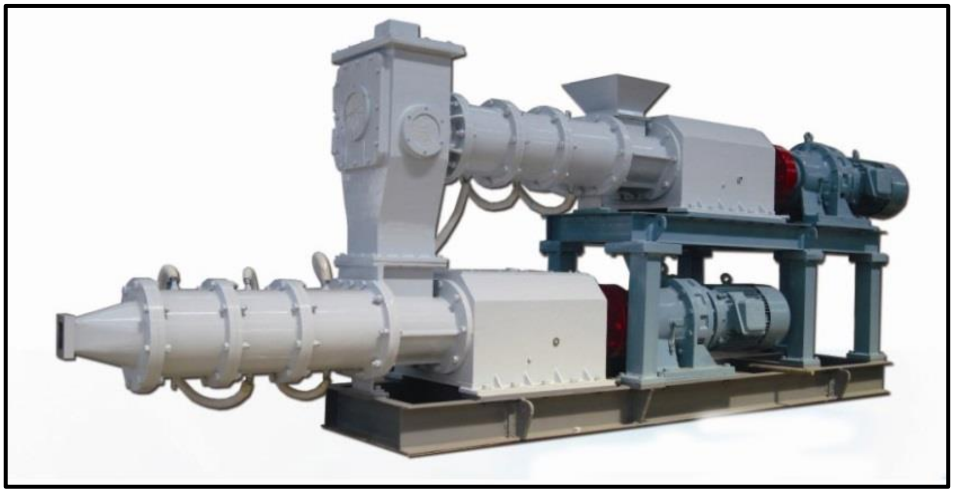
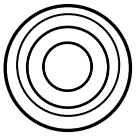
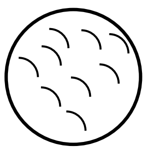
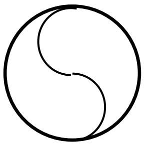
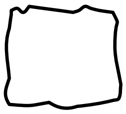


Fig 3.13: Industrial extrusion pug mill

Table 3.1: Defects in extruded clayware

Defect	Cause	Remedy	Appearance
Parallel laminations	Poor die lubrication	Good die lubrication	
Concentric rings	Difference in speed between adjacent parts of the mud column	De-airing	
Crescent laminations	Presence of air bubbles	De-airing	
S- shaped laminations	Auger shaft protrudes beyond the blade end	Use a shaft with a tapered end	
Corrugated edges	Too dry mud	-Add more water -De-airing	

3.3.3 Plastic forming by the soft mud process

(a) The jiggering process

In this forming method, the amount of water in the paste is higher (above 40%). The cake from the filter press is first homogenized in a pug mill then the sectioned products of the pug mill are admitted to a **jiggering machine**. This consists of a vertical shaft the lower end of which is fixed to a shaping template. The mud piece is put on a gypsum mold supported on a high speed vertical shaft and the template is made to contact the surface of the mud piece. This later is then deformed and contoured to give the required shape. A sharp tool trims the edges of the shaped piece. It usually takes less than one minute to form a piece (Figure 3.14). After completion of the operation, the gypsum mold is removed together with the formed piece to be dried in an adjacent dryer. The loss of moisture makes it then possible to remove the formed piece from the mold.

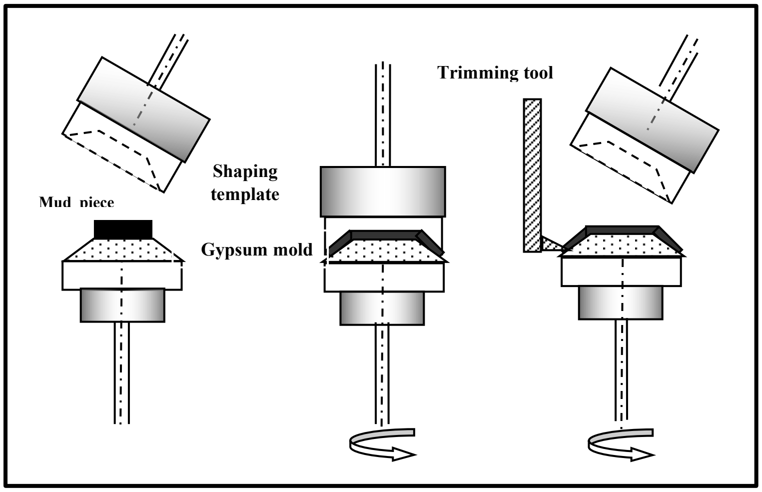


Fig 3.14: Shaping steps in jiggering operation

(b) Products shaped by the soft mud technique

This method is used in shaping ceramic articles having **a circular cross section** such as cups, saucers, electrical porcelain insulators... The accessory parts of irregular shape are formed by slip casting and then fixed to the shaped piece.

3.3.4 Dust Pressing

Dust pressing is the simultaneous compaction and forming of a granular material into a steel die or a flexible mold. The percentage water is normally below 6% and therefore no appreciable during shrinkage takes place. The production of defect free compacts in this method depends largely on a narrow particle size distribution of powder particles. That is why; the slurry has to be spray dried prior to the pressing operation. This way, fine granules of close size are produced.

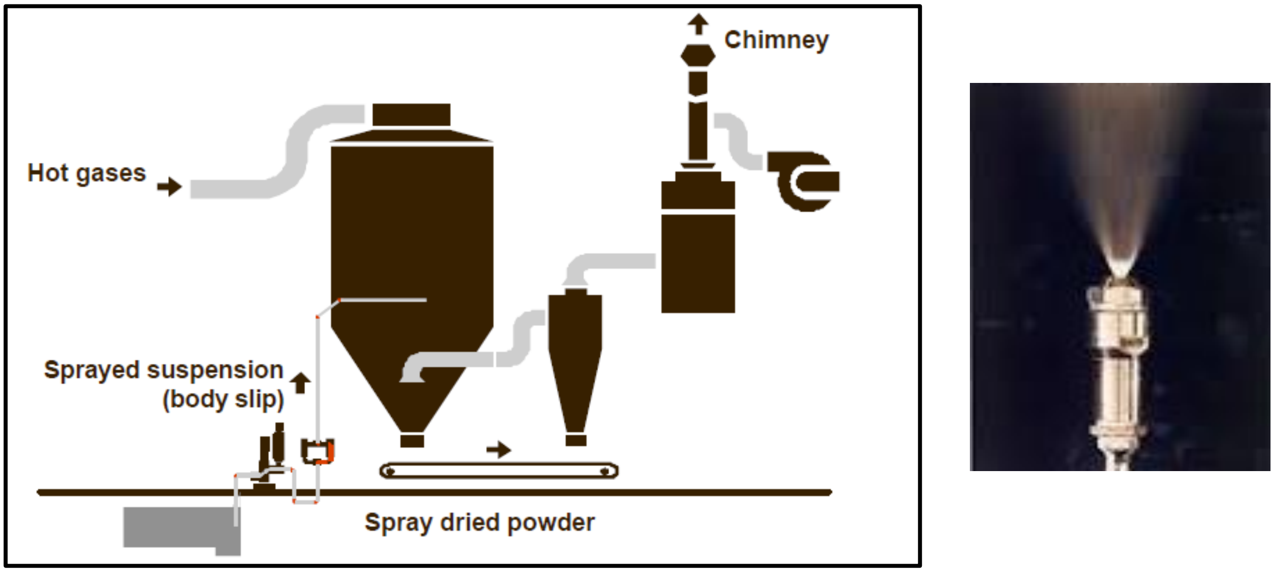


Fig 3.15: Common Spray drying arrangement – vertical atomizer

(a) Spray drying

In this process, slurry is sprayed in a hot air medium at temperatures above 400°C to produce spherical granules of narrow particle size distribution in the range $10^1 - 10^2$ μm. Capacities of industrial spray dryers range from 10 – 100 kg.h^{-1}.

Atomization of the feed slurry is done through either vertical nozzles or a rotary atomizer. In the former case, slurry is accelerated and breaks down into tiny droplets that rapidly evaporate on contact with hot air. A rotary atomizer, on the other hand, revolves at several thousand rpm producing droplets at a higher rate. Besides, nozzles are more subject to clogging. Figure (3.15) shows a common setup for spray drying used in the tile industry.

b) Uniaxial dry pressing

In the ceramic industry, it is common to produce dry pressed parts using the so – called uniaxial pressing technique. In this process, shown in Fig.ure (3.16), feed powder and additives are fed through a hopper to the die cavity of the press. The upper ram then moves down onto the powder applying pressure on it. The pressed part is then lifted upwards to be removed by the upward motion of the lower ram.

One main problem associated with dust pressing is trapping of air inside the pores that produces cracks as pressure is relieved. This can be remediated either by controlling the pressing cycle duration or by having the final applied pressure stepwise: Industrial presses do not usually apply the final pressure in one stroke, rather, about 30 – 40% of the final pressure is first applied then pressure is released to allow for entrapped air to leave the pressed piece. In the following stroke the final pressure is eventually reached. Modern practice increases the pressure over three or more steps to reach the maximum applied pressure. The applied pressure in the manufacture of ceramic tiles is typically in the range 25 – 30 MPa, increasing to 40 MPa for large stoneware articles.

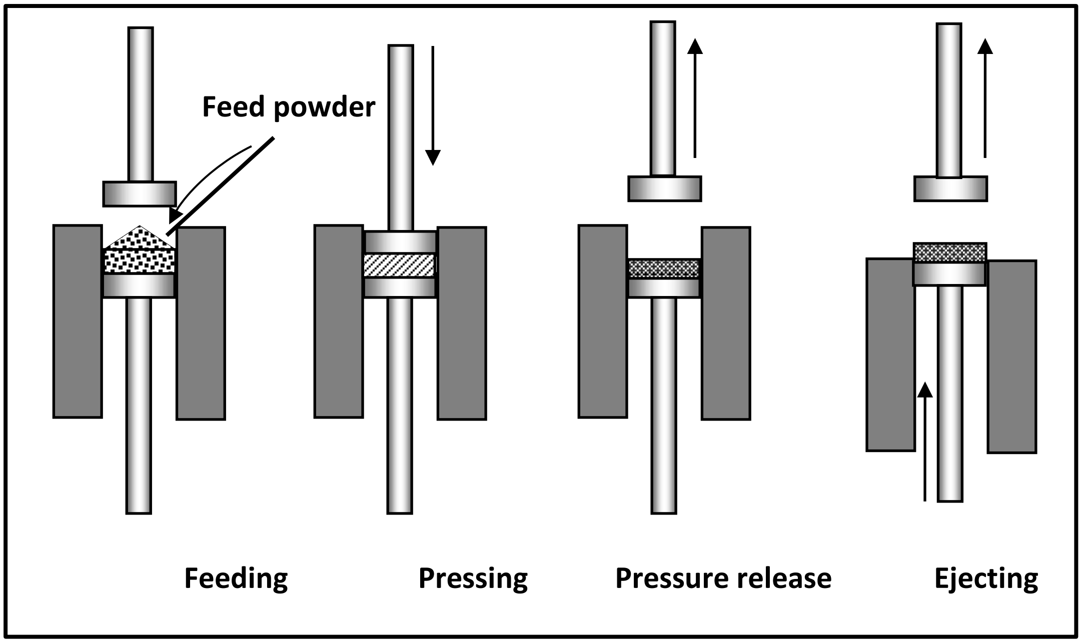


Fig 3.16: Stages of dry pressing

(c) Effect of pressure application on the granulated powder

As pressure is applied by the moving punch, the powder begins to compact. Granules deform by sliding and crushing under pressure leading to a lower porosity. At low pressures, compaction occurs at a high rate and pressures as low as 10 MPa may be sufficient to reach a reasonable pressed density. As the pressure exceeds 50 MPa, little or no densification occurs at all. Air, trapped in pores migrates to the surface and is partly eliminated from the body. Figure (3.17) shows the deformation occurring on applying pressure.

