
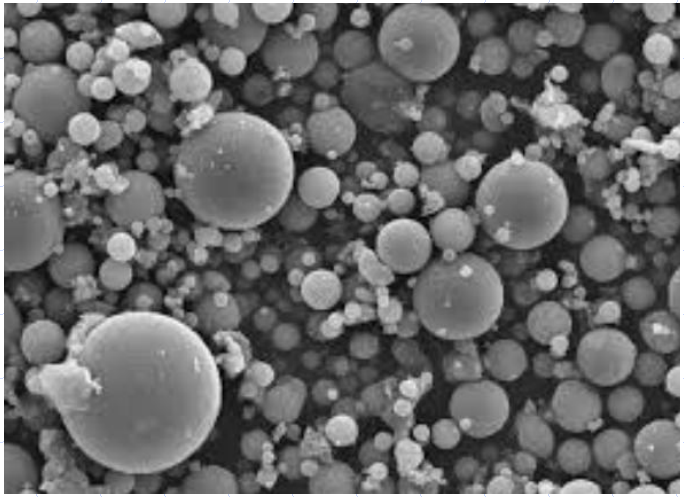


Supplementary Cementitious Materials

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P.E.

Supplementary Cementing Material

- A material, when used in conjunction with portland cement, contributes to the properties of concrete through hydraulic and/or pozzolanic reaction.
- Fly ash, Silica fume, Slag and natural pozzolans

Produced by burning of powdered coal.

Produced in electric arc furnance as byproduct of silicon production

From left to right:

- Fly ash (Class C)
- Metakaolin (calcined clay)
- Silica fume
- Fly ash (Class F)
- Slag
- Calcined shale

Supplementary Cementing Material

- **Pozzolan** — a siliceous or alumino-siliceous material that, in a finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide released by the hydration of portland cement to form compounds possessing cementing properties. ACI 116R
- **Natural Pozzolans** — a natural material which may also be calcined and/or processed (eg. metakaolin, rice husk, volcanic ash, calcined shale)

Prepared by heating china clay to 600-800

Pozzolanic Reaction: Effect 1

- $C_3S + 5.3\ H \Rightarrow C_{1.7}SH_4 + 1.3\ CH$
- $C_2S + 4.3\ H \Rightarrow C_{1.7}SH_4 + 0.3\ CH$

- The hydration of C_3S and C_2S produces:

  - **CSH, which is the binder (glue) responsible for strength**
  - **and CH**, which does **not** have an important **contribution to strength development** and poses certain problems for durability.

Pozzolanic Reaction: Effect 1

- The addition of certain forms of **reactive amorphous silica** (known as pozzolans or supplementary cementing materials) leads to a reaction between silica and CH (**pozzolanic reaction**):

  Calcium Hydroxide Calcium Silicate Hydrate

  - **CH + S ⇒ CSH**: produces more CSH ⇒ refinement of porosity, densification of aggregate-cement paste interface and enhancement to mechanical properties and durability.

- The importance of these improvements, the rate of development with time etc. depends on the form of amorphous silica added.

