Portland Cement

Definition

A hydraulic cement capable of setting, hardening and remaining stable under water. It consists essentially of hydraulic calcium silicates, usually containing calcium sulfate.
Raw Materials

- 2/3 calcareous materials (lime bearing) - limestone
- 1/3 argillaceous materials (silica, alumina, iron) - clay
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Notation

C  CaO
S  SiO$_2$
A  Al$_2$O$_3$
F  Fe$_2$O$_3$
H  H$_2$O
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Cement Minerals

\[ \text{C}_3\text{S} : 3\text{CaOSiO}_2 \]

\[ \text{C}_2\text{S} : 2\text{CaOSiO}_2 \]

\[ \text{C}_3\text{A} : 3\text{CaOAl}_2\text{O}_3 \]

\[ \text{C}_4\text{AF} : 4\text{CaOAl}_2\text{O}_3\text{Fe}_2\text{O}_3 \]
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Chemical Reactions

2C₃S  +  6H  -->  C₃S₂H₃  +  3CH  +  120 cal / g
2C₂S  +  4H  -->  C₃S₂H₃  +  CH  +  62 cal / g
C₃A  +  CSH₂  -->  Ettringite  +  300 cal / g
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Hydrated Paste

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Calcium Silicate Hydrate

Notation:  C-S-H
C/S Ratio:  1.5 to 2.0
Main Characteristics:  High Surface (100 to 700 m²/ g) ----> High *Van der Walls* Force ----> Strength.
Volume % : 50 a 60
Solids in the Cement Paste

Calcium Sulfoaluminate Hydrates

Volume % : 15 to 20

first : ettringite

after : monosulfate hydrated.
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Calcium Hydroxide

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Solids in the Cement Paste

**Calcium Sulfoaluminate Hydrates**

Volume %: 15 to 20

first: ettringite

after: monosulfate hydrated.
Orders of magnitude

Dimensional range of solid and pores in a hydrated cement paste.
ASTM Portland Cements

**Type I**  General Purpose

**Type II**  Moderate heat of hydration and sulfate resistance (C3A < 8%) : general construction, sea water, mass concrete

**Type III**  High early strength (C3A < 15%) : emergency repairs, precast, winter construction.

**Type IV**  Low heat  (C3S < 35%, C3A < 7%, C2S > 40%) : mass concrete

**Type V** - sulfate resistant  (C3A < 5%) : sulfate in soil, sewers
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Main Components of PC

<table>
<thead>
<tr>
<th>Main Components of PC</th>
<th>amount</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3S</td>
<td>50%</td>
<td>very reactive compound, high heat of hydration, high early strength</td>
</tr>
<tr>
<td>C2S</td>
<td>25%</td>
<td>low heat of hydration, slow reaction</td>
</tr>
<tr>
<td>C3A</td>
<td>10%</td>
<td>problems with sulfate attack, high heat of hydration</td>
</tr>
<tr>
<td>C4AF</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>gypsum</td>
<td>5%</td>
<td>used to control the set of cement</td>
</tr>
</tbody>
</table>
**Typical Compound Composition of Various Types of Portland Cement**

<table>
<thead>
<tr>
<th>ASTM type</th>
<th>General description</th>
<th>Compound composition range (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>General purpose</td>
<td>C(_3)S: 45-55, C(_2)S: 20-35, C(_3)A: 8-12, C(_4)AF: 6-10</td>
</tr>
<tr>
<td>II</td>
<td>General purpose with moderate sulfate resistance and moderate heat of hydration</td>
<td>C(_3)S: 40-50, C(_2)S: 25-35, C(_3)A: 5-7, C(_4)AF: 6-10</td>
</tr>
<tr>
<td>III</td>
<td>High early strength</td>
<td>C(_3)S: 50-65, C(_2)S: 15-25, C(_3)A: 8-14, C(_4)AF: 6-10</td>
</tr>
<tr>
<td>V</td>
<td>Sulfate resistant</td>
<td>C(_3)S: 40-50, C(_2)S: 25-35, C(_3)A: 0-4, C(_4)AF: 10-20</td>
</tr>
</tbody>
</table>

ASTM also has Types I-A, II-A, III-A — cements with air entrainment.
Other hydraulic cements

- a) Blended P.C
- b) Modified P.C.
- c) Non-calcium silicate cements
Blended PC

- **Type I-P**  
  P stands for pozzolan. It contains 25 to 30% of fly ash. It has low heat of hydration, develops strength over time.

