MANUFACTURING

OF

PORTLAND CEMENT

Term Project

CL 304: Chemical Process Technology

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Introduction:

What is Portland cement?

Portland cement is a binding substance made by burning and grinding a mixture of limestone and clay or limestone and shale. It is typically a grey, finely crushed powder. The fundamental method was invented in 1824 by English inventor Joseph Aspdin, who gave it the name Portland Stone after the limestone from the Isle of Portland that the cement resembled when set. The anhydrous calcium silicates and other ingredients in Portland cement react chemically with water when combined; they combine (hydration) and break down (hydrolysis), hardening and strengthening the mixture.

Figure 1: Portland Cement Type I

History of Portland cement:

Cement has been made since Roman times, but over time the recipes used to make cement have been refined. The earliest cements were made from lime and pozzolana (a volcanic ash containing significant quantities of SiO_2 and Al_2O_3) mixed with ground brick and water. This cement was not improved upon until 1758, when Smeaton noticed that using a limestone that was 20 - 25 % clay and heating the mixture resulted in a cement that could harden under water. He called this new cement 'hydraulic lime'. When the mixture was heated, a small quantity of it was sintered1. Normally this was discarded as waste, but in the 1800s Aspdin and Johnson discovered that when the entire batch was sintered and then ground, a superior cement was formed. This substance became designated Portland cement (after the region in which they were working) and is the most common cement in use today. Portland cement was first produced commercially in New Zealand in 1886 by James Wilson and Co., and has been produced here ever since. There are currently two companies producing cement in New

Zealand: Golden Bay Cement Ltd. in Whangarei and Milburn New Zealand Ltd. in Westport. Production has increased from aound 5 000 t/annum in 1900 to in excess of 500 000 t/annum in 1991 and a New Zealand market demand in 1996 in excess of 800 000 t/annum. Portland cement is currently defined as a mixture of argillaceous (i.e. clay-like) and calcaneous (i.e. containing $CaCO_3$ or other insoluble calcium salts) materials mixed with gypsum ($CaSO_4 \cdot 2H_2O$) sintered and then pulverised into a fine powder. The precise definition of Portland cement varies between different countries, and in New Zealand are controlled by New Zealand's Standard Specification (NZS) 3122. Portland cement differs from its precursors primarily in the fact that it is sintered.

Hydraulic cements have their roots in classical Greece and Rome. Lime and volcanic ash were the materials employed; these progressively interacted with the lime in the presence of water to form a hard solid. This served as the cementing ingredient for later construction projects in western Europe as well as the mortars and concretes used by the Romans more than 2,000 years ago. The traditional pozzolana cement of the Roman era originated from volcanic ash that was mined close to the present-day Italian city of Pozzuoli. This ash was especially rich in important aluminosilicate minerals. Even now, pozzolana, or pozzolan, can refer to the cement itself or to any finely ground aluminosilicate that forms cement through a reaction with lime in water. (The name "cement" comes from the Latin word "cementum," which originally referred to stone fragments like those used in Roman mortar, not the binding substance itself.)

Photochrome print, circa 1890-1900, depicting Sir James N. Douglass's Eddystone Lighthouse near Plymouth, England. On the left are the ruins of John Smeaton's lighthouse. John Smeaton invented hydraulic lime, which was later used to create Portland cement, in 1756 when he was hired to build the Eddystone Lighthouse off the coast of Plymouth, Devon, England. The next advancement was a substance made by burning clayey limestone nodules, which happened in England and France around 1800. A similar product was later produced in the United States by burning a naturally occurring mineral known as "cement rock." These compounds are part of a family of materials called natural cement; they are similar to Portland cement but have a less regulated composition and burn more gently.

India started making cement in 1914 with the Indian Cement Company Ltd. in Porbundar, Gujarat.However, even before that the first cement plant was set up in India in 1904 in Chennai, Tamil Nadu. South India Industries Limited in Madras, made an initiative to manufacture Portland cement. India ranks as the fourth largest producer of cement in the world after China, Japan and the United States and is poised to emerge as a leader among cement producing countries.

Constituents of Portland Cement:

The composition and grinding size of Portland cement determine how much strength it develops. The strength gained during the first week of hardening is primarily the result of the C_3S, while the strength that follows is primarily the result of the C_2S. The compounds of iron and alumina that are only slightly present don't directly add much to strength.