Pozzolanic Reaction: Effect 1

Cement + water $\Rightarrow$ *calcium silicate hydrate + calcium hydroxide*

$$C_2S \; \& \; C_3S + H \Rightarrow CSH + CH$$

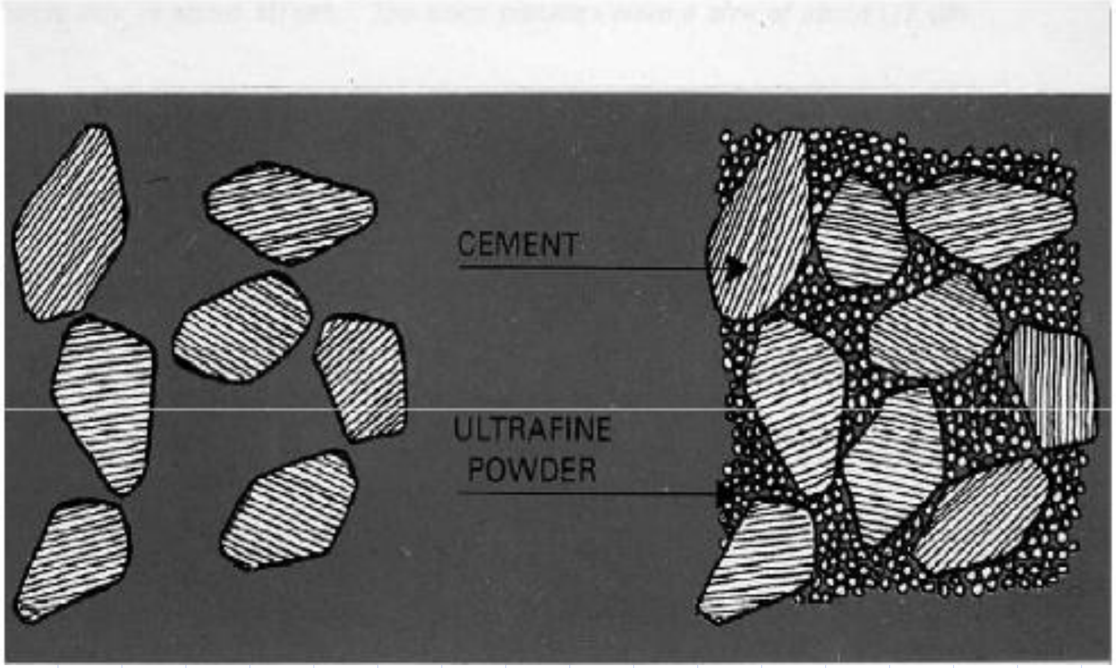
Pozzolan + calcium hydroxide + water $\Rightarrow$ *calcium silicate hydrate*

$$CH + S \Rightarrow CSH$$

Pozzolanic Reaction: Effect 2

Physical filler effect

- In addition to the benefits of the pozzolanic reaction, mineral additions with adequate particle size distribution can lead to a physical filler effect (reduction of porosity between cement grains).



Silica Fume (SF)

Very fine non-crystalline silica produced in electric arc furnaces as a byproduct of the production of elemental silicon or alloys containing silicon; also known as condensed silica fume or microsilica.

Silica Fume

- Smoke by-product from furnaces used in the production of ferrosilicon and silicon metals
- Amorphous silica with high SiO_2 content, extremely small particle size, and large surface area
- Highly reactive pozzolan used to improve mortar and concrete

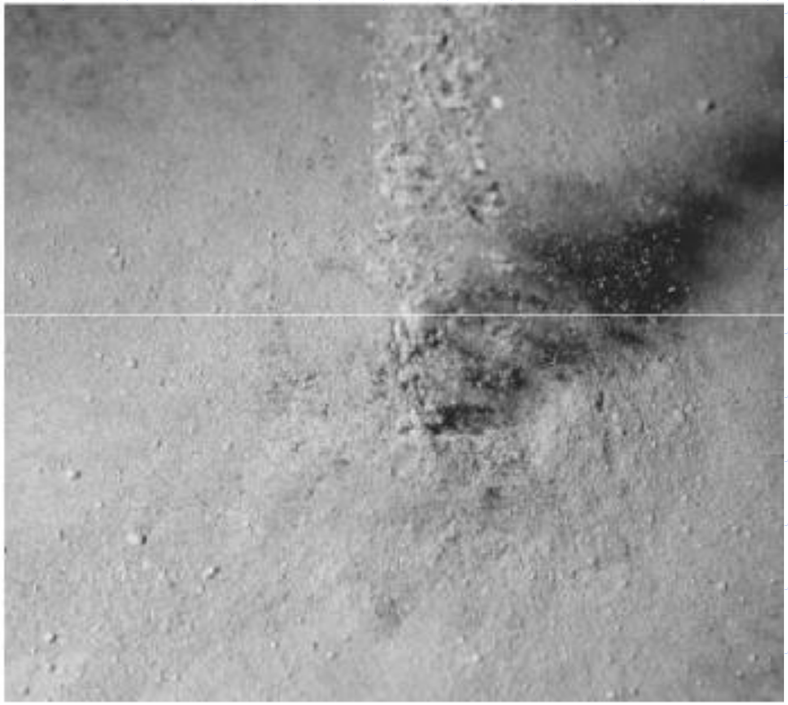
Also known as:

- **Condensed silica fume**
- **Microsilica**
- **"Micropoz" (trademark)**
- **Silica dust**
- **Volatilized silica**