- **Type I-S**  
  S stands for slag. It contains 50 to 60% of Blast-Furnace Slag.
Aggregates for Concrete
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**Significance:**

- Cost
- Provide dimensional stability
- Influence hardness, abrasion resistance, elastic modulus
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**Aggregate Type**

- **Coarse aggregate** > 3/16 in. - 4.75 mm (No. 4 sieve)

- **Fine aggregate** < 3/16 in. and > 150 (No. 200 sieve)
Aggregate Type - mineralogy

- **Sedimentary Rocks** (cost effective - near the surface), about 80% of aggregates

- Natural sand and gravel

- Sandstone, limestone (dolomite), chert, flint, graywacke

- **Metamorphic Rocks**: slate, gneiss

- Excellent to poor
Aggregate Type - mineralogy

- **Igneous Rocks**
  - *Intrusive (plutonic)*: coarse-grained; granite
  - *Shallow Intrusive*: fine-grained; riolite, andesite, basalt
  - *Extrusive*: fine-grained; tuff, pumice, basalt hard,
  - Tough, strong: excellent aggregate.
Industrial by-products used in concrete

- **Slags**: by-product of metallurgic industries
- Not a high quality aggregate because it has some impurities
- Not used for prestressed concrete
- Used for blocks
- Much more value as a cementing material
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Industrial by-products used in concrete

- **Fly-ash:** by-product of burning coal (60 million ton/y in USA)

- Sintered or pelletized fly-ash has been used for LWA

- Good to be used in combination with P.C.
Industrial by-products used in concrete

- **Aggregate from recycled concrete** (demolished concrete buildings)

  - Aggregate is contaminated with cement paste, gypsum, etc.

  - Cost of crushing, grinding, dust control, and separation of undesirable constituents

  - Silt, clay increase water requirement (wash them out)
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Reduction of Voids

![Graphs showing the percentage of voids in mixed aggregates for gravel and granite.](image)

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- Reasons

- (1) Improve or modify some or several properties of portland concrete.

- (2) Compensate for some deficiency
Admixtures

- Classification

- Surfactants (0.05-0.5%; new ones 2%)

- Chemical Admixtures (1-4% by weight of cement)

- Mineral Admixtures (> 15% by weight of cement)
Ice Formation in Concrete
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Air Voids

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Air-Entraining Surfactants

(a) Formula of a typical air-entraining surfactant derived from pine oil or tall oil processing; (b) mechanism of air entrainment when an anionic surfactant with a nonpolar hydro-carbon chain is added to the cement paste.
ASTM Categories (C494) : Water Reducers

- **Low range:** water reduction of 5% (minimum)
  - Type A : normal
  - Type D : WR and retarding
  - Type E : WR and accelerating

- **High range:** water reduction of 12% (minimum)
  - Type F : normal
  - Type G : HRWR and retarding
Citric Acid  Gluconic Acid  Repeating unit of a lignosulphonate polymer (a)
The polar chain is adsorbed alongside the cement particle; instead of directing a nonpolar end toward water, in this case the surfactant directs a polar end, lowering the surface tension of the water and making the cement particle hydrophilic.
As a result of layers of water dipoles surrounding the hydrophilic cement particles, their flocculation is prevented and a well-dispersed system is obtained.
Mode of Action of Superplasticizers

"Physical" binding and dispersion

- Flocculated
- Deflocculated
- Dispersed in less water

"Physical" effects operative in any slurry or paste

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Courtesy from Carmel JOLICOEUR
Illustration of Physical Dispersion Effect

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+10 % water  ⇐  Mineral Paste  ⇒  +0.1 wt% PNS

Courtesy from Carmel JOLICOEUR

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The Pantheon, called the Temple of the Gods, is one of the greatest engineering wonders of the Roman Empire. Built in 128 A.D. by Emperor Hadrian, the Pantheon held the world record for the largest dome diameter (43.2m) for almost 1800 years.
Mineral Admixtures

- Finely divided siliceous materials which are added to concrete in relative large amounts. They react with calcium hydroxide (CH) at ordinary temperature to produce cementitious product.
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Pozzolanic Reaction

- silica + CH $\rightarrow$ C-S-H
Mechanisms of Action

- Control of Bleeding: Channels of bleeding water are obstructed by the small particles.
- Grain Refinement: without pozzolans large CH crystals develop
- Pore Refinement: reduction of porosity
Batching

- measurement of components of concrete
- measurement by weight (water and liquid admixtures both by volume or weight)
- accuracy: cement 1%, aggregates: 2%, water 1%, admixtures 3%
- air-entraining admixtures and other chemical admixtures should be added as solutions.
Ready Mixed Concrete