Certain synthetic or natural chemical agents have the potential to erode concrete and set cement. In soils containing sulfate salts or seawater, the alumina compound is more susceptible to chemical assault; in contrast, the iron compound and the two calcium silicates exhibit greater resistance. Another substance that can be attacked is the calcium hydroxide that is produced when the calcium silicates hydrate. When concrete is installed in enormous masses, like dams, the temperature inside the mass can rise up to 40 °C (70 °F) above the outside temperature because cement releases heat during its hydration process. One possible reason for cracking is subsequent cooling. C_3A exhibits the highest heat of hydration, with C_3S, C_4AF, and C_2S following in decreasing order.

Table 1 : Constituents of Portland Cement

Code	Chemical Formula	Type	%
C_2S	$2CaO.SiO_2$	Silicate	Major(15-30%)
C_3S	$3CaO.SiO_2$	Silicate	Major(50-70%)
C_3A	$3CaO.Al_2O_3$	Aluminate	Major(5-10%)
C_4AF	$4CaO.Al_2O_3.Fe_2O_3$	Aluminate	Minor
–	MgO	-	Minor
–	CaO	-	Minor

Types of Portland cement:

The American Society for Testing and Materials (ASTM) has defined five varieties of Portland cement in the US: sulfate-resistant (Type V), low-heat (Type IV), high-early strength (Type III), modified (Type II), and ordinary (Type I). In other nations, Type III is referred to as rapid-hardening, and Type II is left out. In certain European nations, Type V cement is referred to as Ferrari cement. Varying the percentage of constituents changes the rate of setting, heat evolution, and strength characteristics, there are mainly 5 types of Portland cement :

1. Type I - Regular: 40-60% C_3S, 10-30% Ca_2s, 7-13% Ca_3A; hardens to full strength in 28 days. This is a general-purpose Portland cement suitable for most common applications. It's used in foundations, walls, pavements, and other structural concrete elements where the special properties of other types of Portland cement are not required. It is commonly used in residential and commercial buildings, pavements, bridges, and other general concrete construction.

2.Type II - Modified: Higher C_2S/C_3S to resist sulfate attack. Type II Portland cement has moderate sulfate resistance, making it suitable for use in structures exposed to moderate sulfate concentrations, such as those found in soils and groundwater. It is commonly used in structures like sewage treatment plants and other similar environments. It is used in environments where soil or water has moderate sulfate concentrations, such as in areas with moderate sulfate-rich soils or seawater exposure.

3. Type III - High Early Strength: Attains strength of Type I in only 3 days; high heat rates-useless on massive structures; higher C_3S and C_3A percentage with finer grinding to increase hydration rate. This type of Portland cement has high early strength development, making it ideal for applications where rapid strength gain is required, such as precast concrete elements, cold weather concreting, and in situations where forms need to be removed quickly. It is used in precast concrete elements, high-strength concrete mixes, and projects where rapid construction schedules are required.

4.Type IV - Low Heat: Designed for massive structure work; low C_3S and C_3A which are largest contributors to heat of hydration. Type IV Portland cement is designed to have a low heat of hydration, which makes it suitable for use in massive structures like dams and large foundations where controlling the temperature rise during curing is critical to prevent cracking.

5. Type V - Sulfate Resistant: Type V cement has the highest resistance to sulfate attacks among the different types of Portland cement.Good for sea water contact; $C_3A<4\%$. It's high sulfate resistance, makes it suitable for use in concrete exposed to high concentrations of sulfates, such as seawater environments or soil with high sulfate content.

Relative Compressive Strength Characteristics:

The relative compressive strength characteristics of different types of Portland cement can vary depending on factors such as curing conditions, water-to-cement ratio, aggregate properties, and admixtures used. However, here's a general overview of how the different types of Portland cement typically compare in terms of compressive strength:

- **Type I**: Type I Portland cement usually exhibits good compressive strength characteristics. It's commonly used in general construction where high early strength isn't a requirement.
- **Type II**: Type II Portland cement typically offers similar compressive strength to Type I cement but with moderate sulfate resistance. Its strength development characteristics are suitable for various construction applications.

