Types of Refractories

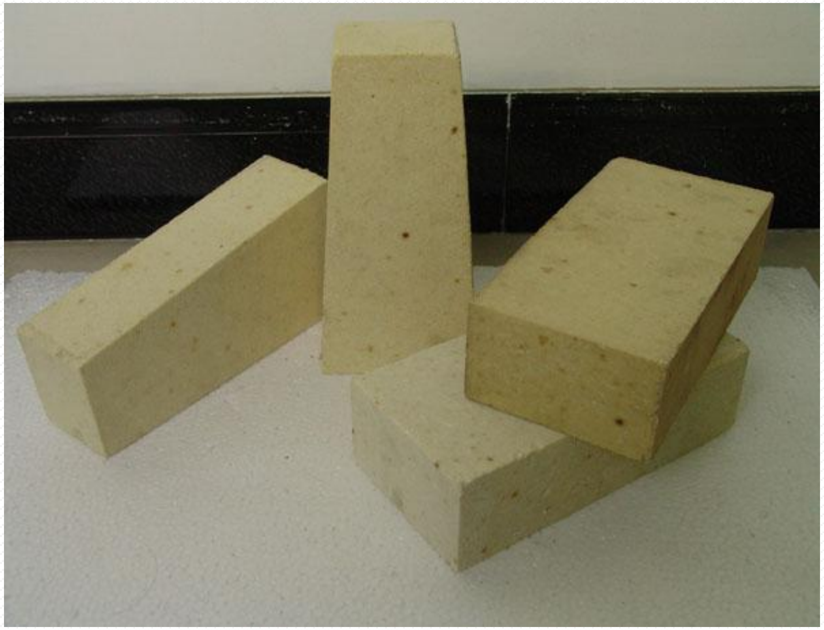
4) Semi Silica Refractories
5) Zirconia Refractory Brick

4) Semi Silica Brick

- Semi silica bricks are made from siliceous materials having silica content of **75 to 92 %.** Semi-silica bricks have less refractoriness than silica bricks.
- Semi silica refractories have ability to withstand alkalis and show thermal shock resistance more than **silica refractories**. They have high volume stability with better spalling resistance than **fire clay bricks**.

- Semi silica refractories are made in a manner similar to silica bricks, these are cheaper and uses where service conditions are not so exacting that the more expansive silica bricks are needed.

- Semi-silica bricks are used as backing layers for silica bricks in coke ovens and kiln.



- **5) Zirconia Refractory Brick**
- Pure Zirconium oxide (Zirconia) has a high melting point (2700°C) and a low thermal conductivity.
- Its **polymorphism**, however, restricts its widespread use in ceramic industry. During a heating process, zirconia (ZrO_2) will undergo a phase transformation process. The change in volume associated with this transformation makes the usage of pure zirconia in many applications impossible.

- Addition of some oxides, such as **CaO**, **MgO**, and Y_2O_3, into the zirconium oxide structure in a certain degree results in a solid solution, which is a cubic form and has no phase transformation during heating and cooling.

- This solid solution material is termed as **stabilized zirconia**, a valuable refractory.

- **Preparation of ZrO_2 Powder**
- The economically available natural sources of ZrO_2, namely, **baddeleyite** and **zircon** ($ZrSiO_4$).
- Zircon is more important because of its wide availability as beach sand deposits.
- The processing of zirconia ore (baddeleyite) is more difficult because it contains a great amount of silica.
- To produce **Zirconia** from **Zircon**, the first step is to convert **zircon** to **zirconyl chloride**. It can be done by:

Zircon ($ZrSiO_4$) + NaOH

↓ Melting

Na_2ZrO_3

↓ + HCl

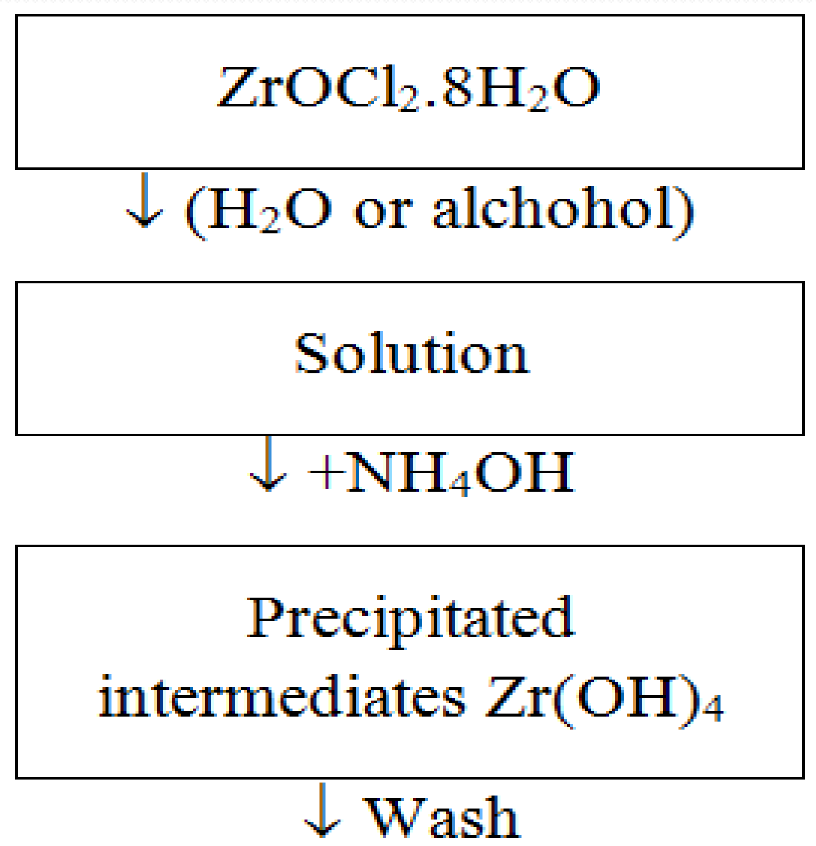
$ZrOCl_2.8H_2O$

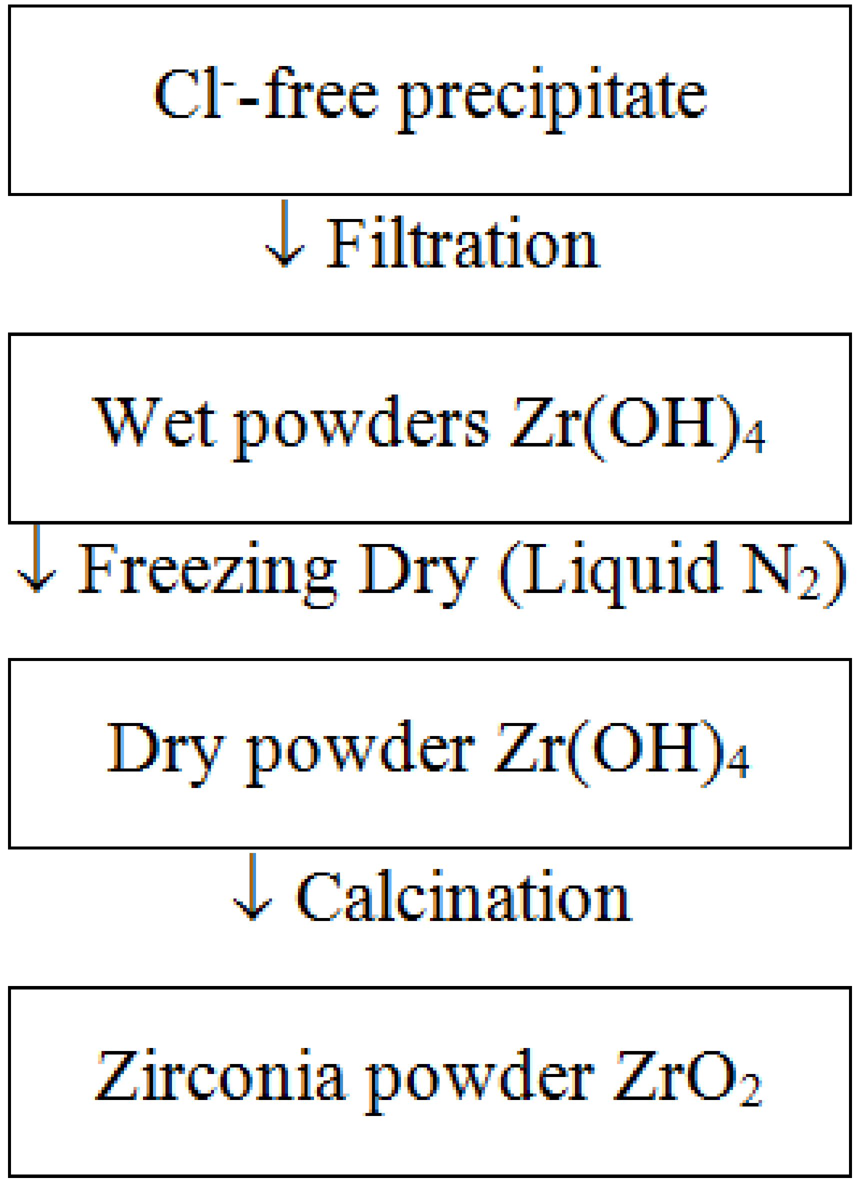
- There are two methods are used to make zirconia from the zirconyl chloride:
- **(A)** thermal decomposition, and
- **(B)** precipitation.