The **fill density** $\boldsymbol{\rho_f}$ is defined as the bulk density of loose powder as it fills the die. It is typically ~ 40% of the particle density. The **compact density** $\boldsymbol{\rho_c}$, on the other hand, is the final bulk density of the compact. It is typically ~ 50% of the particle density. The following relation approximates the effect of pressure on the compact density:

$$\rho_c = \rho_f + k.\ln\frac{P}{P_0} \tag{3.3}$$

Where: k is a constant, P the applied pressure and P_0 the atmospheric pressure.

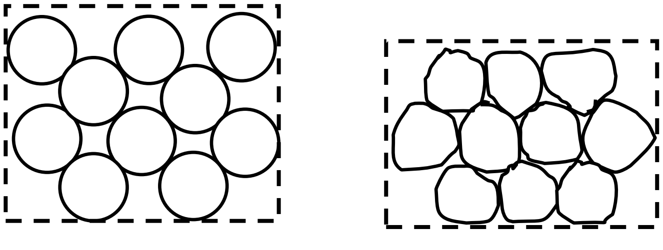


Fig 3.17: Compacting behavior of granules under applied pressure

Example 3.2

Dry pressing is used to form ceramic wall tiles having a thickness = 7 mm using a pressure of 200 bar. The die is 15 mm deep. If it was decided to use the same press to produce tiles of 6.5 mm thickness, what should be the applied pressure?

Solution:

The fill density of the powder is calculated by dividing its mass on the die volume. If the area of the die is *A* and its depth *d*, then:

$$\rho_f = \frac{m}{A.d}$$

A similar expression can be written for the compact density; here, d_c will represent the compact thickness:

$$\rho_c = \frac{m}{A.d_c}$$

Substituting in equation (3.3), we get: $\frac{m}{A.d} = \frac{m}{A.d_c} + k.\ln\frac{P}{P_0}$

Or, $\frac{1}{d} = \frac{1}{d_c} + k'.\ln\frac{P}{P_0}$

This equation can be written twice: in case of wall tiles with d_c = 7 mm and that of wall tiles with d_c = 6.5 mm.

$\frac{1}{7} = \frac{1}{15} + k'.\ln\frac{200}{1.013}$ and $\frac{1}{6.5} = \frac{1}{15} + k'.\ln\frac{P}{1.013}$

From which we get: ***P* = 430 bar**

(d) Additives in dry pressing

Proper dry pressing operation of non – plastic bodies cannot be achieved without the presence of minor additions that play an important role in the pressing operation. These are:

Binders: These consist of polymer molecules of medium to high molecular weight that are adsorbed on the surface of granules and provide interparticle flocculation. They impart high mechanical strength to the pressed compact. Typical such binders are: Gum, polysaccharides such as starch or dextrin, methyl cellulose, PVA, etc.

Plasticizers: The flocculating effect of binders is low at low temperatures (~20°C) since they become brittle and cannot properly coat the granules. This way, there is poor cohesion between the particles. That is why; plasticizers are commonly added that softens the binder and increase its flexibility. Common plasticizers are water, ethylene glycol, glycerol, etc.

Lubricants: These facilitate the sliding of granules under external pressure and reduce the particle – die walls friction, thereby reducing die wear and improve the density distribution in pressed parts. Common lubricants are paraffin wax, steric acid and its salts, oleic acid, talc, etc.

Deflocculants: If the slurry admitted to the spray dryer contains appreciable amounts of ball clay, then the dried particles will tend to agglomerate and form flocs that retain water into their interstices. Suitable deflocculants, such as sodium polyphosphate ($Na_5P_3O_{10}$), have to be added to break these flocs.

All these additives are admixed with the powder after spray drying at levels < 10%. They should be water soluble or easily dispersed in water, non-corrosive or abrasive to the mold, and should contain a minimum amount of mineral salts that can cause problems on firing.

(e) Defects in dry pressed bodies

One common defect in dry pressed bodies is the appearance of **cracks** along its height. This is particularly true in case of bodies having a high *H*/*D* ratio. Cracks (or laminations) are due to one or more of the following causes:

- Gradient of pressure transmitted to the compact due to wall friction. The final pressed piece, prior to its ejection may have a poor pressure distribution in all directions (Figure 3.16). In that case, when subjected to the spring-back pressure of the lower punch, laminations will tend to form. Proper die lubrication will minimize this defect.
- Due to non-uniformity of granule size, air will be preferentially trapped in large pores. Compressed air will tend to flow out of the pressed piece upon its ejection causing cracks to appear. A pressing cycle that continuously allow for air to leave the pressed compact will decrease this effect. Poor die lubrication, on the other hand, may produce a **capping effect** in which sharp corners of pressed compacts tend to detach from the main body. This defect is also seen when the spring-back pressure of the lower punch is high.

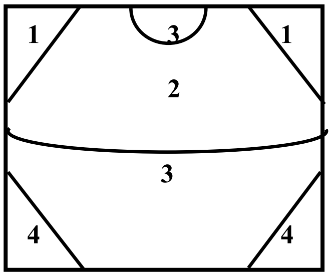


Fig 3.18: $P1 > P2 > P3 > P4$

(f) Products shaped by the dust pressing technique

This method of forming is used to shape a variety of products of more complex shapes, such as wall and floor tiles, flat dinnerware, spark plug insulators, refractory bricks etc. The drying shrinkage is low and the pressed parts needs little or no drying.

(g) Recent trends in the manufacture of dry pressed bodies

Because of the fact that the spray dryer unit has an elevated fixed cost besides the high running cost associated with the need to raise the temperature of air, research has been directed towards finding more economical alternatives. In 2010 was commercialized the first production line of the so – called **dry milling technique** for the production of ceramic tiles. In this method of production, raw materials are dry ground using a vertical roller mill of the OK type which delivers spherical shaped fine particles. The fine powder is then humidified for homogenization and stored in silos to ensure uniform distribution of moisture. Then the moist powder containing 6 – 7% moisture is fed to the pressing unit. Despite the advantages gained by energy saving, the resulting powder for the dry process suffers from broad particle size distribution and low bulk density. This latter causes problems in the pressing step.

(h) Isostatic pressing

Poor pressure distribution in uniaxial pressing can be overcome by subjecting the pressed piece to equal pressure from all sides. In the isostatic pressing technique, granulated powder is filled in flexible molds usually made from rubber, and put in a liquid medium to which external pressure is applied.

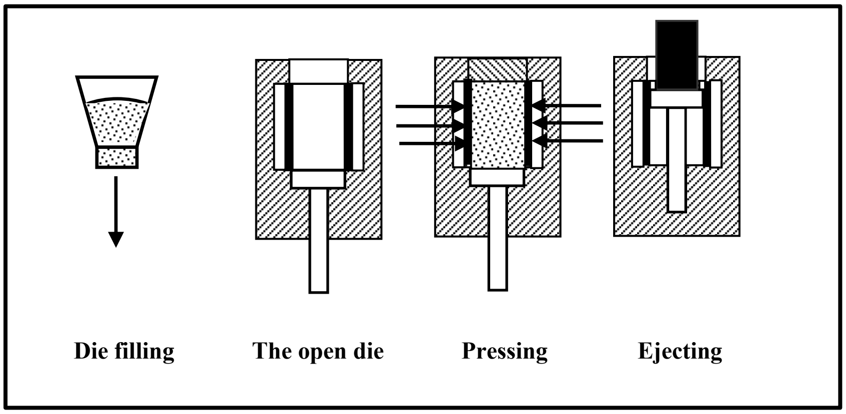


Fig 3.19: Dry isostatic pressing

Figure (3.19) shows one of the isostatic pressing techniques in which the pressurized liquid is placed between the flexible mold and a rigid shell. This technique is used to produce spark plug insulators and hollow tubes. The liquid used should be incompressible as much as possible, mineral oils and glycerin being common choices. Pressures applied to the liquid are in the range ~ 10^2 MPa.

3.3.5 Other forming techniques

The previous forming methods are the most used techniques. In the following, some other forming methods are presented, particularly for shaping technical ceramics for special purpose such as magnetic, electrical, high abrasion resistant ceramics.

(a) Hot pressing

When a near zero porosity is required, ceramic compacts can be produced by simultaneously heating and pressing granulated powder in graphite dies in an inert atmosphere. Pressures up to 200 MPa and firing temperatures up to 1600ºC are common. Figure (3.18) shows the details of a small scale hot press. Uniaxial hot pressing is not commonly used on an industrial scale. Rather, hot isostatic pressing **HIP,** is used to produce special refractory parts, heavy duty abrasives, etc. The powder is first fired to produce a high degree of sintering then subjected to further heating in presence of a highly pressurized inert gas.

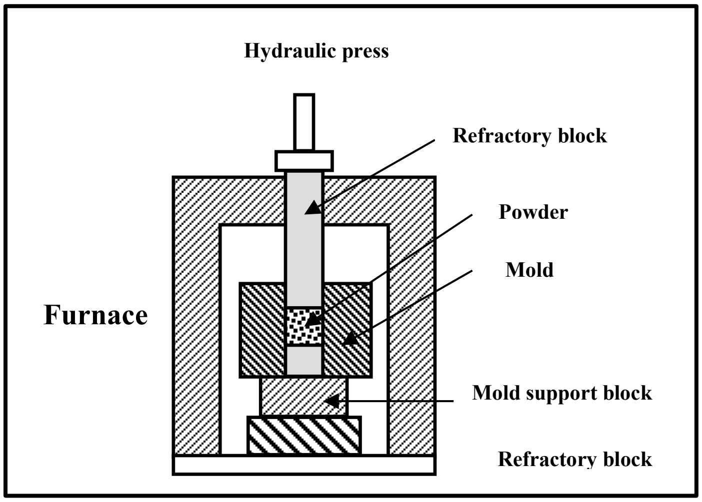


Fig 3.20: Experimental hot press

b) Precipitation from solution

Some ceramic products, such as magnetic ferrites when manufactured by dry mixing of oxide raw materials, do not produce, after firing a homogeneous isotropic body. That is why; it is becoming more common to precipitate the parent oxides from their salt solutions to obtain an extremely homogeneous mix. For example, nickel ferrite can be prepared by adding to a solution of nickel sulfate and iron (II) sulfate, a solution of ammonium oxalate. Nickel – iron oxalate will precipitate, according to the reaction:

$$0.33NiSO_4 + 0.67FeSO_4 + (NH_4)_2C_2O_4 = (Ni_{0.33}Fe_{0.67})\,C_2O_4 + (NH_4)_2SO_4$$

The precipitated oxalate is then fired to about 500°C to produce a ferrite ($NiFe_2O_4$). Its properties are superior to that prepared by the conventional dry method consisting of milling together iron and nickel oxides.