- central-mixed concrete is mixed in a stationary mixer and then delivered in trucks.
- concrete is mixed partially in a stationary mixer and completed in truck mixer.
- truck-mixed concrete is mixed completely in a truck mixer.
Transport – Truck agitator

- Range: Used to transport concrete to all uses in pavements, structures and buildings.
- Advantages
  - Good quality control (from central mixing plants).
  - Well-controlled discharge from agitadors.
- Points to watch for
  - Careful timing of deliveries
  - Concrete crew and equipment must be ready
Truck mixer

- **Type and range:** Mix and transport concrete to site over short and long hauls.

- **Advantages:**
  - No central mixing plant is needed
  - Concrete is mixed completely in truck mixer.

- **Points to watch for:**
  - Control of concrete quality is not as good as with central mixing.
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Crane

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Aerial Cable

Courtesy from Jose Marques Filho

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Belt Conveyors

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Shotcrete

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Formation of ettringite and monosulfate

\[
C_3A + 3CS\bar{S}H_2 + 26H \rightarrow C_3A.3CS\bar{S}.H_{32}
\]

ettringite

\[
2C_3A + C_3A.3CS\bar{S}.H_{32} + 4H \rightarrow 3C_3A.CS\bar{S}.H_{12}
\]

monosulfate

In the presence of sulfates, the monosulfate can form ettringite which may lead to expansion
Sodium sulfate attack:

- \( \text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \)

- The formation of sodium hydroxide as a by-product of the reaction ensures the continuation of high alkalinity in the system, which is essential for the stability of the cementitious material C-S-H.
Magnesium sulfate attack

- \( \text{MgSO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2 \)
- \( 3 \text{MgSO}_4 + 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 8 \text{H}_2\text{O} \rightarrow 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 3 \text{Mg(OH)}_2 + 2\text{SiO}_2 \cdot \text{H}_2\text{O} \)

- The conversion of calcium hydroxide to gypsum is accompanied by the simultaneous formation of relatively insoluble magnesium hydroxide.
- In the absence of hydroxyl ions in the solution C-S-H is no longer stable and is also attacked by the sulfate solution.
- The magnesium sulfate attack is, therefore, more severe on concrete.
Negligible attack: When the sulfate content is under 0.1 percent in soil, or under 150 ppm (mg/liter) in water, there shall be no restriction on the cement type and water/cement ratio.

Moderate attack: When the sulfate content is 0.1 to 0.2 percent in soil, or 150 to 1500 ppm in water, ASTM Type II portland cement or portland Pozzolan or portland slag cement shall be used, with less than an 0.5 water/cement ratio for normal-weight concrete.
This deleterious reaction is known for a long time.

California, 1936

Map cracks

Vertical cracks
Examples of damage

Built in 1965, this deteriorated bridge is located 9.7 miles west of Lee Vining at 9400 feet elevation on the eastern slope of the Sierra Nevada.
The chemistry is simple

1) The high pH in the cement paste promotes the hydrolysis of silica

\[
\text{Si-O-Si} + \text{OH}^{-} + \text{H}^{+} \rightarrow \text{Si-OH} + \text{Si-OH}
\]

aggregate paste

2) Si-OH react with the paste to form Si-O-

3) Si-O-, adsorbs Na, K, and Ca to form a gel.

Which chemical composition causes the gel to expand?
Corrosion damage

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Electrochemical process of steel corrosion in concrete

Cathode Process
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

Anode Process
\[ Fe \rightarrow Fe^{++} + 2e^- \]

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Volumetric change

![Volumetric change graph showing different compounds and their volumes.]

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Problems:

- Aggregate, cement, and water will be at cold temperature
- Low temperature --> slow hydration
- Influences setting, hardening, strength development
Time of Set

Penetration Resistance

Initial Final

2 4 6

73 F 40 F

Time (h)
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Strength

Strength (psi)

1000

Time (h)

73 F

50 F

20 F

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Precautions/Solutions

1) Materials and Proportions (indirect way)
   • Set Accelerators
   • Type III cement
   • Use more cement (more heat generation)

2) Mix Temperature
   • Heat aggregates
   • Replace some of the mixing water with hot water
- Insulating formwork (keep heat inside)
- Use blankets, heaters
- Air shelters (small jobs)
- Keep formwork for a longer period of time
Hot Weather Concreting

- Problems
  - High temperature --> fast hydration --> loss of water
  - Form hydration products quickly
  - Loss of slump, time of set reduced
  - Loss of consistency
Rapid Hydration

- 1) More mixing water required due to the loss of consistency
- 2) Rapid Setting time
Solution:

- Selection of material and mix proportions.
  1) Set retarders
  2) Cement Type II, IP
  3) Less cement
  4) Air entrainment to control slump
  5) Mineral admixtures
  6) Use cooled water or ice
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Schmidt rebound hammer

Watch the video

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The type and amount of aggregate play an important role in the penetration resistance.