Silica Fume Product Forms

- As-produced powder
- Water-based slurry
- Densified
- Blended silica-fume cement
- Pelletized (dustless, pellets 10-25 mm will not disperse in concrete, needs to be ground to be used in concrete)

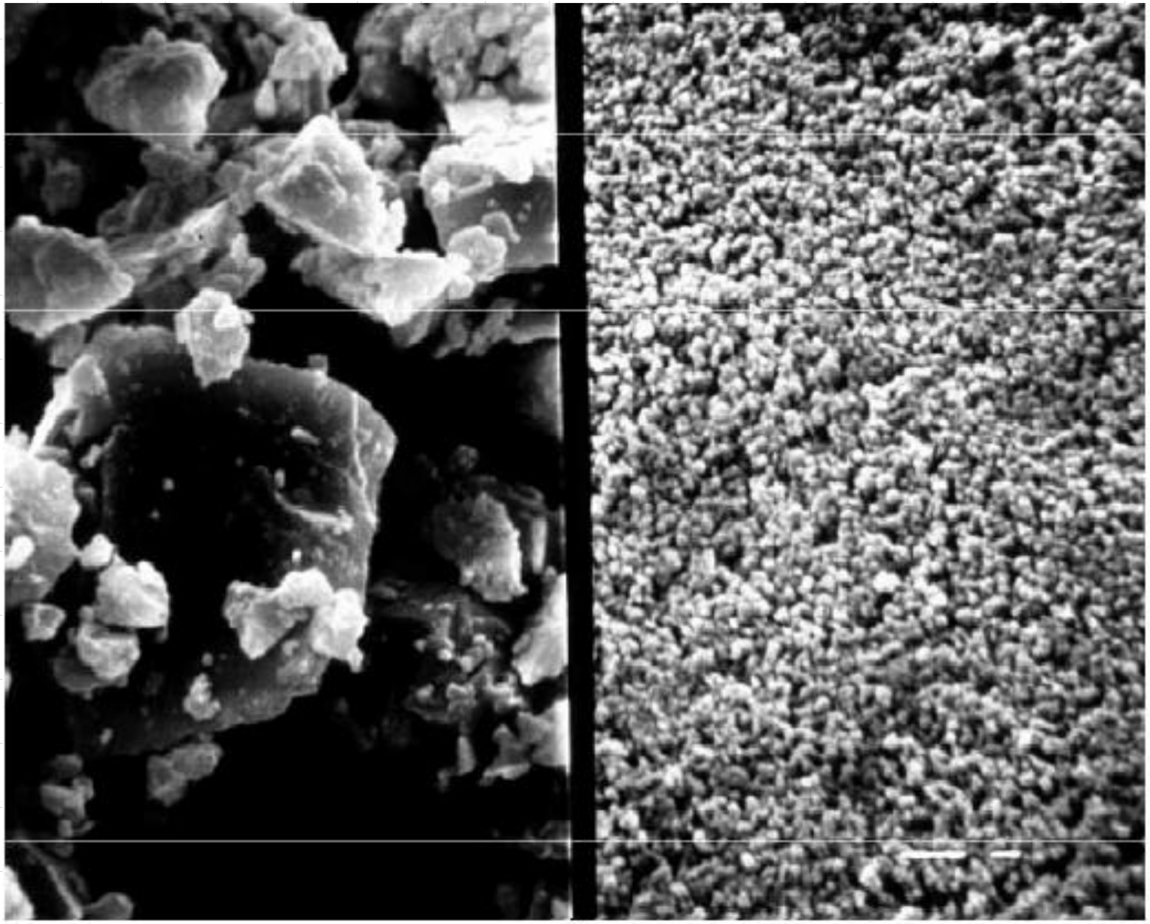
Silica Fume



- **As produced silica fume**: Extremely fine and dusty
- Difficult to handle pneumatically -- sticky
- Self-agglomerating with tendency to create small lumps

Silica Fume Colors

Silica Fume Grain Size



Cement grains (left) and silica fume particles (right) at the same magnification.

The ACI 234R-96 report estimates that for a 15 percent silica fume replacement of cement, there are approximately 2,000,000 particles of silica fume for each grain of portland cement.