- **Type III**: Type III Portland cement is known for its high early strength development. While it may not necessarily have significantly higher ultimate compressive strength compared to other types, it achieves its strength rapidly, making it suitable for projects where early formwork removal or rapid construction is necessary.
- **Type IV**: Type IV Portland cement is designed to have a low heat of hydration, which may slightly impact its ultimate compressive strength compared to other types. However, its strength development over time is still sufficient for its intended use in massive structures.
- **Type V**: Type V Portland cement typically exhibits good compressive strength characteristics similar to Type I cement, but with enhanced sulfate resistance. It maintains its strength in environments where sulfates are present, such as in marine structures or soil with high sulfate content.

It's important to note that while the compressive strength characteristics vary among the different types of Portland cement, proper mix design, curing procedures, and construction practices play crucial roles in achieving desired strength levels for specific applications. Additionally, testing and evaluation of concrete mixes should be conducted to determine the actual compressive strength characteristics under specific project conditions.

Table 2: Relative Compressive Strength

Type	Compressive Strength, kg/cm^2		
	1 Day	3 Days	28 Days
Type I	37	120	340
Type II	28	83	260
Type III	103	240	440
Type IV	20	49	177
Type V	28	88	214

Methods of Production:

Classification of Processes:

1. Cement Rock Beneficiation
2. Portland Cement Production

Cement Rock Beneficiation:

The beneficiation process aims to enhance the quality of locally available limestone by removing undesirable constituents, ultimately ensuring that the limestone meets the stringent requirements for cement manufacturing. Through grinding, classification, flotation, thickening, and recycling, the beneficiation process maximizes the utilization of resources while minimizing environmental impact. The process of limestone beneficiation for cement manufacturing involves a series of steps, each based on fluid mechanics and adsorption principles. These steps are crucial for ensuring that the limestone meets the desired quality standards for cement production.

1. **Grinding:** The first step in the beneficiation process is grinding. Limestone rock is typically hard and needs to be reduced to smaller particle sizes to increase its surface area. Grinding is done using wet methods to minimize dust and to ensure efficient particle size reduction.
2. **Classification:** After grinding, the limestone slurry is classified based on particle size. Classification separates the ground limestone into different size fractions, allowing for more efficient processing in subsequent steps.
3. **Hydroseparator:** The classified material is fed into a hydroseparator. The overflow from the hydroseparator is sent directly to final separation thickener if it meets satisfactory composition criteria.If not, it proceeds to the flotation separator.
4. **Flotation:** Flotation is a key beneficiation technique used to remove undesirable impurities from the limestone. The flotation process relies on the ability of certain chemicals, called collectors, to selectively wet the surfaces of specific minerals. In this case, the collectors are chosen to selectively bind to minerals like silica, mica, and talc, making them hydrophobic. Air bubbles are then introduced into the slurry, causing the hydrophobic minerals to attach to the bubbles and float to the surface as a froth. The froth, containing the unwanted minerals, is then removed from the top of the flotation cell and sent to further processing.
5. **Thickening:** The overflow from the flotation cell, which now contains the beneficiated limestone, is directed to a final separation thickener. In the thickener, the slurry undergoes further separation, allowing for the removal of any remaining impurities. The thickener operates on the principle of gravity settling, where denser particles settle to the bottom while clearer liquid overflows from the top. The overflow from the thickener typically meets the required composition for direct use in cement manufacturing. However, if the composition is not satisfactory, it may undergo additional flotation or other beneficiation steps.

6. **Recycling:** In the thickener cascade, the clarified liquid (or overflow) is recycled back into the beneficiation process, ensuring efficient use of water and chemicals. The beneficiated limestone slurry, now free from impurities, is directed to cement kilns for further processing.