(c) Sol – gel techniques

This method is of particular interest in the preparation of thin film coatings. A sol is a colloidal solution of a monomer, which, in presence of a suitable liquid, will polymerize to a gel – like polymer. An example is the preparation of fine titania powder from titanium ethoxide sol. Partial hydrolysis of this sol is followed by condensation to produce the gel

$$Ti(OC_2H_5)_4 + 4H_2O = (OC_2H_5)_3Ti - OH + C_2H_5OH$$

$$(OC_2H_5)_3\,Ti - OH + OH - (OC_2H_5)_3\,Ti = (OC_2H_5)_3\,Ti - O - (OC_2H_5)_3\,Ti + H_2O$$

The gel formed is then dried and fired to give extremely fine TiO_2 having a homogeneous particle size distribution.

Sometimes, linear polymerization taking place, ceramic fibers can be produced. If cross – linking occurs, then three-dimensional spherical particles can be obtained. Powders obtained by the sol – gel technique often have very high specific surface (~ 100 $m^2.g^{-1}$) and porosity (~ 70%). Some oxide catalysts may be obtained this way. Figure (3.21)

(d) Chemical vapor deposition

This technique involves precipitation of a solid phase from a vapor phase. A compound is vaporized or reacted with another vapor to produce a non – volatile material that readily deposits on a solid substrate as a very thin coating. This deposition occurs on a molecular level; that is, there is a continuous build-up of molecular layers on the solid substrate. For example, extremely fine and pure silicon carbide can be deposited by the reduction of trichloro-methyl silane at 1000°C. $CH_3SiCl_3 + H_2 = SiC + 3\ HCl$

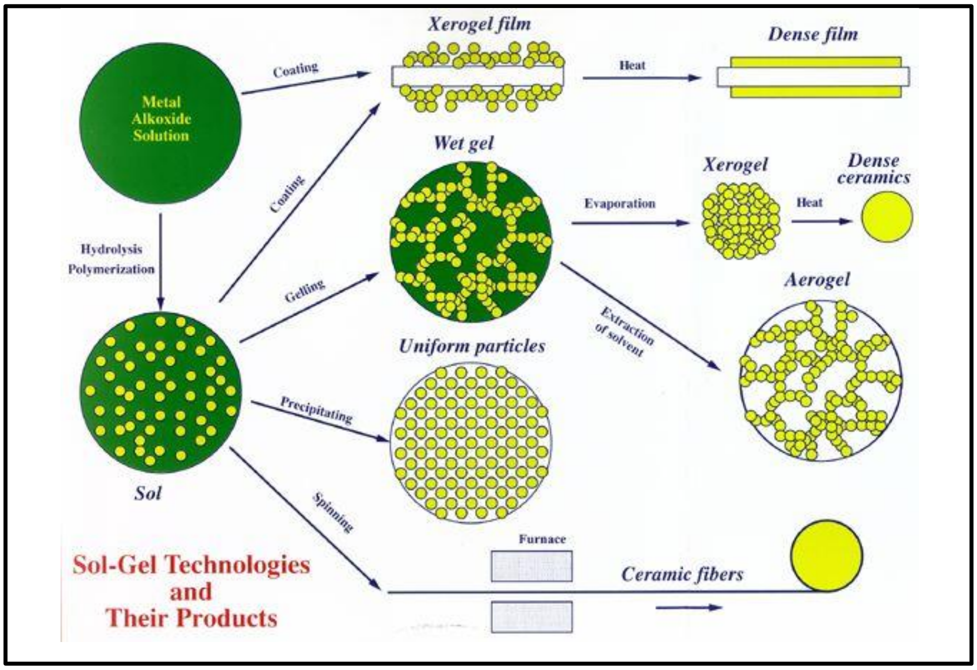


Fig 3.21: Sol – gel products

3.4 Drying

3.4.1 Theory

(a) Water distribution in clay based pastes

To form a paste out of clay, silica, feldspar and other possible ingredients, one has to add water to such an extent that a plastic mass is obtained. The total quantity of water necessary to form this plastic mass is called **water of plasticity**. This is the sum of two terms: **pore water**, which is the mass of water necessary just to fill the pores and **layer water,** which reduces the inter-particle contact by distancing the particles from each other.

(b) Drying mechanism

As the plastic body begins to dry, layer water is first eliminated (Figure 3.22). In this stage, water droplets have a direct access to the surface and the rate at which they reach the surface is equal to the rate at which evaporation takes place. This is called the **constant rate period**. This is associated with the elimination of layer water and is responsible for the **drying shrinkage** occurring. After completion of that stage, water droplets have to reach the surface through tortuous paths, and the rate is highly reduced. This stage is called the **falling rate**

period and is not accompanied by any shrinkage. At the end of this stage, most of the pore water will have been eliminated.

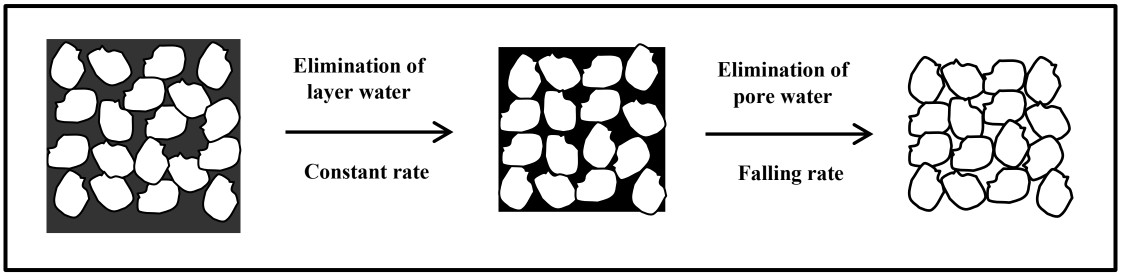


Fig 3.22: Elimination of water during drying

Moisture content (M.C. = *X*) is defined as the mass of water present per unit mass of dry body (*D*). So the mass of water is:

$$m_w = D.X \tag{3.4}$$

The rate of drying (*r)* is the rate at which mass is lost per unit area of the body (kg.m^{-2}.s^{-1}):

$$r = -\frac{D}{A}\frac{dX}{dt} \tag{3.5}$$

Figure (3.23) shows the variation of volume and that of drying rate with moisture content. The initial M.C. is X_i, while X_c represents the critical moisture content (C.M.C.) which is the M.C. at which the drying mechanism changes from constant rate to falling rate. Its value depends on the nature of the body and its particle size. For traditional mixes it usually ranges around 6%. On the other hand, X_f represents the final M.C. which depends on the quantity of water allowed in bodies to be fired. It is usually less than 1%. The rate of drying is proportional to the driving force for drying, which is the difference between the water content at the hot gas – water interface and the air humidity.

The definition of drying rate (Equation 3.5) can be used to evaluate the time required for drying a wet body from an initial M.C. of X_i to a final M.C. of X_f. To do so, one has to consider two periods:

- The time required for constant rate period can be readily obtained by integrating equation (3.5) between the limits X_i and X_c. Integration yields:

$$t_1 = \frac{D\ (X_i - X_c)}{r_c.A} \tag{3.6}$$

Where, r_c is the constant rate of drying.

- The time required for drying in the falling rate period is more difficult to calculate, since it involves graphical integration:

$$t_2 = \frac{D}{A}\int_{X_c}^{X_f}\frac{dX}{r} \tag{3.7}$$

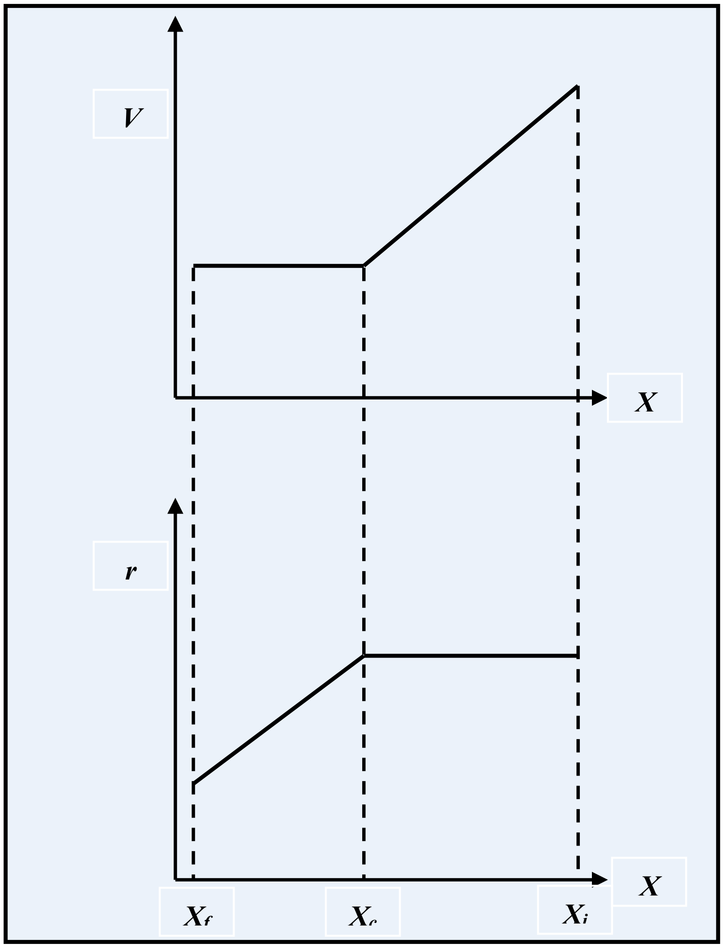


Fig 3.23 Variation of volume and drying rate with M.C.

Since the falling rate period usually involves a linear dependence of rate on M.C., one may write:

$$r = a.X + b$$

Substituting in equation (3.7) and integrating, we get:

$$t_2 = \frac{D}{a,A} \ln \frac{aX_c+b}{aX_f+b} = \frac{D}{a,A} \ln \frac{r_c}{r_f}$$

Now, a = slope of the $r - X$ relation = $\frac{r_c - r_f}{X_c - X_f}$

We finally get:

$$t_2 = \frac{D\,(X_i - X_c)}{r_{lm}.A} \qquad (3.8)$$

Where, r_{lm} is the logarithmic mean rate = $\frac{r_c - r_f}{\ln\frac{r_c}{r_f}}$

Adding t_1 and t_2, we get the time required for drying. Computational procedures can be understood by the following example.