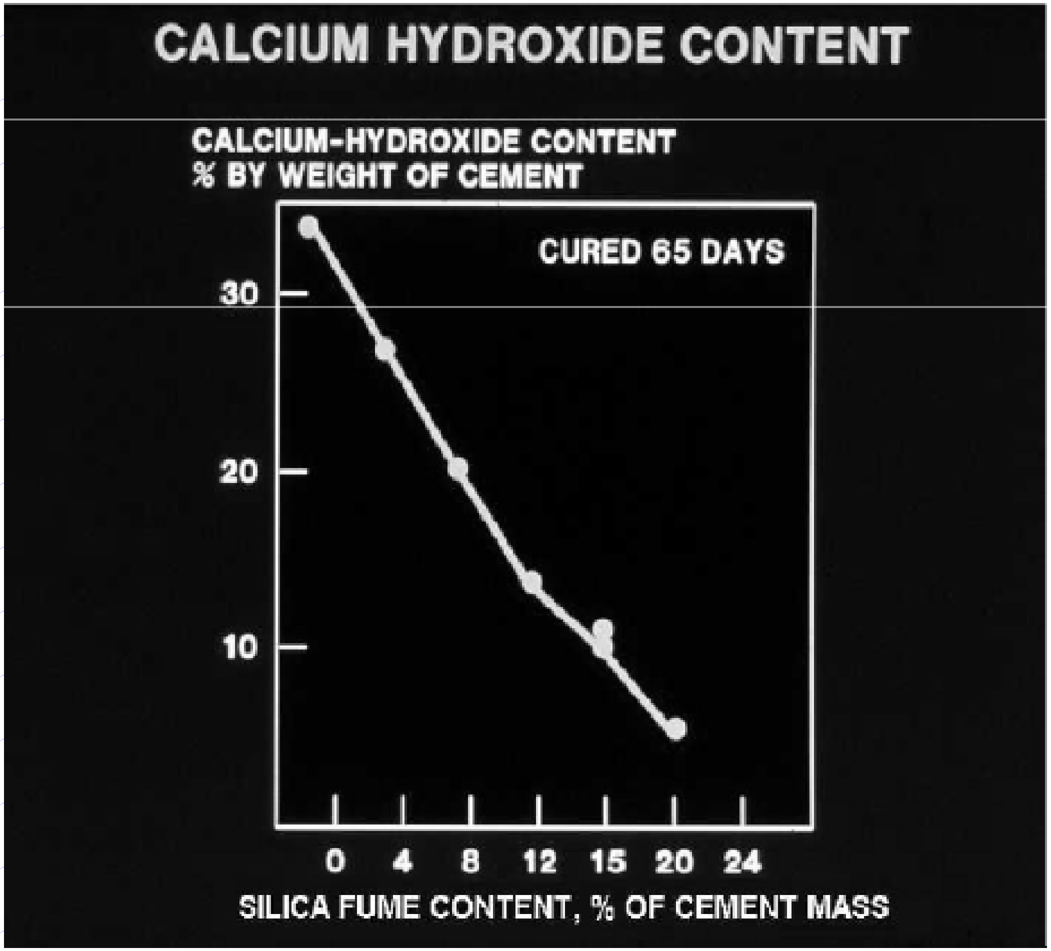
Silica Fume: Physical Properties

Particle size (typical)	< 1 μ m
Bulk density	
(as-produced)	130 to 430 kg/m^3
(slurry)	1320 to 1440 kg/m^3
(densified)	480 to 720 kg/m^3
Specific gravity	2.2
Surface area (BET)	13,000 to 30,000 m^2/kg