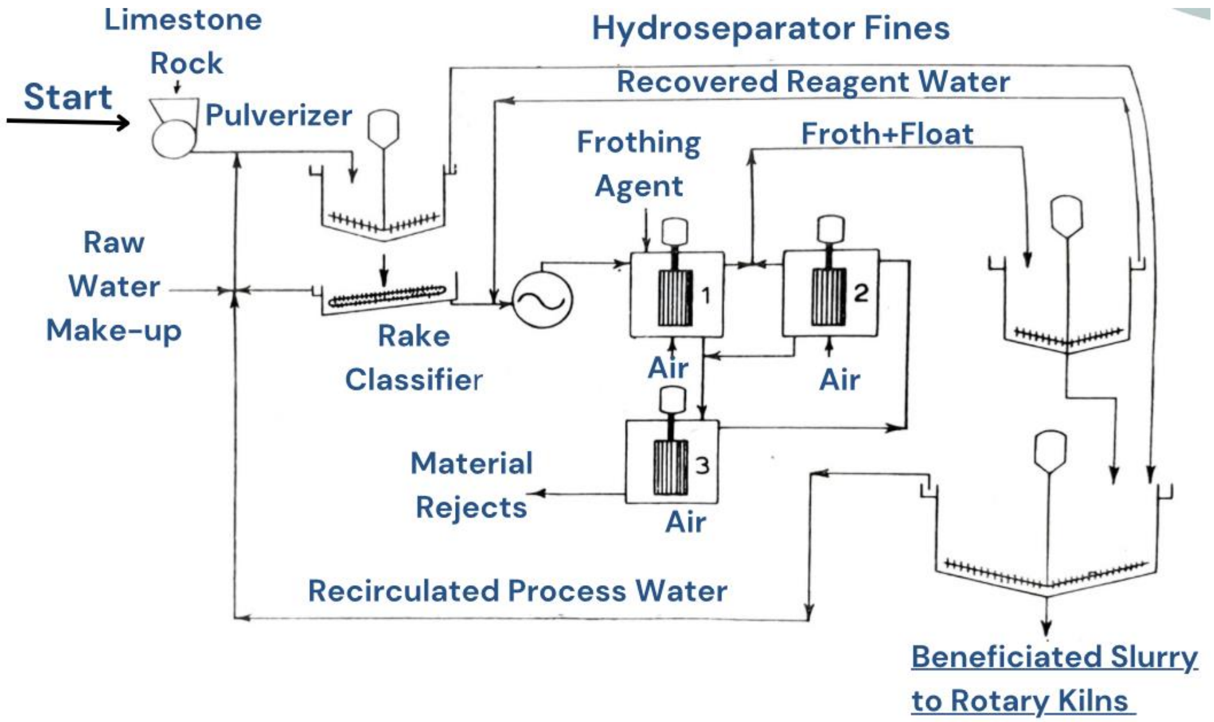

Figure 2: Flow Sheet of Limestone Beneficiation

Quantitive Requirements:

- Basis: 1 ton of low grade limestone
    - Water: 2-3 tons
    - Reagents: 50-200 grams
    - Electricity: 2.5 KWH
- Plant capacities: 300-1,000 tons/day

Major engineering problems:

1. Choice of flotation agents- necessary for selective wetting. Older type is oleic acid @ 200 gm/ton. Newer types of detergents have better selectivity and lower consumption.
2. Grinding-optimizing particle size range with power input

Portland Cement Production:

Cement-grade limestone (and possibly oyster shells) plus clay or shale, sand, iron containing materials (such as blast furnace slag), gypsum and coal (especially in India where it is more plentiful than oil or gas for heating) are ground together Grinding may be a wet or dry process, but dry process plants now predominale because of savings in heat (less water to evaporate) and accurate control possible. The sequence may include rough crushing, followed by gyratory and hammer mills then drying and fine grinding in tube mills followed by air separation and pneumatic blending. The dry powdered feed (or wet slurry) is then fed to a direct-fired counter-current rotary kiln. The residence time is 1-3 hours and the feed mixture is decarbonated and fused to form the cement compounds (C_2S, C,S, C_3A). The hot clinker (3-10 mm size) is dropped to rotary cooler which also preheats combustion air for the kiln. The product from tube milling the clinker is a powder of which 90% passes 200 mesh; it is bagged or bulk stored and shipped.

Cement production is thought to be responsible for 4–8% of global carbon dioxide (CO_2) emissions, which makes it a significant contributor to global warming. Certain strategies to reduce these emissions of greenhouse gases are also applicable to other industries. These include making cement factories more energy efficient, switching to renewable energy sources in place of fossil fuels, and trapping and storing the CO_2 emissions. Additionally, new cements and alternative formulations that lessen the need for clinker are an important area of attention, since a large share of the emissions are an inherent element of the clinker production process.

