COVENANT UNIVERSITY NIGERIA

TUTORIAL KIT
OMEGA SEMESTER

PROGRAMME: CHEMISTRY

COURSE: CHM 425

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1. Write short notes on the following:

    i. Firing of clay body (8 mks)
    ii. Loss of ignition in clay firing (8 mks)
    iii. 3-point and 4-point flexure testing of ceramics (7 mks)

2. (a) Describe how ceramics are formed. (7 mks)

   (b) By means of a diagram, explain the term “*sintering of ceramics*”. (3 mks)

   (c) What is the processing method for clay-based ceramics? (8 mks)

   (d) Highlight the general characteristics of ceramics? (5 mks)

3. (a) What is fracture in ceramic terms? (2 mks)

   (b) Explain brittle fracture and describe why ceramics tends to fail brittle mechanism (5 mks)

   (c) Define the following intensity factors terms: K, K_C, K_{IC}, K_{IIC}, K_{IIIC} and state the differences between plane stress and plain stress? (10 mks)

    i. Which of these intensity factors are used for metallic materials and are not useful for ceramic materials? (3 mks)
    ii. Which of the intensity factor is used for both metallic and ceramic materials? (3 mks)

4. Give the procedure for moisture content determination in clay.

5. Write short note on simple clay chemistry.

6. Explain how shrinkage can be determined in clay.

7. What do you understand by the term ‘clay melt’

8. Write short notes on the following

    i. Glass – fiber reinforced composites (GFRPS)

ii. Carbon – fiber reinforced composites (CFRPS)
iii. Glass
iv. Cullet

9. What do you understand by the term ‘cement’

10. With the aid of a flow chart, describe the manufacturing process of cement.

SOLUTION

Question 1 (a)

(i) The clay body goes through a number of stages during firing.

Up to 120° C **Water smoking**:

The water of plasticity evaporates first and then the pore water. Rapid increase of temperature will build up steam pressure, and may crack the clay.

220° C **Cristobalite expansion**: Cristobalite is created from silica at temperatures above 900° C. When the clay is fired a second time it will expand nearly 3% at 220° C. On cooling, cristobalite shrinks again. Rapid cooling at this temperature may crack ware.

350 - 600° C **Ceramic change**:

As described above, the chemically bound water of the clay crystal is released. The clay is very fragile and porous at this point. The clay particles are held together by a sort of "spot welding" at the points of contact. This process is called sintering.

573° C **Quartz expansion**:

The quartz crystal (SiO_2) expands suddenly and will shrink again at this point during cooling (about 1%). The clay structure during heating is still open enough to accommodate this change, but if cooling is too rapid, the ware may crack.

500° - 900° C **Oxidation**:

Organic matter in the clay is burned out. If the clay has a black core after firing, then this stage of firing was done too fast. When the rise of temperature is very rapid, the surface may vitrify before the carbon dioxide inside the clay has escaped, and the entrapped gas will bloat the clay at a later stage of firing. Limestone ($CaCO_3$) gives off its carbon dioxide (CO_2) at 825° C.

900° C - **upwards Vitrification**:

At this temperature the soda and potash in the clay will start to form a glass by combining with the free silica. As the temperature rises, more and more glass will be formed, involving materials like limestone, talc and iron oxide. The melted glass will gradually fill the pores between the clay particles. This vitrification process also causes the clay to shrink. (8 mks)

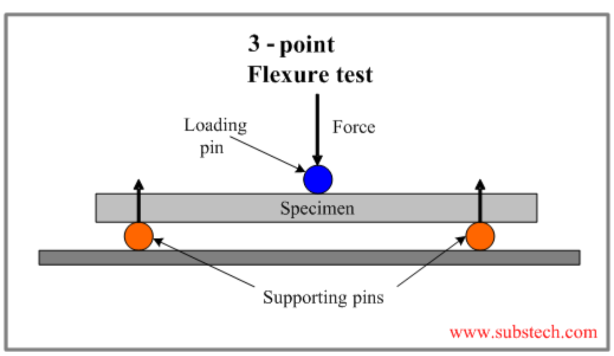
1 (c)