Comparison of Silica Fume

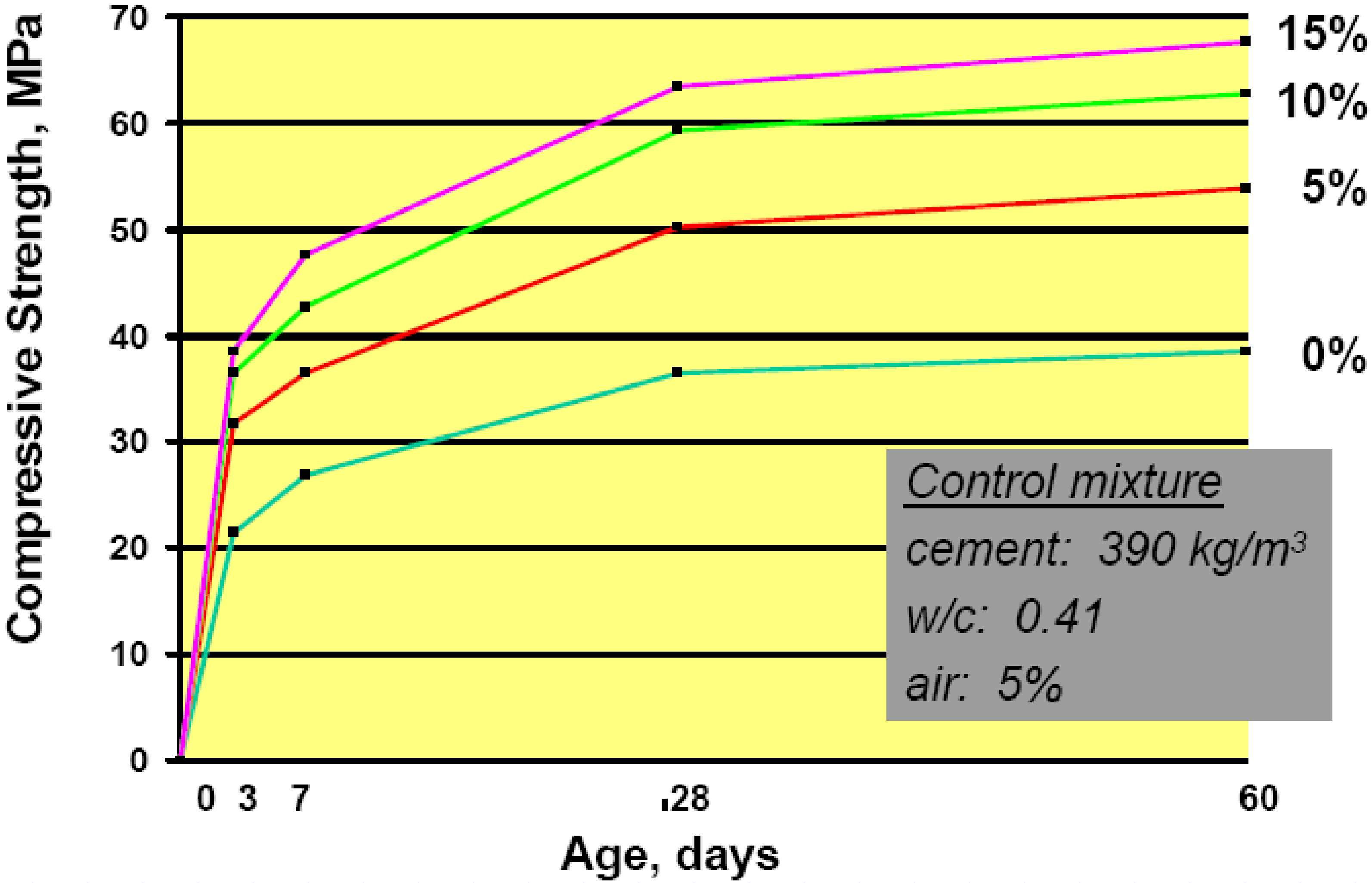
	Silica Fume	Fly Ash	Cement
SiO_2 Content	85- 97	35 - 48	20 -25
Surface Area m^2/kg	17,000 - 30,000	400 - 700	300 - 500
Pozzolanic Activity (with cement, %)	120 - 210	85 - 110	n/a
Pozzolanic Activity (with lime, psi) (MPa)	1,200 - 1,660 (8.3 - 11.4)	800 - 1,000 (5.5 - 6.9)	n/a