Example 3.3

The following table shows experimental results obtained on drying a clay sample of dimensions 20×20×150 mm using hot air at 90°C and 30% RH to a final moisture content of 0.01. This sample was prepared by mixing 80 g dry clay with 35 g water.

Time min	0	20	40	60	80	100	120	140	300
Mass g	115	107	99	91	86	83	82	81	80.8

Deduce the C.M.C., the constant drying rate and the drying rate at a moisture content = 0.01.

These values are used to calculate the time required for drying 2000 bricks having an initial M.C. of 0.3 to a final M.C. of 0.01 under the same conditions. The mass of dry brick is 2 kg, and its total area is 0.1 m^2. Estimate the time required for drying.

Solution

First, we calculate the M.C. by dividing the loss in weight in the table by the dry weight (80g). We get the following table:

***t* h**	0	0.33	0.67	1	1.33	1.67	2	2.33	5
X	0.4375	0.3375	0.2375	0.1375	0.075	0.0375	0.025	0.0125	0.001

Experimental results: We plot *X* vs *t* and get the curve shown in Figure (3.24)

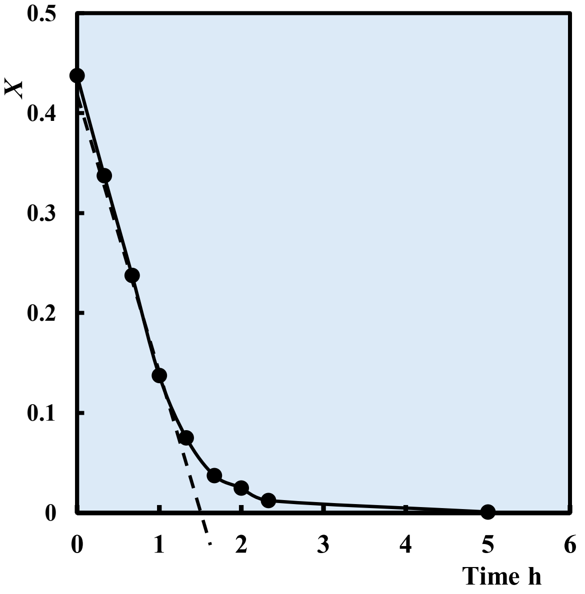


Fig 3.24: Plot of M.C. vs time

The slope $\frac{dX}{dt}$ is almost constant for the first four points. It is equal (numerically) to 0.3 h^{-1}.

The area of sample = 2×(20×20 + 20×150 + 20×150) = 12800 mm^2 ≡ 0.0128 m^2 and its dry weight = 0.08 kg

Since $r_c = -\frac{D}{A}\frac{dX}{dt}$, then $|r_c| = 6.25 \times 0.3 =$ **1.875 kg.m^{-2}.h^{-1}**

Also, the CMC is approximately equal to the value of X at the end of the constant rate period: $\boldsymbol{X_c}$ **= 0.1375**

The final rate can be obtained by fitting an exponential function through the points of the falling rate portion at time ≥ 1 h.

This equation can be obtained by curve fitting. It takes the form:

$$X = 0.31e^{-1.186t} \qquad \text{(i)}$$

Differentiating, we get: $\frac{dX}{dt} = -1.186 \times 0.31e^{-1.186t} = -1.186X$ h^{-1} (ii)

The final M.C. being $X_f = 0.01$, this corresponds from equation (ii) to:

$$\left|\frac{dX}{dt}\right| = 1.186 \times 0.01 \text{ kg.h}^{-1} = 0.01186 \text{ kg.h}^{-1}$$

Hence $r_f = 6.25 \times 0.01186 =$ **0.0741 kg.m^{-2}.h^{-1}**

Practical application: From equation (3.6), the time required for drying at constant rate for bricks with initial M.C. = 0.3 and D = 4000 kg and A = 200 m^2 is:

$$t_1 = 4000\times\frac{(0.3-0.1375)}{1.875\times200} = \mathbf{1.73\ h}$$

$$\text{The mean logarithmic rate} = \frac{1.875-0.074125}{\ln\frac{1.875}{0.074125}} = 0.557 \text{ kg.m}^{-2}.\text{h}^{-1}$$

$$t_2 = 4000\times\frac{(0.1375-0.01)}{0.557\times200} = \mathbf{4.58\ h}$$

Total time = 1.73 + 4.58 = **6.31 h**

(c) Drying shrinkage

As shown in Fig. (3.13), the evolution of layer water has for effect to cause shrinkage of the body. This drying shrinkage can be based on a linear dimension or on the whole volume of the body. The classical definition of the linear drying shrinkage S_{dL} is:

$$S_{dL} = \frac{L_i - L_d}{L_i} \qquad (3.9)$$

This usually expressed as percentage.

Where, L_i and L_d are the initial (wet) and final (dry) lengths respectively.

On the other hand, the volume shrinkage S_{dV} is defined by:

$$S_{dV} = \frac{V_i - V_d}{V_i} \tag{3.10}$$

Where, V_i and V_d are the initial and final volumes respectively.

To obtain the relation between the drying shrinkages S_{dL} and S_{dV} , consider a wet cube of edge measuring L_i.

Hence, $V_i = L_i^3$, and $V_d = L_d^3$

Denoting $L_i - L_d$ by ΔL and $V_i - V_d$ by ΔV, we can write:

$$V_i - \Delta V = (L_i - \Delta L)^3 \tag{3.11}$$

Hence: $V_i - \Delta V = L_i^3 - 3L_i^2.\Delta L + 3L_i.\Delta L^2 - \Delta L^3$

Or, since $V_i = L_i^3$, hence: $\Delta V = 3L_i^2.\Delta L - 3L_i.\Delta L^2 + \Delta L^3$

Dividing both sides by $V_i = L_i^3$, we get:

$$S_{dV} = 3.S_{dL} - 3.S_{dL}^2 + S_{dL}^3 \tag{3.12}$$

If the linear shrinkage is less than 0.05, so that the above equation can be approximated to:

$$S_{dV} \approx 3.S_{dL} \tag{3.13}$$

Drying shrinkage occurs only in the constant rate period. In theory, the amount of volume shrinkage ΔV is equal to the volume of layer water eliminated through this step. Shrinkage causes deformation of the dried body and has to be carefully controlled. This is done by adding some non-plastic material to the mix (like sand or grog) or using not too fine a particle size. Also, some types of clay are associated with a high shrinkage, such as ball clays. Their amount in the original mix should be carefully dosed. It should be noted, however, that bodies who do not exhibit a large shrinkage, will tend to have a poor dry strength and will cause troubles in handling prior to firing. A compromise is usually reached in this respect.

3.4.2 Defects occurring on drying

There are two main types of defects occurring on drying wet ceramic articles. Those are **warping** and **cracks**. These are due, in turns, to two types of causes: Those related to the properties of the body and those related to process conditions.

(a) Cracks

The appearance of cracks is mainly due to rapid evolution of moisture from the body. In the constant rate period of drying, while shrinkage takes place, if the rate of supply of moisture to the external surface is lower than the rate at which evaporation takes place, then water droplets will force their way out by forming cracks. This takes place if the gaseous drying medium is too dry, too hot or flows at a high rate. This can also take place when there is a moisture gradient across the body, in case of large parts. Wet regions will tend to shrink more than dryer regions, resulting in crack formation.

(b) Warping

By warping is meant the distortion of the shape of the body. A moisture gradient or a density gradient can cause that defect. Also, the presence of particles having a broad particle size distribution can cause this defect. On the other hand, if the flow of the drying medium (usually air) is not uniform, then the surface subjected to the medium will tend to shrink more than the hidden surface. Warping can take place accordingly. (Fig.3.25).This effect can be overcome by proper routing of the drying medium across the articles in the dryer.

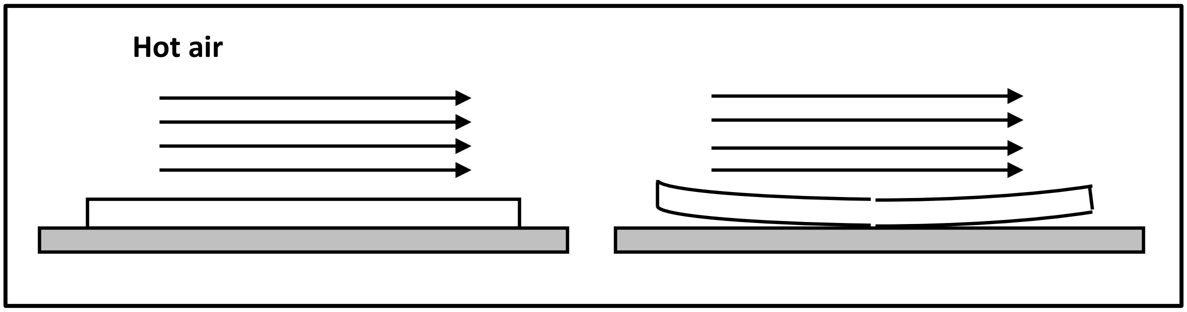


Fig 3.25: Warping on drying

3.4.3 Industrial dryers

There are several ways of drying wet ceramic products. Sometimes, as in drying of fragile slip cast articles, these can simply be placed on shelves in the casting department. Pipes carrying hot air are made to pass through this department so that these articles are eventually dried after some hours. However, the majority of ceramic products are dried into either batch or continuous dryers. Most of the defects occurring on drying take place during the constant rate period, associated with shrinkage. That is why; the drying rate has to be carefully controlled throughout this period where relatively mild conditions are required: "cold" air ($T < 80^oC$), "humid" air, and a relatively low flow rate ($v < 2$ m/s). After the C.M.C. has been reached, the rate of drying drops and no more shrinkage occurs. In this final stage, more drastic conditions can be applied: Hotter and dryer air and a higher flow rate, to help increasing the drying rate.

(a) Batch dryers: the compartment dryer

The compartment dryer is a typical batch dryer used in drying a variety of wet ceramic products such as bricks, pipes, dinnerware, etc. It consists of a chamber where the ware is placed either on shelves or on cars.

Hot air (or alternatively hot flue gases from the firing kiln) is circulated through the chamber for the required period. Care should be taken that the temperature of the drying gas should not drop below its dew point otherwise condensation will take place, accompanied by corrosion of metallic parts. Figure (3.26) shows the general aspects of compartment shelf dryer used for large scale drying of dinnerware. It is a shuttle dryer where articles are introduced on metallic cars moving on tracks.