The variation in the Windsor probe-test results is higher when compared with the variation in standard compressive strength tests on companion specimens.

This method is excellent for measuring the relative rate of strength development of concrete at early ages, especially for determining stripping time for formwork.
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Windsor probe

Compressive strength as a function of exposed probe

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Schematic diagram of the pullout test

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MATURITY METHOD

A simple maturity function $M(t)$ can be defined as the product between time and temperature:

$$M(t) = \sum (T_a - T_o) \Delta t$$

or in the limit

$$M(t) = \int_0^t (T_a - T_o) \, dt$$

where $\Delta t$, $T_a$, and $T_o$ are time interval, average concrete temperature during the time interval $\Delta t$, and the datum temperature, respectively. Traditionally, $-10^\circ C$ or $14^\circ F$ is assumed to be the datum temperature below which there is no additional gain in strength. ASTM C 1074 recommends a datum temperature of $0 ^\circ C$ or $32 ^\circ F$. 

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Influence of curing temperature at early ages on the strength-maturity relationship when equation (1) is used with $T_0 = -10 \, ^\circ C$. This early-age difference can be reduced when better maturity functions are used.
Reflection and refraction

\[
\frac{\sin \theta_1}{\sin \theta_2} = \frac{V_1}{V_2}
\]

\[
\theta_{ic} = \sin^{-1} \left( \frac{V_1}{V_2} \right)
\]
Ultrasonic Pulse Velocity Methods

Watch the video
Many receivers

slope: 1/V
Impact-echo

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Generation, propagation, and detection of Acoustic Emission
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Equipment II

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Radiographic (left) and CT (right) image.
Thermal Stresses

Thermal Shrinkage

Temperature (°C)

Time (days)

T_{max}

ΔT

T_{placement}

T_{ambient}

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Thermal stresses

where:

\( \sigma_t \): tensile stress

\( K_r \): degree of restraint

\( E \): elastic modulus

\( \alpha \): coefficient of thermal expansion

\( \Delta T \): temperature change

\( \phi \): creep coefficient

\[
\sigma_t = K_r \frac{E}{1 + \phi} \alpha \Delta T
\]
\[ \Delta T = \text{placement temperature of fresh concrete} + \text{adiabatic temperature rise} - \text{ambient or service temperature} - \text{heat losses.} \]
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Sequence of placement
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**Sequence of placement**

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Sequence of placement

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Compaction

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Repair of Reinforced Concrete Structures

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1. Repair Materials
   a. portland cement
   b. polymer modified concrete
   c. resin mixtures
   d. substitute materials
Nomenclature

- **polymer concrete (PC):** formed by polymerizing a mixture of a monomer and aggregate (no other bonding material)
- **latex-modified concrete (LMC):** also known as polymer portland cement concrete. Conventional concrete made by replacing part of mixing water with a latex.
- **polymer-impregnated concrete (PIC):** produced by impregnating or infiltrating a hardened concrete with a monomer and subsequently polymerizing the monomer in situ.
Significance -- LMC

- LMC possess excellent bonding ability to old concrete, and high durability to aggressive solutions; it has therefore been used mainly for overlays in industrial floors, and for rehabilitation of deteriorated bridge decks.
Significance -- PIC

- In the case of PIC, by effectively sealing the microcracks and capillary pores, it is possible to produce a virtually impermeable product which gives an ultimate strength of the same order as that of PC.

- PIC has been used for the production of high-strength precast products and for improving the durability of bridge deck surfaces.
Polymer concrete (PC) is a mixture of aggregates with a polymer as the sole binder. To minimize the amount of the expensive binder, it is very important to achieve the maximum possible dry-packed density of the aggregate.
Commercial products are available with a variety of formulations, some capable of hardening to 105 MPa (15,000 psi) within a few minutes without thermal treatment.

Epoxy resins are higher in cost but offer advantages such as adhesion to wet surfaces.

Styrene monomer, and methyl methacrylate (MMA) with benzoyl peroxide catalyst and an amine promoter are often used.