Chemical Reactions:

$$CaCO_3 \longrightarrow CaO + CO_2 + 44Kcal$$

$$CaO + Al_2O_3 + SiO_2 \longrightarrow \text{Mixture of } C_3S, C_2S, C_3A$$

Process Description:

1. **Raw Material Preparation**: Limestone, clay or shale, sand, iron-containing materials (e.g., blast furnace slag), gypsum, and coal are gathered. These materials are ground together. Grinding can be done via wet or dry processes, with dry processes being more common due to cost savings and better control.
2. **Crushing and Grinding**: The raw materials undergo rough crushing. Gyratory and hammer mills are utilized for further size reduction.
3. **Drying and Fine Grinding**: The crushed materials are dried to reduce moisture content. Tube mills are used for fine grinding, ensuring a finely powdered consistency.
4. **Mixing and Blending**: Air separation and pneumatic blending techniques are employed to ensure uniformity in the mixture.

5. **Kiln Feeding and Processing**: The dried and finely ground feed or slurry is fed into a direct-fired counter-current rotary kiln. Inside the kiln, the mixture undergoes decarbonation and fusion, forming cement compounds like C_2S, C_3S, and C_3A. The residence time in the kiln ranges from 1 to 3 hours.
6. **Clinker Cooling**: The hot clinker, ranging from 3 to 10 mm in size, is discharged from the kiln and passed through a rotary cooler. This cooling process not only reduces the temperature of the clinker but also preheats the combustion air for the kiln.
7. **Tube Milling**: The cooled clinker is finely ground in tube mills to produce a powder. Approximately 90% of the resulting powder passes through a 200 mesh sieve, ensuring a fine consistency.
8. **Packaging and Shipping**: The powdered cement is either bagged or bulk-stored for transportation and distribution. It is then shipped to various destinations for use in construction and other applications.

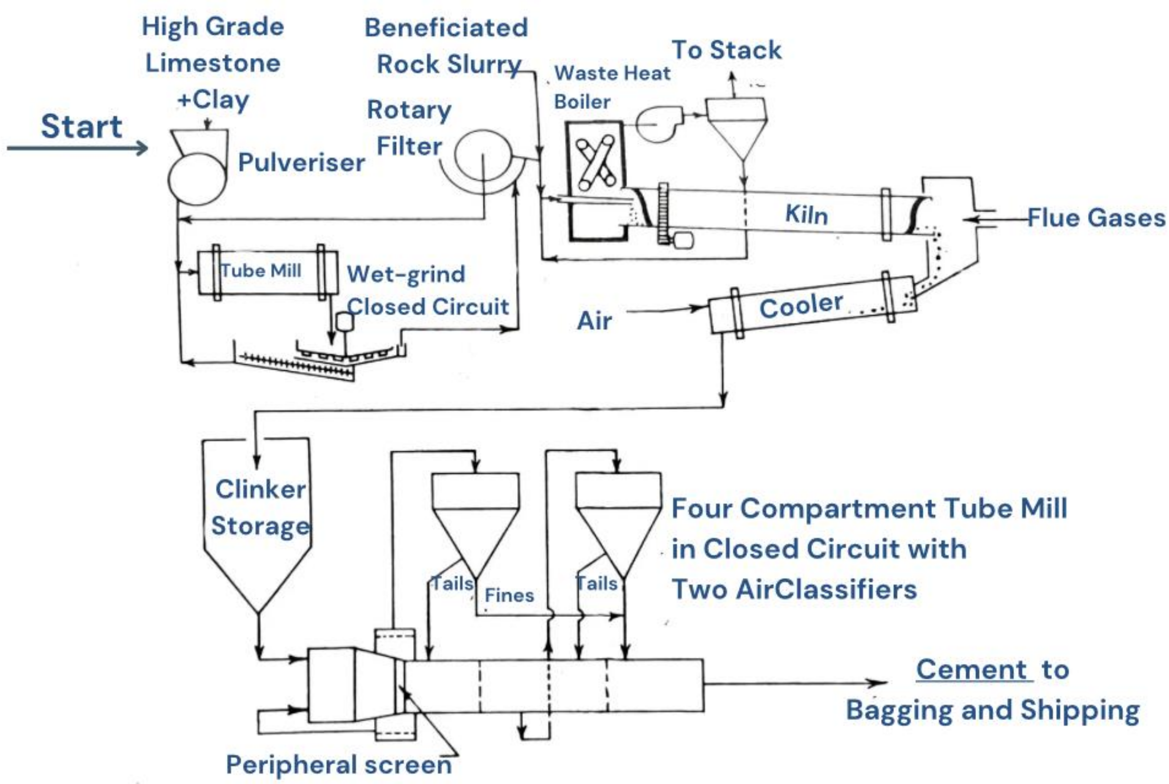

Figure 3: Flow Sheet of Portland cement manufacture

Quantitive Requirements:

- Basis: 1 ton of low grade limestone
  - Clay: 0.1-0.3 ton
  - Limestone: 1.2-1.3 tons
  - Gypsum: 0.03-0.05 ton
  - Coal: 0.25-0.40 ton

    - Water: 3 tons
    - Electricity: 80 KWH
- Plant capacities: 300-1,000 tons/day

Major engineering problems:

1. Types of grinding: Wet or dry grinding may be used with dry grinding being used in most new plants. The importance of good design here is emphasized by the fact that about 80% of the total power consumed in the manufacture of cement is used in the crushing, grinding and blending operations.
2. Kiln Design: Calcining is a process that decomposes calcium carbonate (CaCO3) into calcium oxide (CaO) by firing at temperatures between 1,400°C to 1,500°C. This temperature range promotes compound formation. Heat duty is essential for various purposes, including water evaporation, oxidizing organic materials, and volatilization of sulfates, chlorides, water, and alkalies. For wet process feed, kilns typically range from 90 to 170 meters in length and have diameters of 2.5 to 6 meters. They rotate at speeds between 2 and 4 rpm. Dry process kilns may be shorter, around 50 meters in length.
3. Heat Economy: Minimizing fuel consumption S an economic balance between fuel costs and addition of waste-heat boiler and air preheater with the equipment usually specified because of favorable incremental investment. The theoretical heat requirement is 430 Kcal/kg of Portland cement clinker. down Actual to to heat heat r (yQualiy 700-1,000 requirements control Kcal/kg vary for from processes 1,300-1, using 800 dry Kcal/kg for processes using wet grinding.
4. Quality Control: Product performance is sensitive to rock composition, particle size and degree of calcining.

Economics of Cement Industry:

Raw Materials:

The main ingredients of Portland cement are lime (calcium oxide, CaO) molecules combined with alumina (aluminum oxide, Al_2O_3) and silica (silicon dioxide, SiO_2). The other oxides are formed from an argillaceous (clayey) substance, whereas the lime is obtained from a calcareous (lime-containing) raw material. To achieve the required composition, other raw materials in lower amounts, such as silica sand, iron oxide (Fe_2O_3), and bauxite (which contains hydrated aluminum, $Al(OH)_3$), may be employed.

In order to conserve native limestone, high grade and beneficiated circuit rock are blended with burnt clays and blast furnace slag. An example is the utilization of calcium carbonate sludge from Fertilizer Corp. of India Ltd., Sindri, in cement production. This sludge, a byproduct of the reaction involving $CaSO_4$, ammonium carbonate, and ammonium sulfate, is used to produce 600 tons of cement per day by Associated Cement Companies Ltd. Additionally, cement production can occur as a co-product during the production of sulfuric acid from gypsum, resulting in cement clinker and a gas containing 9% SO_2 as co-products. This process involves heating gypsum, coke, and shale in a coal-fired kiln at 2500°F.

$CaSO_4 + (NH_4)_2CO_3 \longrightarrow (NH_4)_2SO_4 + CaCO_3$

Gypsum. fertiliser grade ammonium sulfate sludge

Overall Factors to be considered in Cement Industry:

a. Process Technology
b. Industry Problems including:
   i. Capital availability
   ii. Power
   iii. Locational problems
   iv. Raw material problems
   v. Transport problems
   vi. Export problems
c. The advent of mini-plants
d. The impact of research and development
e. Future market influences and trends

Production:

1. **Global Cement Production**: Exceeding one billion tons indicates the substantial scale and importance of the cement industry worldwide. Cement is a crucial material for infrastructure and construction projects, so its production is a significant indicator of economic activity.
2. **Indian Cement Industry**: The Indian cement industry is highlighted as it's approaching a significant milestone of 100 million tons in production capacity. This growth underscores the rapid development and urbanization occurring in India, driving demand for construction materials like cement.
3. **Production Targets and Achievements**:
   - ✓ For the year 1992-93, the government set a production target of 56.5 million tons for the cement industry, implying a monthly target of 4.9 million tons.
   - ✓ In 1991-92, actual production reached approximately 50.61 million tons, slightly below the target but still showing significant output.
   - ✓ Capacity utilization of large cement plants improved from 83.7% in 1990-91 to 87.9% in 1991-92. This indicates enhanced operational efficiency and possibly increased demand for cement.
   - ✓ The Planning Commission has set a production target.

Technology:

The cement manufacturing industry has evolved through various technological stages, from the outdated wet process to the more efficient dry process and the latest precalcinator technology. The precalcinator technology, particularly, allows for partial or complete calcination of raw materials before entering the rotary kiln, reducing thermal load and enabling increased capacity by 30-50%.

Modernization is crucial to address technological obsolescence in the industry. This involves shutting down uneconomic units and converting others to semi-dry or completely dry processes. Process conversion costs less than setting up new units, and it's essential to upgrade existing facilities. However, this modernization requires a significant investment of around Rs. 1,500 crore, which the cement units cannot afford on their own.

To address this financial challenge, the government could establish a modernization fund similar to that of the textile industry. Additionally, financial institutions could offer soft loan schemes tailored for modernization projects. It's also imperative for companies to allocate funds for research and development (R&D) to enhance existing technologies and adapt foreign expertise to Indian conditions. Currently, the industry's commitment to R&D is minimal, highlighting the need for increased investment in this area to drive innovation and efficiency improvements.

Applications of Portland cement:

- **Production of Concrete:** The main component of concrete, the most used building material in the world, is Portland cement. It generates a paste that hardens and binds the aggregates together to form a solid structure when combined with aggregates (such as sand, gravel, or crushed stone) and water. Many different types of structures, including pavements, roads, bridges, dams, and buildings, are made of concrete.
- **Mortar**: Portland cement, fine aggregates (like sand), and water are combined to create mortar, which is a binding agent used in construction to keep bricks, stones, and other masonry components together. Building walls, chimneys, and other brick or stone constructions requires mortar.
- **Grouts:** In construction projects, the spaces between tiles, bricks, or other masonry units are filled with grouts made of Portland cement. Grouts improve the completed surface's look, offer structural stability, and stop water intrusion.
- **Stucco and Plaster:** Portland cement is an essential component of stucco and plaster, two materials that are used as coatings on walls and ceilings to give them a long- lasting and attractive appearance. Plaster is typically used for internal walls and ceilings, while stucco is typically utilized for external surfaces.
- **Soil Stabilization:** The process of strengthening and stabilizing soil by mixing it with Portland cement is called soil stabilization. In regions with poor soil quality, this approach is frequently employed for foundation stabilization, road construction, and embankment reinforcement.

- **Precast Concrete goods:** A variety of precast concrete goods, such as pipes, blocks, panels, beams, and slabs, are made using concrete that is based on Portland cement. In construction projects, precast concrete has benefits including quality control, efficiency, and versatility.
- **Shotcrete:** Also referred to as sprayed concrete, shotcrete is a high-velocity building material that is applied pneumatically to a surface. Shotcrete made of Portland cement is frequently used for building swimming pools, tunnel linings, slope stabilization, and structural rehabilitation.
- **Road Construction:** Where extreme strength and endurance are needed, Portland cement is utilized to build rigid pavements like roads and airport runways. Additionally, base layers coated with cement are employed to increase the road foundations' ability to support loads
- **Industrial Uses:** Portland cement is employed in the manufacturing of concrete pipes, precast concrete components, railroad sleepers, and building blocks, among other industrial uses. Additionally, it is employed in the production of cement-based goods like pavers, bricks, and tiles.
- **Specialized Uses:** Portland cement can be made to meet specific needs. For example, it can be made to set quickly for emergency repairs, low-heat for large-scale concrete pours, and sulfate-resistant for subterranean and maritime constructions.

References:

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- https://en.wikipedia.org/wiki/Portland_cement