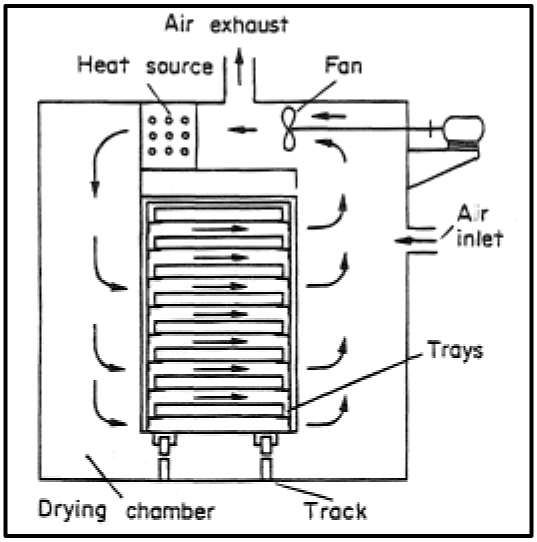


Fig 3.26 A compartment shelf dryer

(b) Continuous dryers: the tunnel dryer

Large scale production of several ceramic products necessitates the use of such dryers. This is the case in the manufacture of different porcelain products, sewer pipes, dinnerware, etc. The tunnel dryer is a typical continuous dryer shown schematically in Figure (3.27) where wet articles are either introduced on a belt or rollers or by cars into a long tunnel and hot air counter-currently flown in the opposite direction. A system of fans ensures the proper flow of the drying medium across the ware.

The countercurrent nature of operation ensures that drying will take place under the most appropriate conditions: As can be seen from the figure, the inlet hot dry air encounters the almost dried ware in its falling rate period where drastic drying conditions are required. On the other hand, the outlet colder and moister air encounters the incoming wet solids and mild conditions proper to the initial constant rate period are fulfilled. Figure (3.28) displays a continuous tunnel dryer for tiles.

A special type of continuous dryers is the **infrared dryer** that is used to dry high value thin commercial products. These are moved through a narrow opening on a belt. Heaters are arranged under the roof to provide infrared radiation. The intensity of these radiations increase as the ware gets dryer. Infrared is provided by the combustion of a gas such as acetylene in bulbs that emit intense heat.

3.5 Firing

3.3.1 Firing schemes

This is probably the most important step in the manufacture of ceramic products. It involves conferring to the product its final consistency and strength. In some cases, when the body is to be glazed, it is necessary first to fire the greenware, prior to glazing, at a relatively low temperature to impart reasonable strength and seal off surface open pores thus allowing for the glaze to apply properly besides driving off all gases from the body before glazing.

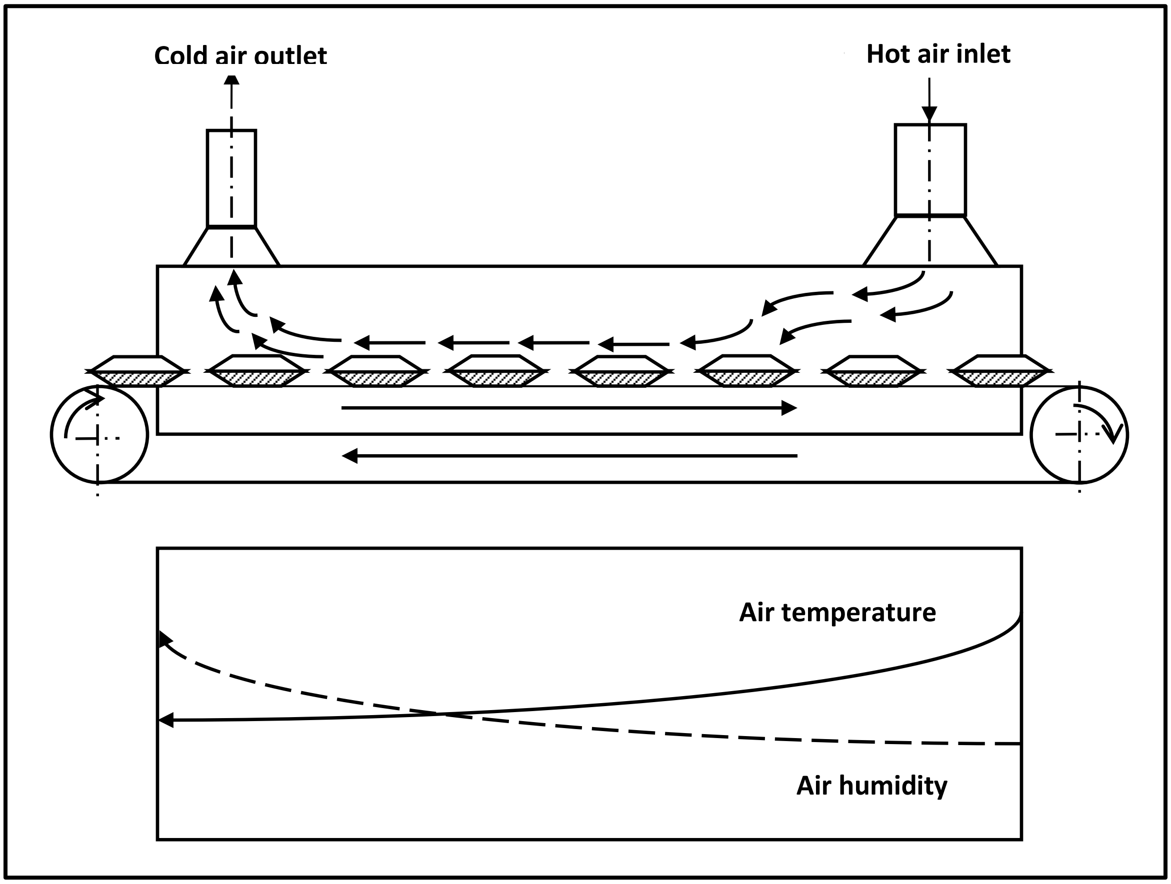


Fig 3.27: Tunnel dryer for drying gypsum molds + jiggered products

Fig 3.28: Tunnel dryer for ceramic tiles

This step is known as **biscuit firing**. Following glazing, the articles are then fired to a higher temperature in step known as **gloss firing**. This is the case in the production of household porcelain articles and often wall tiles where a two fire schedule is applied. The biscuit temperature is below 1000°C, while the gloss temperature may exceed 1250°C. Other glazed articles can be fired in one single step such as floor tiles and sanitary ware.

There are several operations and processes that can occur on firing ceramic ware; these are sintering, grain growth, vitrification, solid state reactions and solid state transitions. In what follows are reviewed the main aspects of these changes.

3.5.2 Sintering

(a) Definition

Sintering is a physical operation resulting in consolidation of the body, thus raising its bulk density by reducing the porosity. Whenever sintering is discussed it is usually meant solid state sintering without melt formation. This latter is referred to as liquid phase sintering and will be discussed in a separate section. On a macroscopic scale, sintering can be viewed as coalescence of particles so that their total surface area is reduced as depicted in Figure (3.29), assuming spherical particles. As seen in that figure, a neck is formed and there is a center to center movement of the original spherical particles. The figure also shows the formation of a new boundary between the sintered particles. A more general pattern is exhibited if we consider several particles of different sizes where a large number of grain boundaries will develop. (Figure 3.30)

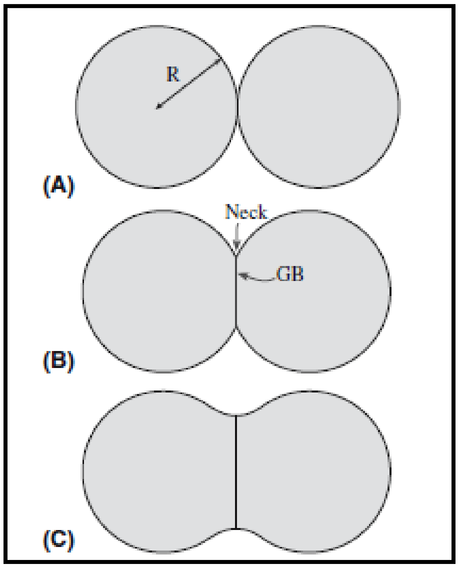


Fig 3.29: Sintering of two spherical particles

(c) Densification curves

These are curves drawn to follow the extent of densification with time. The percent densification is defined as the ratio between the bulk and the true (particle) density of the fired body. It is related to the total porosity of the fired body (ε) by the expression:

$$\frac{\rho_f}{\rho_p}\times 100\% = (1-\varepsilon)\times 100\% \qquad (3.14)$$

The development of dense body is initially rapid, slowing down with time as shown in Figure (3.31) As expected, the total porosity will decrease on firing. Open pores will gradually be converted to closed pores so that the final body will usually contain both types of pores.

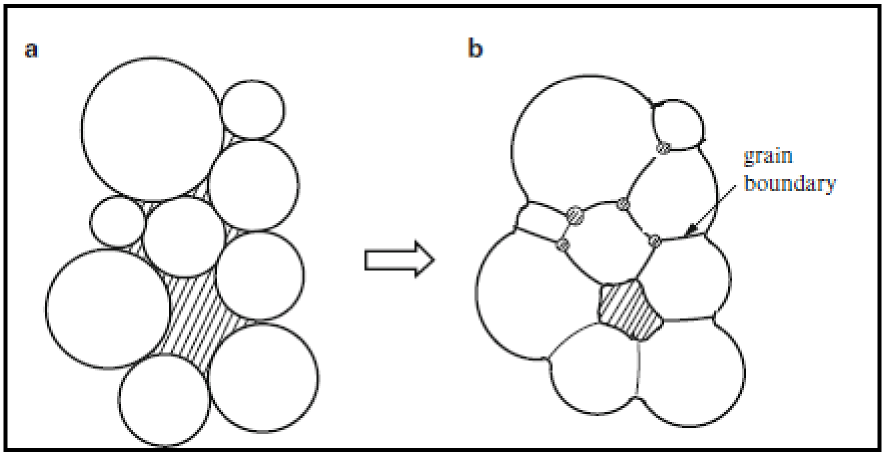


Fig 3.30: Solid state sintering (Multiple particles model)