Products with increased strength have been obtained by adding to the PC monomer system a silane coupling agent, which increases the interfacial bond between the polymer and aggregate.
Latex-Modified Concrete

- The materials and the production technology for concrete in LMC are the same as those used in normal portland cement concrete except that latex, which is a colloidal suspension of polymer in water, is used as an admixture.
Earlier latexes were based on polyvinyl acetate or polyvinylidene chloride, but these are seldom used now because of the risk of corrosion of steel in concrete in the latter case, and low wet strengths in the former.

Elastomeric or rubberlike polymers based on styrenebutadiene and polyacrylate copolymers are more commonly used now.
The hardening of a latex takes place by drying or loss of water.

Dry curing is mandatory for LMC; the material cured in air is believed to form a continuous and coherent polymer film which coats the cement hydration products, aggregate particles, and even the capillary pores.
Polymer-Impregnated Concrete

- The concept underlying PIC is that if voids are responsible for low strength as well as poor durability of concrete in severe environments, then eliminating them by filling with a polymer should improve the characteristics of the material.
It is difficult for a liquid to penetrate it if the viscosity of the liquid is high and the voids in concrete are not empty (they contain water and air). Therefore, for producing PIC, it is essential not only to select a low-viscosity liquid for penetration but also to dry and evacuate the concrete before subjecting it to the penetration process.
Repair Materials and Methods

- Goals:
- Strength of repair work should be, at least, as much as the old concrete.
- Bond between old and new concrete should be very good.
Parameters Affecting the Repair

- 1) Permeability
  - The subbase can be wet leading to a significant amount of moisture below the repair. The moisture will evaporate and it will develop vapor pressure; therefore overlays should be able to breath.
  - If the permeability is too low the repair will delaminate. Portland cement concrete is able to breadh causing delamination.
2) Drying Shrinkage

If the same mix is used the concrete will shrink and crack, losing the bond. This causes the development of microcracks at the interfacial bond producing delamination.
Parameters Affecting the Repair

3) Coefficient of Thermal Expansion ($\alpha$)
   • quartz sand has a high $\alpha$ value.
   • differences in $\alpha$ between old and new concrete will cause differential strains.
   • use $\alpha$ as close as possible to the old concrete.

4) Elastic Modulus
a) Cast in place formwork
- section thickness: 6-8 in
- remove old concrete --> clean --> use water jets
- (sand blast is not as used because of pollution)
DRY-MIX SHOTCRETE PROCESS

- Cementitious binder and aggregates thoroughly mixed (central mixing, transit mixer, volumetric proportioning mixer or dry bagged premix)
- Water Added if necessary to bring shotcrete to “Earth Dry” consistency – 3 to 6% moisture content.
- Mix added to shotcrete delivery equipment or gun.
Compressed air conveys the shotcrete from the gun down the hose.

Water introduced under pressure through a water ring at the nozzle.

Shotcrete jetted from a nozzle at high speed onto a surface with the force of the impacting jet compacting the material.
Wet-Mix Shotcrete Process

- All ingredients including mixing water thoroughly mixed.
- The mortar or concrete is added to the chamber of the delivery equipment.
- The mix is either pumped or pneumatically conveyed down the hose by compressed air.
- High-pressure air is added at the nozzle to jet the shotcrete at high velocity onto the impacting surface.
Comparison of Wet and Dry Mix Shotcretes

- Wet Mix Shotcrete
- Advantages
- Less Rebound
- Less Dust
- Less Nozzleman Skill Required
- Air Entrainment Possible
- Large Volume Rates of Placement Possible
- Lower Cost Ready Mix Supply Often Possible
Wet Mix Shotcrete

- Disadvantages
- Generally Lower Compressive Strengths (unless silica fume and superplasticizers used)
- Cannot Adjust Moisture Content at Nozzle when Shooting Wet Areas
- Restricted to Layers 2 to 3 inches thick in a single pass
- Not suitable for small volume, intermittent work
Dry Mix Shotcrete

- Advantages
- Generally Higher Compressive Strengths
- Nozzleman Can Adjust Water For Better Adherence in Wet Substrate Conditions
- Available in Premixed Dry Bags Form for Stop-Start Type Work
- Air Entrainment Possible
- Greater Thickness of Application Possible on Vertical and Overhead Surfaces
Dry Mix Shotcrete

- Disadvantages
- Higher Rebound
- More Dust
- Larger Air Compressor Required
- High Level of Nozzleman Skill Required
- Potential for Laminations, sand lenses, dry pockets, etc.
- Difficult to entrain air
- Lower volume rates of placement