Reduction in CH with Silica Fume

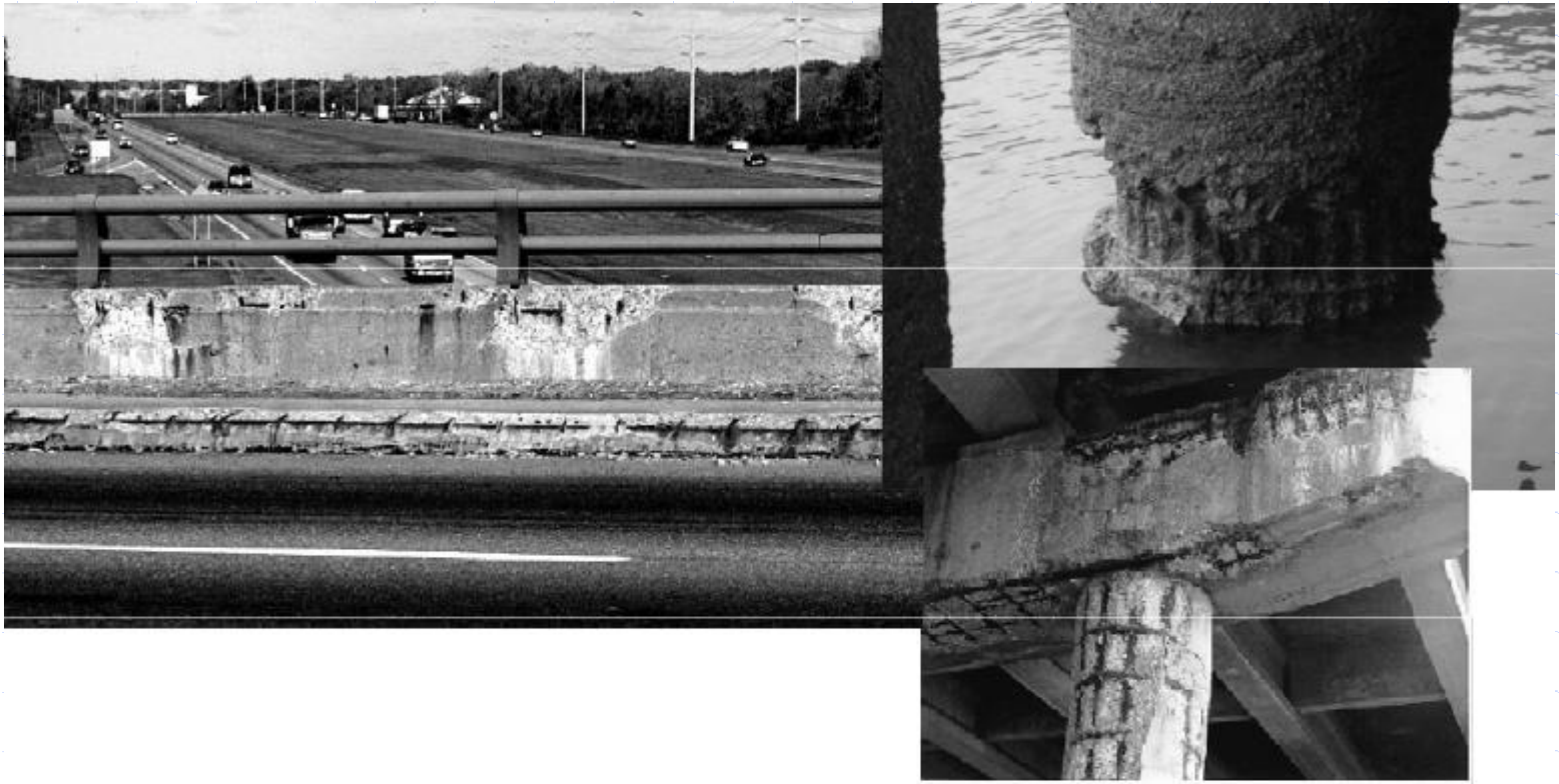


This figure shows the reduction in calcium hydroxide (CH) content of a mature cement-silica fume paste with a water-cement ratio of 0.60. (CH consumed to make more CSH!)

Strength with Silica Fume (SF)