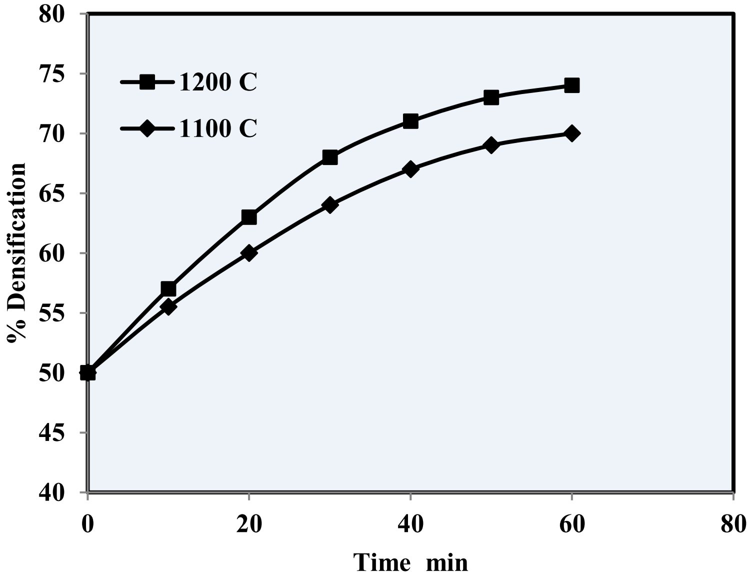


Fig 3.31: Sintering curves for ceramic wall tiles

(d) Firing shrinkage

If a dry body has a linear dimension L_d, then after firing this dimension will shrink to $L_f < L_d$. The linear firing shrinkage S_{fL} is defined as:

$$S_{fL} = \frac{L_d - L_f}{L_d} \tag{3.15}$$

Similarly, the volume shrinkage S_{fV} is defined as:

$$S_{fV} = \frac{V_d - V_f}{V_d} \tag{3.16}$$

The relation between volume firing shrinkage and the corresponding linear shrinkage follows an expression similar to (3.12):

$$S_{fV} = 3S_{fL} - 3S_{fL}^2 + S_{fL}^3 \tag{3.17}$$

If the linear firing shrinkage is < 0.05, this can be approximated to:

$$S_{fV} \approx 3S_{fL} \tag{3.18}$$

On the other hand, the total linear shrinkage S_{TL} is defined as follows:

$$S_{TL} = \frac{L_i - L_f}{L_i} \tag{3.19}$$

The total linear shrinkage is related to both drying and firing shrinkages as follows:

From equation (3.9), we get:

$$L_d = L_i(1 - S_{dL}) \tag{3.20}$$

A similar expression can be deduced from equation (3.15):

$$L_f = L_d(1 - S_{fL}) \tag{3.21}$$

Substituting from (3.20) in (3.21), we get:

$$L_f = L_i(1 - S_{dL}).(1 - S_{fL}) \tag{3.22}$$

From equation (3.19), we can write:

$$L_f = L_i(1 - S_{TL}) \tag{3.23}$$

Comparing equations (3.22) and (3.23), we get:

$$S_{TL} = S_{fL} + S_{dL} - S_{fL}S_{dL} \tag{3.24}$$

Finally, the total volume shrinkage is related to total fractioanl linear shrinkage by an expression similar to (3.20):

$$S_{TV} = 3.S_{TL} - 3.S_{TL}^2 + S_{TL}^3 \tag{3.25}$$

Example 3.4

A ceramic specimen was molded by adding 35 g. water to 100 g. clay to form a stick of dimensions 20×20×200 mm. After drying, the length of this specimen decreased to 188 m, and after firing to 180 mm.

Estimate the following:

(a) The amount of layer water and that of pore water
(b) The total volume shrinkage

Solution:

The fractional linear drying shrinkage is calculated as:

$S_{dL} = \frac{200-188}{200} = 0.06$

The volume drying shrinkage, as calculated from equation (3.12) is:

$S_{dV} = 3 \times 0.06 - 3 \times 0.06^2 + 0.06^3 = 0.169$

From equation (3.10), we get:

$V_d = V_i(1 - S_{dV}) = 20 \times 20 \times 200 \times (1 - 0.169) = 66480$ mm^3

Since the wet volume = $20 \times 20 \times 200 = 80000$ mm^3, hence the amount of volume shrinkage is: $80000 - 66480 = 13520$ mm^3.

This represents the volume of layer water eliminated in the constant rate drying period. It corresponds to a mass of **13.52 g**.

The amount of pore water is therefore $35 - 13.52 = \mathbf{21.48}$ **g**.

The total linear shrinkage is: $\frac{200-180}{200} = 0.1$

From equation (3.25): $S_{TV} = 3 \times 0.1 - 3 \times 0.01^2 + 0.01^3 = \mathbf{0.271}$

Example 3.5

Clay bricks have final dimensions of 6 × 12 × 25 mm^3. The linear drying shrinkage = 8% and the firing shrinkage = 3%. Find the dimensions of the extrusion die.

Solution:

The extrusion die is rectangular so and the produced body is cut in the direction of its thickness.

The total linear shrinkage is obtained from equation (3.24):

$S_{dL} = 0.08 + 0.03 - 0.08 \times 0.03 = 0.1076$

The original wet length is obtained from equation (3.23):

$25 = L_i(1 - 0.1076)$ Hence $\boldsymbol{L_i} = \mathbf{28.01}$ **mm**

Similarly for the breadth:

$12 = B_i(1 - 0.1076)$ Hence $\boldsymbol{B_i} = \mathbf{13.45}$ **mm**

3.3.3 Grain growth

(a) Theory

During firing, there occurs a coarsening of grain. The reason behind this behavior can be understood from the following discussion. Consider Figure (3.32) which shows a boundary between two grains, the atoms of which being in different plane sets.

It can be proved that atoms on the concave side of the boundary have higher energy than those on the convex side. So that, as their mobility increases on raising temperature, these high energy atoms will jump across the boundary to the lower energy convex region and the boundary will move **towards its center of curvature** (dashed position in figure).

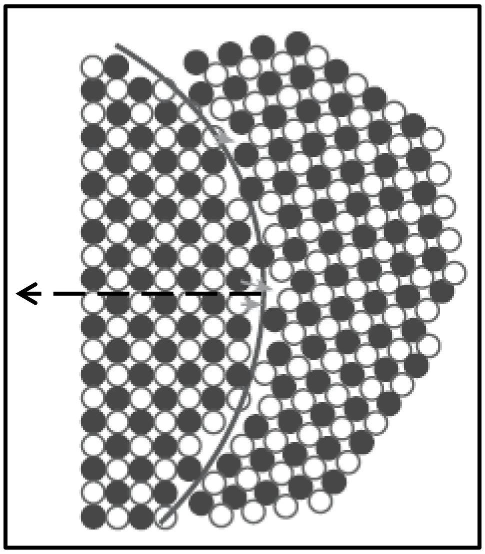


Fig 3.32: Atomic representation of a grain boundary

Consider now the point of intersection of three grain boundaries in a one phase material. The interfacial tension forces holding the grain together are therefore equal. So, for equilibrium to occur at this point, the angles between these forces have to be equal = 120°. This is the case in six sided grains. Hence such grain will have fixed linear boundaries. Such grains will neither grow nor shrink. If a grain has a number of sides < 6, then in order that the angles between the boundaries be equal to 120°, the boundaries have to be curved outwards. This means that these boundaries will move inwards and such grains will shrink and, given enough time, will ultimately disappear. Conversely, grains with sides > 6 will have convex boundaries and will tend to grow on the expense on their neighbors which have less than 6 sides. Figure (3.33)

The speed at which grains grow is governed by the equation:

$$D^2 - D_0^2 = k.t \qquad (3.26)$$

Where: D_0 is the average grain size at zero time and D its size at time = t.

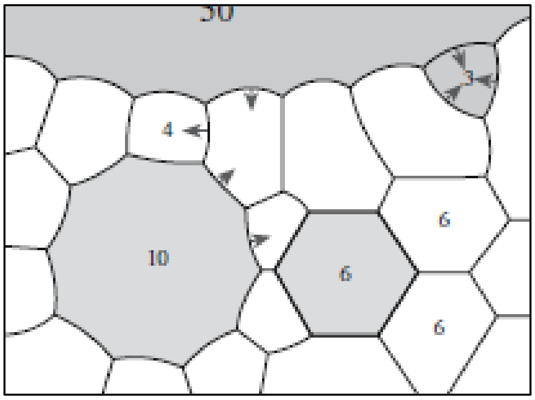


Fig 3.33: Boundary motion causing grain growth or shrinkage

(b) Grain growth inhibition

It has been seen earlier that large grains are associated with lower mechanical properties. Another important reason why excessive grain growth should be prevented has to do with the elimination of porosity on firing. Pores are usually eliminated by diffusing towards the grain boundaries. As they reach these boundaries, they tend to move along them to the external surface where they ultimately disappear. Therefore, the extent to which the elimination of pores proceeds will depend on their reaching the boundaries during the available firing time. If the grains are too large, then pores will have to move a longer distance across the grain, and it may not be possible for them to reach its boundaries during the available firing time. This will result in residual porosity in the fired body that will negatively affect its mechanical properties.

Prohibiting grain growth is done by adding, in small amounts, a foreign material the atoms of which can easily diffuse to align themselves along boundaries. These will exert a drag force on this boundary and reduce its mobility. For example, adding strontium zirconate to alumina can stop grain growth to an appreciable extent.

To conclude this section, it is worth mentioning that in some rare instances, grain growth is encouraged despite its negative impact on mechanical properties. A typical such instance occurs on firing magnesite or dolomite refractories. These products can slowly react with atmospheric water vapor and carbon dioxide. When their grains are left to coarsen on firing, their reduced surface area will decrease this effect.

3.3.4 Vitrification

This is the formation of a viscous liquid phase at high temperature due to partial melting. It is sometimes a major process in smoothing the surface and imparting reasonable strength as in firing of porcelain and some refractory products. The formed liquid flows into the available pores. By surface tension, it will pull the particles together causing more shrinkage. Also, sintering can occur as mass transfer can occur from the convex parts of the particles, by diffusion through the melt, to be precipitated along the concave region between particles. This called **liquid phase sintering**. Too much vitrification is undesirable, as flow under gravity may take place, causing **warping**. Also, in some cases, vitrification should be totally prevented, as the presence of any glassy phase along the surface will give a defective product. This is the case in the production of building bricks, where a non-porous glassy surface will not retain the cement coat because of the absence of capillary action on water present in the cement paste.

3.3.5 Solid state reactions

Different solid-state reactions can take place on firing a ceramic body. Some examples are given:

- Decomposition: solid = solid + gas

Examples are the calcination of calcium carbonate or dehydration of kaolinite.

- Decomposition: solid = solid + solid

A classic example is the decomposition of m – kaolinite to alumina and silica.

- Solid – solid reaction: solid + solid = solid or solid + solid = solid + gas

Examples are the reaction between Fe_2O_3 and NiO to produce $NiFe_2O_4$ or the reaction between Na_2CO_3 and SiO_2 to produce sodium silicate and CO_2.

(i) Thermodynamic considerations:

For any of these reactions to take place, it should have a negative free energy at the operating temperature.

For reaction in the form: A (s) + B(s) = C(s), the standard free energy is obtained from the expression:

$$\Delta G^0 = \Delta H^0 - T.\Delta S^0 = -RT.\ln K \qquad (3.27)$$

The equilibrium constant $K = \dfrac{a_C}{a_A.a_B}$

Here, a_A, a_B, a_C are the activities of the three compounds.

If, however, the reaction involves evolution of a gas, in the form: A (s) + B(s) = C(s) + G(g) and if A, B and C are pure phases, then equation (3.30) takes the form:

$$\Delta G^0 = \Delta H^0 - T.\Delta s^0 = -RT.\ln p_G \qquad (3.28)$$

Here, p_G is the partial pressure of the gas (atm.)