3-point Flexure Test

In this test a specimen with round, rectangular or flat cross-section is placed on two parallel supporting pins. The loading force is applied in the middle by means loading pin. The supporting and loading pinsare mounted in a way, allowing their free rotation about:

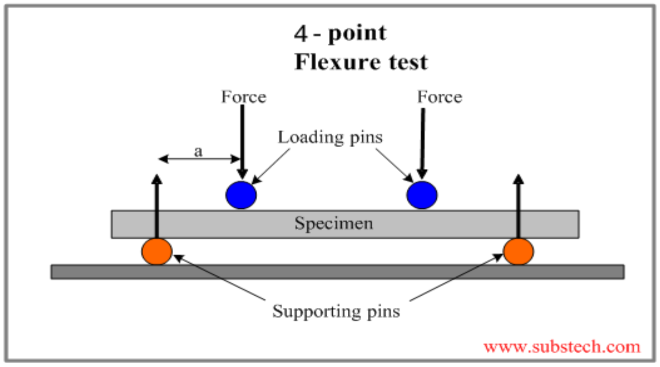
- axis parallel to the pin axis;
- axis parallel to the specimen axis.

This configuration provides uniform loading of the specimen and prevents friction betweenthespecimen and the supporting pins.



4-point Flexure Test

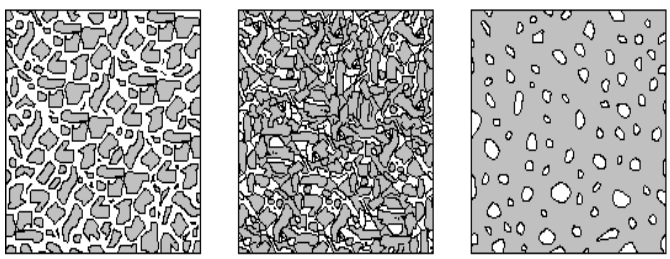
In this test the loading force is applied by means of two loading pins with a distance between them equal to a half of the distance between the supporting pins.



(7 mks)

Question 2(a)

Ceramics are formed by basically sintering of fine powders to formed hard, brittle and chemically stable solid. Well what is sintering? This can be illustrated by the following diagram:



This figure composed of fine grain (usually on the order of microns in diameter), loosely piled, pressedor bonded together. It could be silicon nitride having been compressed in a steel die, aluminum oxide with an organic binder (which burns out), or clay which has the nice property of bonding itself with the helpof water. The particles are basically pile together, having little or no “green” strength. The center picture is a cross-section after sintering: the particles are tighter; the interfaces are wider – bonds have formed – and explanation of porosity after furling. At any rate, the pores close up and it becomes dense, bonds form, thickens and for very fine powder, pressed while being heated near the melting point, becomes almost fully dense – without having been melted.

There is also another method of forming ceramics which is known as liquid phase sintering. In this case, instead of a melt solution, a eutectic mixture forms between the grains; first partially melting them, then depositing the materials on the grains, then on cooling it solidifies in place, increasing bond strength and reducing porosity. Since oxide crystals form very slowly (quartz is an extremely complex structure), this eutectic is often a supercooled liquid, otherwise known as glass, in pottery. You can imagine liquid-phase sintered pottery as the far right diagram above, hard particles (which are either insoluble, or were not melted during the firing) suspended in a glassy matrix. (7 mks with just 2 mks for the sketch)

2 (c)

Clay-based ceramics were formed by mixing clay and other ingredients with some amount of watertoget a consistency that was acceptable for the forming method of choice. Even though the emphasis in the field of ceramic engineering has shifted away from traditional ceramics to advanced materials,processing science still focuses on processing methods that rely on controlled plastic deformation during forming, thus mimicking the behavior of clay–water pastes. Some of these processing methods include dry pressing, extrusion, tape casting, and slip casting. The clay is then air dried after which is then firedathigh temperature to form ceramics.