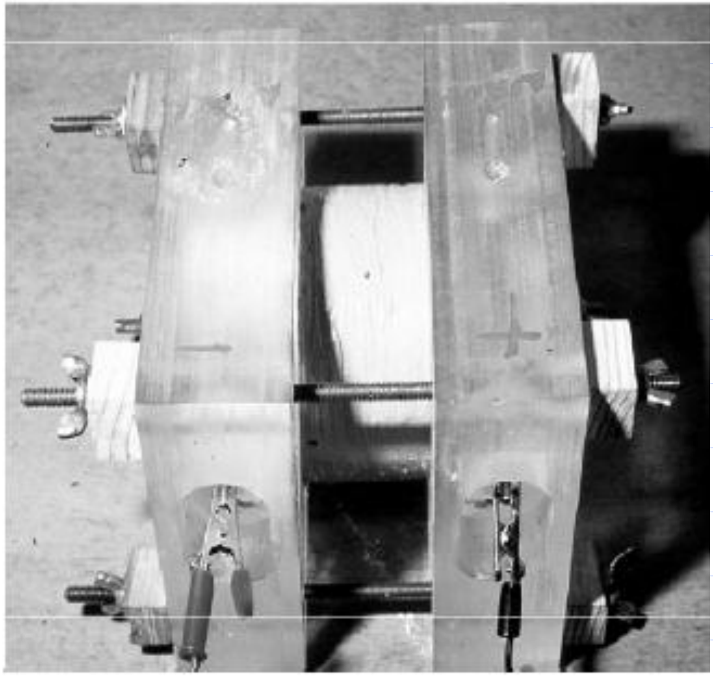
Durability Improvements with Silica Fume



Silica fume reduces permeability of concrete and diffusion of chlorides, which substantially enhances durability to corrosion provided that adequate curing is provided to eliminate drying shrinkage cracks.

Durability Improvements with Silica Fume

- 5-10% silica fume added by mass of cement
- Mixture may include fly ash or slag
- w/cm < 0.40: use HRWR
- Total cementitious materials < 415 kg/m^3
- Permeability estimated using ASTM C 1202



Silica Fume: Chloride Penetration

Silica fume (by mass of cement)	RCP	Compressive Strength
0%	> 3,000 coulombs	= 35 MPa
7-10%	< 1,000 coulombs	> 50 MPa
>10%	< 500 coulombs	> 65 MPa

Silica Fume Shotcrete

- Reduction of rebound loss up to 50%
- Increased one-pass thickness up to 12 in. (300 mm)
- Higher bond strength
- Improved cohesion to resist washout in tidal rehabilitation of piles and seawalls

Silica Fume increases Workability

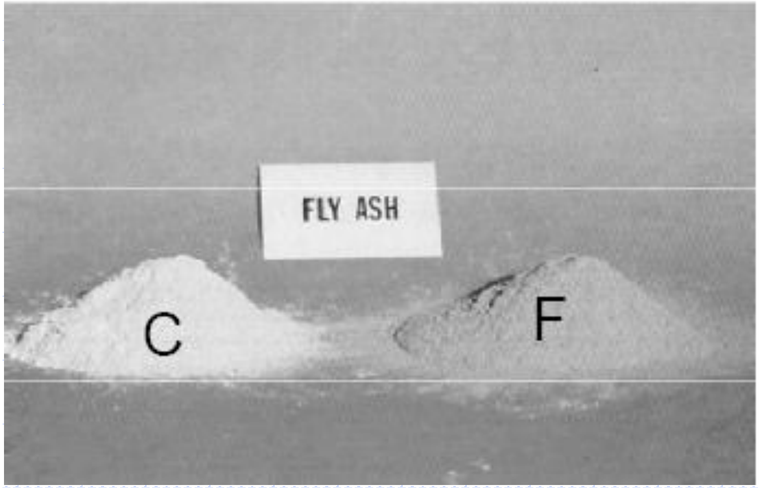
Because of the silica-fume addition and the low w/cm ratio, silica-fume concrete is cohesive and less prone to segregation. Increasing the slump by about 50 mm will make placement much easier. Addition of silica fume is often required.

Fly Ash

- Fly ash is a by-product of coal burned power plants. It is a pozzolanic material made mostly of spherical particles (< 1 mm à > 150 mm).
- ASTM C 618: 2 classes of fly ash; Class F & Class C.
- Class F fly ash, also called low calcium oxide fly ash is generally produced by calcination of bituminous coal.
- Class C fly ash, also called high calcium oxide fly ash is generally produced by calcination of sub-bituminous coal or lignite.