(ii) Kinetic considerations:

This type of reactions differs from homogeneous fluid phase reactions in the following respects:

i. The reaction involves a surface contact between the particles and the gas phase or other particles and the product phase is first formed on the interface. Its molecules then diffuse inside the particles.
ii. The rate of a solid state reaction is defined in a different way than that of a homogeneous reaction. It is usually expressed as the rate of change of the weight of the reactant phase with respect to time: $r = -\dfrac{dW}{dt}$ or: $r = -\dfrac{d\alpha}{dt}$, α being the conversion.
iii. The rate controlling step can be the reaction at interface in case the product layer formed is porous enough to allow for rapid diffusion of the unreacted species; or it can be the diffusion across the product layer in case this layer is of low porosity.

In some instances, when the particle size is extremely small (~ 10^0 μm), the reaction may proceed at a molecular level. It is then treated as if it were a homogeneous reaction. Several kinetic models have been proposed to interpret solid state reactions data, this subject being however out of the scope of the present course.

3.3.6 Allotropic transitions

Some allotropic transitions that take place upon firing, or on cooling, can have a negative effect on the properties of the fired product. We have previously mentioned the case of low – high quartz transition and the associated dimensional changes that may cause collapse of the fired article. Another well – known example is the allotropic transition of zirconia. On cooling, the tetragonal form suddenly transforms to the monoclinic form, which is accompanied with a large dimensional change. Adding calcium oxide forms a solid solution which, on cooling, undergoes a gradual and milder change.

3.3.7 Defects occurring on firing

The presence of water or an appreciable amount of organic materials in the fired body may cause **shuttering** of the product since these will force their way out at an early stage. When the furnace atmosphere is reducing, organic impurities are transformed to carbon. This forms a **black core** inside the body. The presence of decomposable or highly volatile salts will produce vapors at a later stage of sintering which may cause undue expansion of the body; a phenomenon known as **bloating**. Finally, too high a firing temperature will increase the level of vitrification and causes **warping**.

3.3.8 Kilns for firing ceramic ware

Ceramic articles are fired either in batch or continuous kilns. The former are used for small scale production while the latter are associated with large production capacities such as ceramic tiles and refractory blocks. The following is a brief outlook on the most important types.

(a) Updraft kilns

This is a type of vertical shaft kiln particularly used for the batch production of building bricks. It can be also used in the small scale production of vitrified clay pipes and dinnerware. This type consists of a perforated refractory floor beneath which is the combustion chamber on which is placed the ware to be fired.

Flue gases then pass through this ware. Figure (3.34) shows such a kiln.

Batch kilns in general and updraft kilns in particular have the following advantages:

- They are cheap to build
- Their operation does not necessitate skilled labor.

They suffer, however, from the following disadvantages:

- The setting and drawing of articles are tedious
- The fuel economy of such kilns is very low. Their thermal efficiency hardly exceeds 20%, most of the heat being lost with the flue gases.
- Since the refractory walls are subjected to alternative cycles of heating and cooling, they ultimately shutter because of repeated thermal strains in the brickwork; a phenomenon is known as thermal spalling.
- Another type of batch kilns is the **downdraft kiln**, which is similar to the previous type except that flue gases are made to collide against a crown before passing through ware in a downwards direction.
- A more common batch kiln that is used in the manufacture of a variety of products, such as sewer pipes, porcelain ware, artware, etc. is the **shuttle kiln** shown diagrammatically in Figure (3.35). In this kiln, articles to be fired are placed onto a refractory board placed on the top of a car that is pushed inside the kiln. The kiln door is then closed and firing begun. At the end of the process, the articles are left to cool inside the kiln to a reasonably low temperature then the door is opened and the car withdrawn. The main merit of this type over the updraft kiln is the ease of setting and drawing of articles.

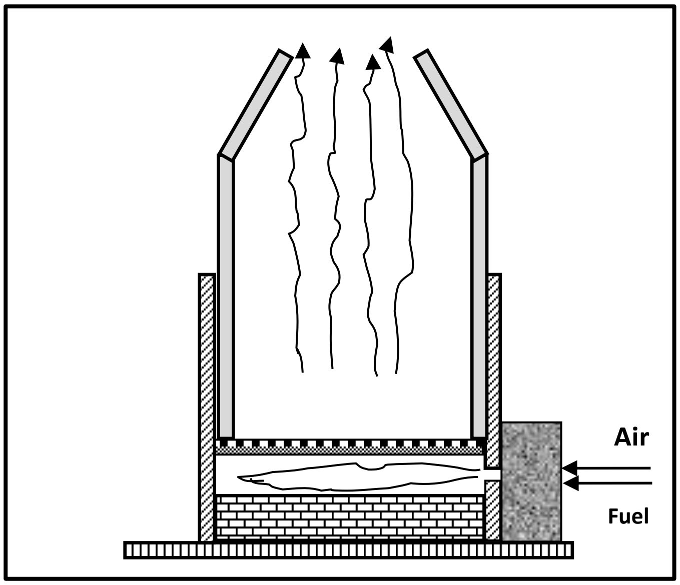


Fig 3.34: Updraft kiln

In the following are given some features of this kiln:

- Firing is performed through side burners, although top firing is also available.
- A refractory crown at the top of the kiln reflects the heat to the batch, thereby increasing the thermal efficiency to about 30%.
- Vertical steel beams are fixed at the two sides of the kiln to "tighten" its structure, as thermal expansion increases its dimensions. These beams are fastened to horizontal transversal bars by bolts. When the structure expands, these bolts are loosened.

(b) Ring kilns

This type of kiln is categorized as semi – continuous since gases flow continuously across its chambers while the articles are fired in a batch way. One common type is the **Hoffmann kiln**. This kiln consists of a series of chambers, each being a separate kiln that can be fired under conditions different from those of other chambers.

Figure (3.36) shows a schematic view of this kiln. Ware to be fired is placed into chambers. One chamber is fired at a time. Fuel and hot air are mixed in the burners of this particular chamber. The hot flue gases emanating from that chamber are directed through a duct to the next chambers where green ware awaits to be fired. This way, green ware is preheated and flue gases cooled down until they are cold enough to be rooted out from the kiln through a central stack. Air for combustion, on the other hand, is blown, as cold, through the system and made to pass through the chambers containing the hot fired ware. As it passes through successive hotter chambers, it heats up to such an extent that it can be directed towards the burner of the next chamber where firing is due.

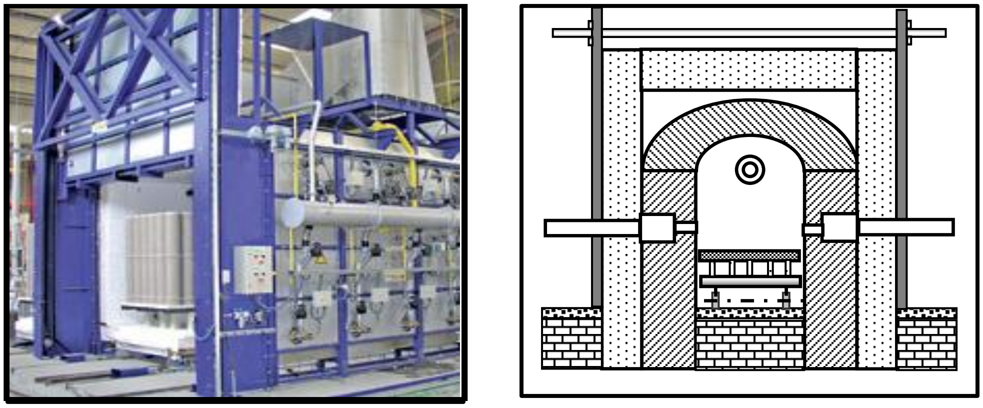


Fig 3.35: Shuttle kiln

This scheme makes use of the heat contained in flue gases to preheat incoming ware and the heat contained in the fired ware to preheat combustion air. The thermal efficiency is highly raised (>60%) and setting and drawing can be eased up by using moving cars to introduce and draw the ware. Also, ring kilns can be used to fire simultaneously different types of products. It is said that they are **flexible** in their operation. However, the problem associated with spalling of refractories remains.

(c) The tunnel kiln

This kiln is of the continuous type. It is especially suited for large scale production of refractory materials, sanitary ware. Porcelain ware, sewer pipes, clay bricks, etc…It has also been traditionally used for the production of small and flat ware such as tiles and cups, but has been largely been supplanted by the more practical roller kiln.

It consists of a long tunnel (up to 200 m.) along which is maintained a constant temperature distribution. Ware to be fired is carried on cars moving on a railway along the kiln. This train of carriages is moved periodically by a hydraulic pusher through a certain distance at constant thrust.

The length of the tunnel, as can be seen from the schematic diagram Figure (3.37) is divided into three main portions: The **preheating zone**, where flue gases and part of hot air from the cooling zone are circulated to preheat the incoming ware. Next is the **firing zone** where burners are located. Burning takes place laterally in most cases, and in this zone sintering and possibly vitrification take place. Finally, in the **cooling zone** cold air is made to pass over the fired hot ware.

As it heats up, air, from positions close to the firing zone, is driven, as secondary air for combustion towards the burners, whereas air from positions in the cooling zone is circulated into the preheating section of the kiln. Cars are fitted with side blades that run along their length and fit into two channels fixed at the walls and filled with ground grog. These channels run along the whole length of the kiln. This is in order to minimize heat dissipation to the cars bottom.

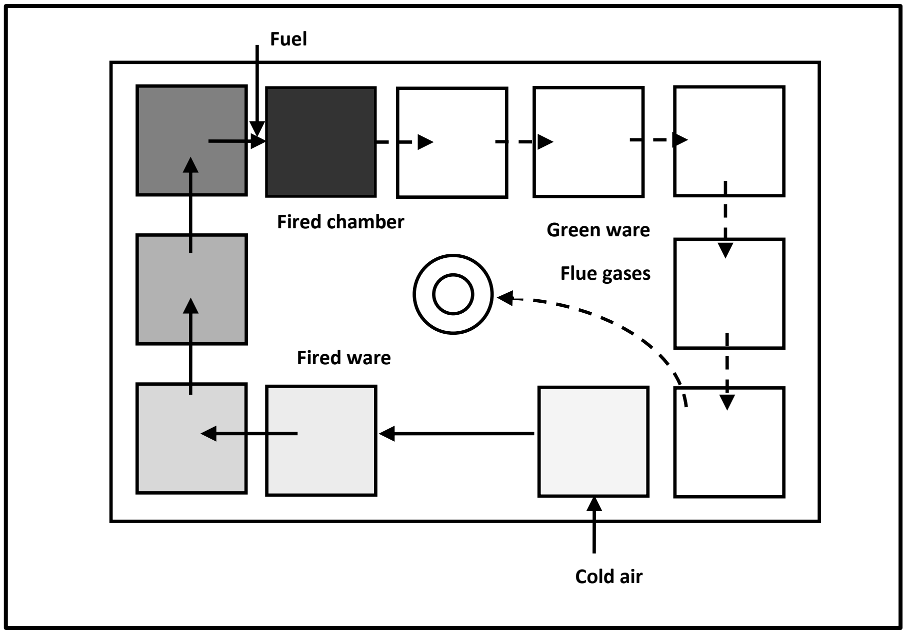


Fig 3.36: Hoffmann ring (compartment) kiln

Also, Figure (3.38) shows a cross section of a tunnel kiln showing that the carriage and its load totally fill this cross section, and that an inspection tunnel is located beneath the kiln in case of emergency operation. This figure also shows the two side blades fitted to a car dipping into the side channels fixed at the kiln walls. It is also apparent from this section that provision is taken to minimize the heat load on car bottom by charging the ware on a refractory plate supported on insulating refractory block. Figure (3.40) shows a photo of a tunnel kiln used to fire dinner ware.