Question 3(a)

Fracture is a process of breaking a solid into pieces as a result of stress. There are two principal stages of the fracture process which are: *Crack formation and Crack propagation*. (2 mks)

3(c)

Stress-intensity Factor (K) is a quantitative parameter of fracture toughness determining a maximum value of stress which may be applied to a specimen containing a crack (notch) of a certain length. Depending on the direction of the specimen loading and the specimen thickness, four types of stress-intensity factors are used: $\mathbf{K_C}$, $\mathbf{K_{IC}}$, $\mathbf{K_{IIC}}$, $\mathbf{K_{IIIC}}$. (3 mks)

$\mathbf{K_C}$ This is stress-intensity factor of a specimen, thickness of which is less than a critical value. It depends on the specimen thickness and this condition is called **plane stress**. (3 mks)

$\mathbf{K_{IC}}$,$\mathbf{K_{IIC}}$, $\mathbf{K_{IIIC}}$ are stress-intensity factors, relating to the specimens, thickness of which is above the critical value therefore the values of $\mathbf{K_{IC}}$, $\mathbf{K_{IIC}}$, $\mathbf{K_{IIIC}}$ do not depend on the specimen thickness. This condition is called **plane strain**. (4 mks)

K_{IIC} and **K_{IIIC}** – stress-intensity factors relating to the fracture modes in which the loading direction is parallel to the crack plane. These factors are rarely used for metallic materials and are not used for ceramics. (3 mks)

K_{IC} – plane strain stress-intensity factor relating to the fracture modes in which the loading direction is normal to the crack plane. This factor is widely used for both metallic and ceramic materials. (3 mks)

4. Moisture content determination

Procedure:

- Sample clay by quartering.
- Weigh out 200 g (W moist) of the moist clay.
- Place the clay in a clean cup and heat it to 150° C for 2 hrs.
- Find the weight (W dry) in g of the dry clay.

5. Shrinkage determination in clay

Procedure:

- Mix the clay with water to plastic consistency and knead it well.
- Form 10 test bars of each clay to be tested. The test bars are molded in a standard mould.
- Mark the test bars with two incised lines exactly 100 mm apart.
- Turn the test bars several times while they dry to prevent warping.
- After the test bars are completely dry (open air) measure the distance between the two cuts in mm.
- Drying shrinkage in % = 100 - dry length (mm). For the most accuracy, take the average of 10 test bars.
- Firing shrinkage is found by firing 5 of the test bars to the intended firing temperature.
- Measure the distance between the lines on the test bars in mm.
- Firing shrinkage in % = dry length - fired length(mm)
- Total shrinkage in per cent = 100 - fired length (mm). The firing shrinkage is found as an average of 5 test bars.

7. Glass melt:

Prevention of sudden collapse in clay from the stiff melted glass.

8.

Glass-fiber reinforced composites (GFRPs): Glass fibers (made from E-glass: 55% SiO_2, 20% CaO, 15% Al_2O_3, and 10% B_2O_3) are easily drawn, relatively strong, chemically inert, and cheap. They can be imbedded in a wide variety of (usually thermoset) polymers (for use in car, small aircraft & boat bodies, flooring, and piping). They are not very stiff, however, and use temperatures are limited by the polymer to below 200°C.

Carbon-fiber reinforced composites (CFRPs): These fibers can be either pure graphite (under very controlled conditions) or a mixture of graphite with some amorphous carbon phase (carbon glass). They can be produced from rayon, pitch (a petroleum by-product), or PAN (polyacrylonitrile – a synthetic polymer). They have very high specific modulus and specific strength (even at high Temperature), are fairly inert, can be engineered to exhibit a range of properties, and are relatively inexpensive. They are used in sporting goods, rocket casings, pressure vessels, and aircraft structures.