- **(A) Thermal decomposition:**
- Once the zircornyl chloride ($ZrOCl_2.8H_2O$) is heated to **200°C**, it starts dehydration and becomes **dehydrated $ZrOCl_2$**.
- On next step, $ZrOCl_2$ decomposes into **chlorine gas** and becomes **zirconia** at a much higher temperature.
- Zirconia lumps obtained from the calcination then undergo a **size reduction** process, such as ball milling, into the particle size range needed, usually up to -325 mesh.

- This method is associates with
- **low production cost**.
- However, it is not easy to produce zirconia powders with **high purity** and **fine particle size** by the method.

- **(B) Precipitation method:**
- On other hand, uses **chemical reactions** to obtain the **zirconia hydroxides** as an intermediate. Its processing can be described as following:




Cl^--free precipitate
↓ Filtration
Wet powders $Zr(OH)_4$
↓ Freezing Dry (Liquid N_2)
Dry powder $Zr(OH)_4$
↓ Calcination
Zirconia powder ZrO_2

- **Preparation of Stabilized Zirconia Powders**
- In order to achieve the requirement of the presence of **cubic** and **tetragonal** phases in their microstructure, stabilizers (**magnesia**, **calcia**, or **yttria**) must to be introduced into pure zirconia powders prior to sintering.

- Stabilized zirconia can be formed during a process called **in-situ stabilizing**.
- Before the forming processes, such as molding, pressing or casting, fine particles of **stabilizer** and **monoclinic zirconia** are well mixed.
- Then the mixture is used for forming of green body. The phase conversion **is accomplished by sintering the doped zirconia at 1700°C**. During the firing (sintering), the phase conversion takes place.

High quality stabilized zirconia powder is made by **Co-precipitation process**.

Stabilizers are introduced during chemical processing, before zirconium hydroxide's precipitation. (See following flow chart):