Tunnel kilns possess several **advantages** over other types of kilns:

- They lend themselves for continuous production and hence have high productivities.
- The charge fills the kiln cross section and hence heat transmission is uniform.
- The firing schedule can be regulated beforehand depending to the articles to be fired.
- Setting and drawing are easily and regular

- The refractory brickwork at any section of the kiln is at a uniform temperature, thus minimizing spalling.
- A thermal efficiency exceeding 80% is usually achieved.

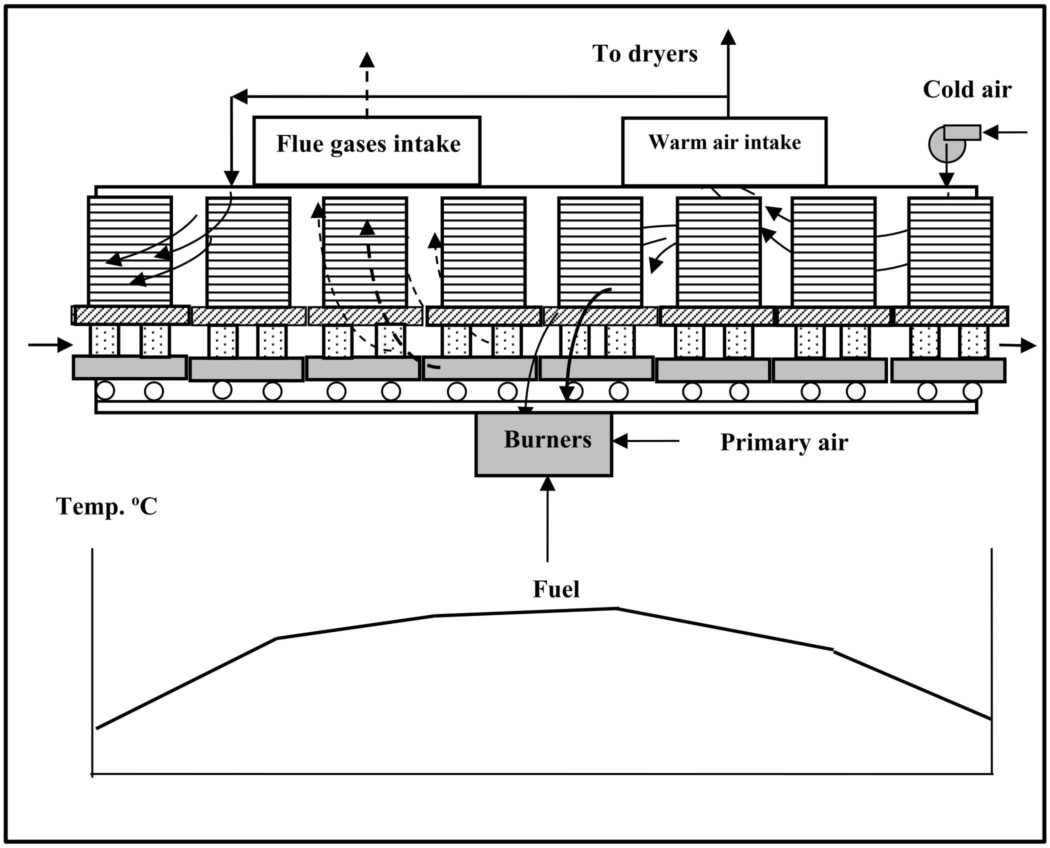


Fig 3.37: Schematic operation and temperature profile along a tunnel kiln

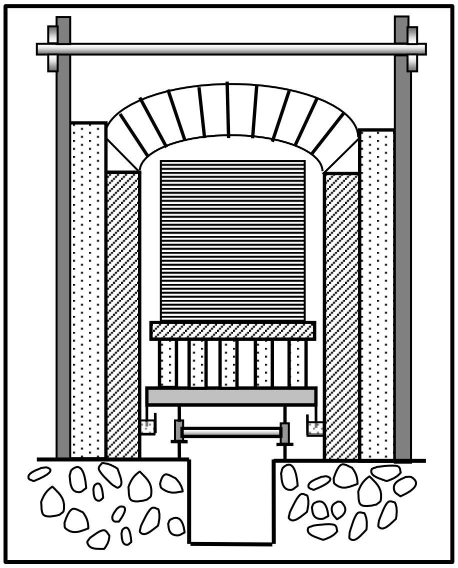


Fig 3.38: Cross section of a tunnel kiln

Tunnel kilns, on the other hand, suffer from some **drawbacks** (disadvantages)**,** the main one being:

- Their capital cost is high (Tens of MUSD)
- They require considerable floor length
- The upkeep of cars is high due to their repeated heating and cooling.
- A shutdown ties up the whole unit up to 4 weeks.
- They cannot be run efficiently at low capacity.
- Their burning schedule should be kept constant as much as possible for any specific product. That is why it is customary to have a certain kiln run to fire a specific type of articles. In this respect such kilns lack flexibility of operation.
- It is not easily adapted to fast firing operation. (Residence time ranges from a few hours to several days).

Fig 3.39: Tunnel kiln for firing dinnerware

(d) The roller kiln

This type of kilns has supplanted tunnel kilns in the tile industry and to a lesser extent in porcelain production. It consists of a set of stationary parallel horizontal rollers spaced at a convenient distance and situated in a row along the length of the kiln. The drive system as well as gears are located outside the kiln, at relatively low temperature (Figure 3.40). The width of such kilns usually lies between 1 and 2 m. and its height hardly exceeds half a meter. Their length ranges from 30 – 60 m. They are heated by natural gas and burners are located both over and under the rollers for uniform heat transmission to the ware. The flow pattern of air and flue gases is similar to that of a tunnel kiln. Some roller kilns are also heated electrically.

Dry ware is either directly placed on the rollers or placed on supporting plates. In the former case, the distance between rollers must be so adjusted not to have too high a clearance. This is since the ware may soften on firing and an excessive clearance will result in deformation of shape. In softening of the ware is excessive, it is preferable to have the ware admitted on supporting plate. This way, there will be no relative movement between this ware and the rollers. Figure (3.40) shows a schematic view of a roller kiln and Figure (3.41), the drive system of rollers On the other hand, Figure (3.42) shows a photo of a kiln for firing tiles.

This type of kilns has been successfully used in the last two decades to fire tiles in a fast firing mode. In this technique, a higher temperature is used to increase the rate of processes occurring on firing. This has made it possible to fire tiles and some types of technical ceramics in less than one hour, compared with a much longer firing time in conventional tunnel kilns.

Rollers are made from steel for firing temperatures up to 1050ºC, porcelain or alumina up to 1250ºC and silicon carbide for temperatures exceeding 1600ºC.

The main **advantages** of this type of kilns are:

- No kiln furniture is required (e.g. cars).
- Heat transfer is uniform because of the narrow firing space.
- This kiln can be shut down in a reasonable time and started up after a few hours. One reason is that the refractory walls do not consist of bricks but rather of monolithic layers or ceramic fibers of much higher spalling resistance.
- Its energy consumption is low compared to tunnel kilns.
- It has a high flexibility of operation.

Fig 3.40: Tranmission of motion to rollers

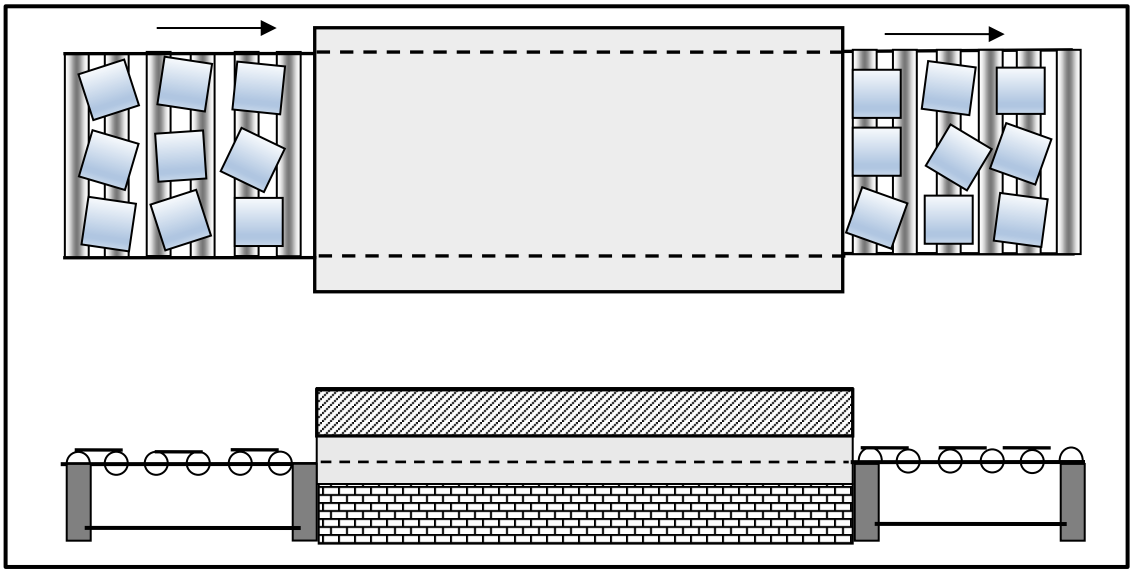


Fig 3.41: Schematic view of a roller kiln

Fig 3.42: Photo of a roller kiln

Suggested additional reading

1. D.W. Richerson, *Modern Ceramic Engineering,* 3rd ed., Taylor and Francis group, London, N.Y., 2007
2. F. Shiner, *Ceramics: Materials, processing and Properties,* N.Y. Research, 2022

Suggested sites:

Manufacture of ceramic tiles: https://www.youtube.com/watch?v=USE8j2EJgdE

Tunnel kiln operation: https://www.youtube.com/watch?v=L6HyYqFe7X8

Roller kiln for ceramic tiles: https://www.youtube.com/watch?v=NA9hgP6ZWMk