Glass

Glass is a hard, transparent or translucent brittle material that is insoluble and non -flammable. It is capable of withstanding high temperatures and many corrosive substances. The primary raw material of glass is high silica sand (silicon dioxide), which is heated until it melts and then allowed to cool in a controlled process. The temperature needed to melt sand is very high (about 1700ºC) so materials are added to the sand to reduce the melting point to about 800ºC. The commonest of these materials is sodium oxide (Na_2O), which is obtained from sodium carbonate (soda ash, Na_2CO_3). Potassium oxide (K_2O) is also used frequently. This mixture is unstable, however, so a stabilizer such as calcium oxide, derived from calcium carbonate (limestone, $CaCO_3$), or magnesium oxide (dolomite, MgO) is added to the mixture. A number of other materials may be added, depending on the type of glass desired. Metal oxides, for example, such as iron, manganese, chromium, or copper, may be used to produce glass in colors ranging from light green to deep blue to topaz yellow. Lead oxide or potassium oxide, obtained from potash, is used to make very clear glass. Most glasses are silicate materials with added impurities to lower the softening point, which aids in fabricating articles and reduces processing costs.

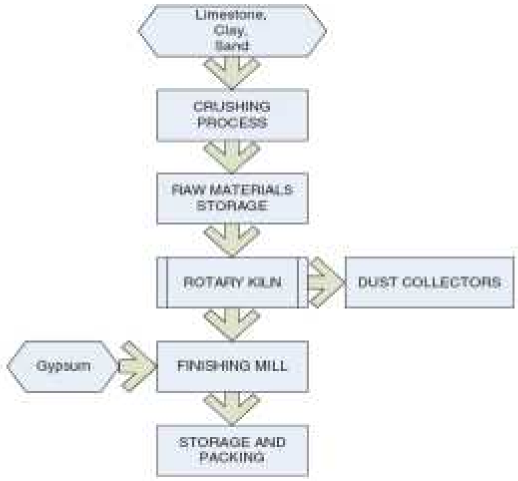
Cullet

Another important ingredient in glass manufacture is cullet, which is scrap or recycled glass that is cleaned and crushed specifically to be remelted and reused. The principal source of most cullet is waste or rejects glass from the manufacturing operation. However, glass from other sources can be used. This is particularly true in the glass container industry, where composition does not vary substantially from one manufacturer to another. It is evident that when uniform composition must be maintained, the composition of the cullet must be the same as the composition of the glass being produced. Cullet is normally crushed and stored in much the same way as the other raw materials are. The use of cullet serves two purposes. The first is that reusing the scrap glass saves the cost of raw materials. The second is that cullet aids in the melting process. Some glass melting operations use up to 60 percent cullet. For some purposes, it is possible to make glass entirely of cullet.

CEMENT

Cement is a binder that sets and hardens by itself or binds other materials together. The most widely known application of cements is in construction; a second one is the area of “bone cements.” Cements used in construction are characterized as hydraulic or nonhydraulic and mostly for the production of mortars and concrete. Hydraulic cements set and harden after combining with water. Most construction cements are hydraulic and based on Portland cement, which consists of calcium silicates (at least 2/3 by weight). Nonhydraulic cements include the use of nonhydraulic materials such as lime and gypsum plasters. Bone cements and bone cement composites refer to compounds that have a polymer matrix with a dispersed phase of particles. For instance, polymethylmethacrylate (PMMA) is reinforced with barium sulphate crystals (for radio-opacity) or with hydroxyapatite to form a bioactive cement. These composites are currently used in orthopaedics for bone trauma repair.

Two types of manufacturing processes have become prevalent in the cement industry: “wet process” and “dry process.” Although these processes are similar in many respects, in the older “wet process,” ground raw materials are mixed with water to form thick liquid slurry, while in the “dry process,” crushed limestone is used and raw materials are mixed together, with consequent higher energy efficiency as drying is eliminated. The figure below represents schematically the cement manufacturing process and the rotary kiln for clinker production.



Flow diagram of the main process