$ZrOCl_2$ $8H_2O$

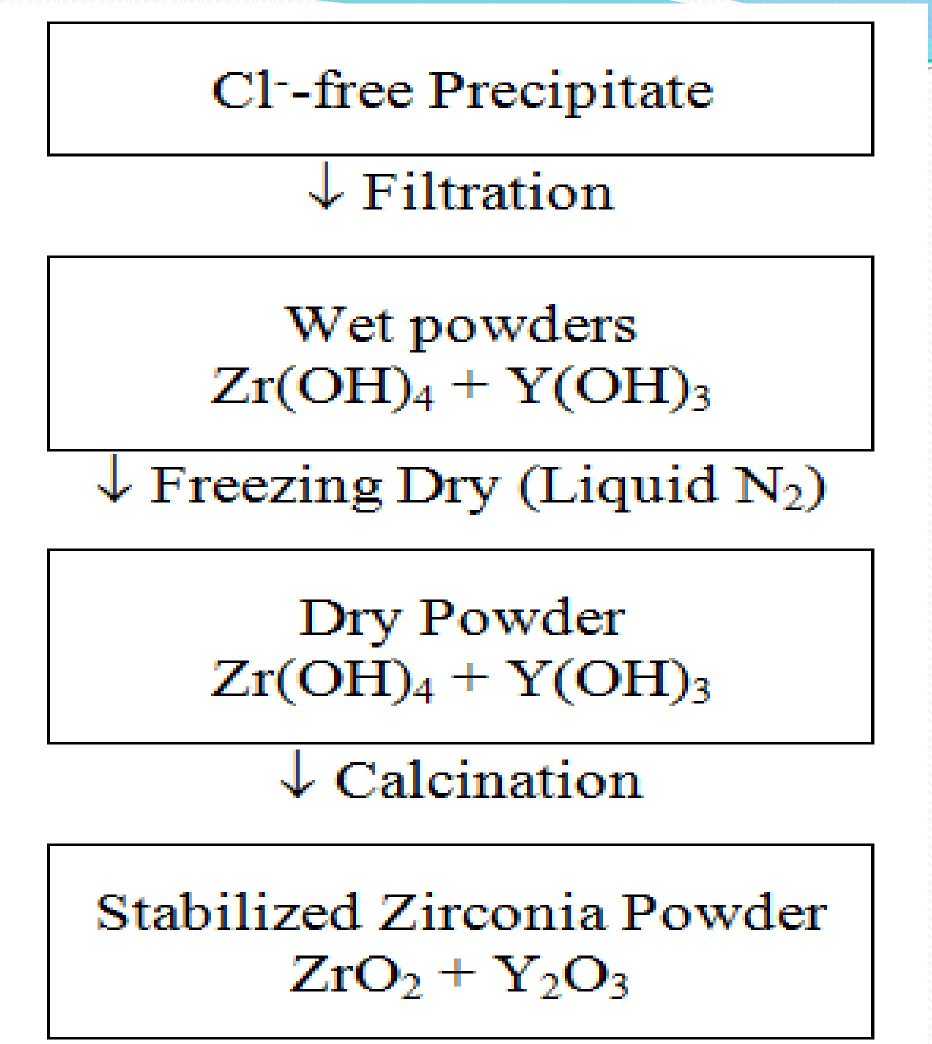
↓ + Stabilizer (Y_2O_3, for example) + HCl

Solution

↓ + NH_4OH

Co-precipitated intermediates $Zr(OH)_4 + Y(OH)_3$

↓ Wash



These powders have chemically higher uniformity than in-situ stabilizing powder.

- **Properties of Zirconia Refractory**
- Zirconia properties depend mainly on **degree of stabilization** and **quantity of stabilizer** as well as the quality of original raw material.
- Pure zirconia (fusion point **2677°C**) reacts with **H_2** and **N_2** above **2200°C** but below this temperature is stable in both oxidizing and reducing atmosphere.
- **Thermal conductivity** of zirconia is found to be **<u>much lower</u>** than that of most other refractories and the material is therefore used as a high temperature **insulating refractory.**

- Zirconia is useful refractory material for **glass furnaces** primarily since it is **not easily** wetted by molten glass and because of its low reaction with them.
- It has **low spalling resistance** due to susceptibility of zirconia to **structural changes** on heating thereby obviating its use in those places where fluctuating temperature conditions exist.
- It has **high electrical conductivity** at high temperature, therefore it is used as inductors in high frequency induction furnaces.

- **Uses of Zirconia Bricks**
- Zirconia bricks are **very expensive** and are used only when the temperature is very high as in high frequency electric furnaces.

- Zirconia **does not react** with any metal (except titanium) and hence is used in receptacles used for refractory metals and alloys at high temperatures.

- Zirconia is also used for:
- lining high temperature ceramic kilns,
- thermal barrier coatings for jet engines,
- crucibles, and
- insulating bricks for furnaces used for melting precious metals, enamels, glazes, special glasses etc.