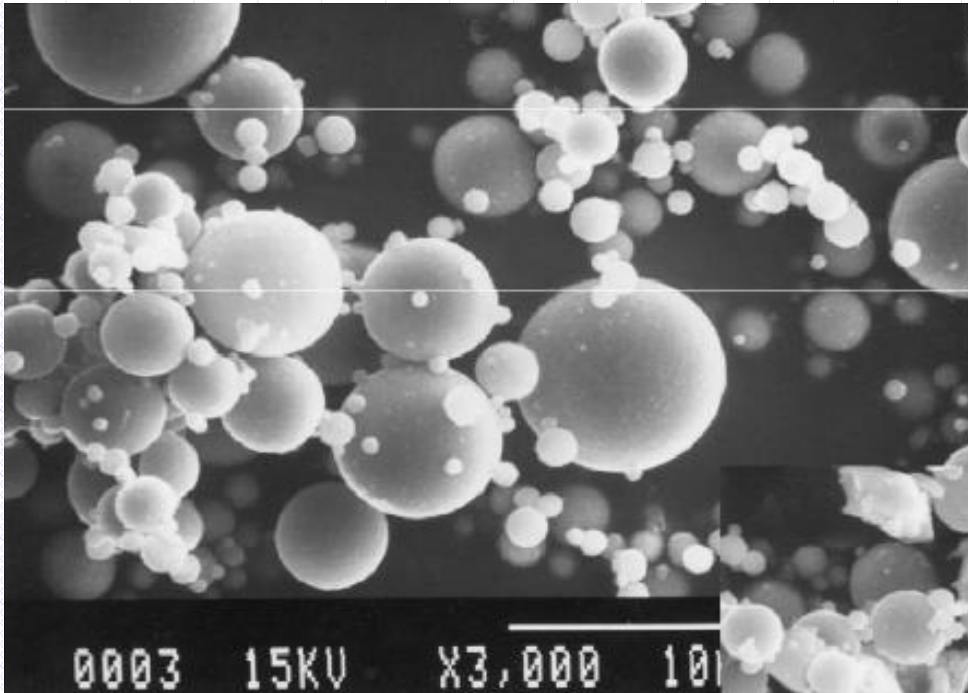
Specifications and Classes of Fly Ash

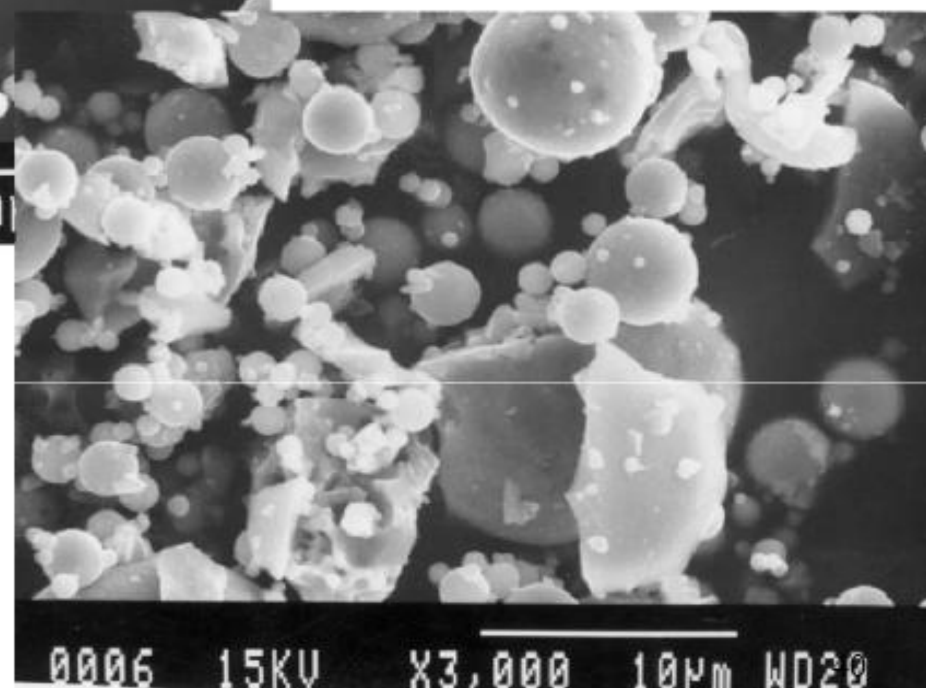
ASTM C 618 (AASHTO M 295)



- **Class F**—Fly ash with pozzolanic properties
- **Class C**—Fly ash with pozzolanic and cementitious properties

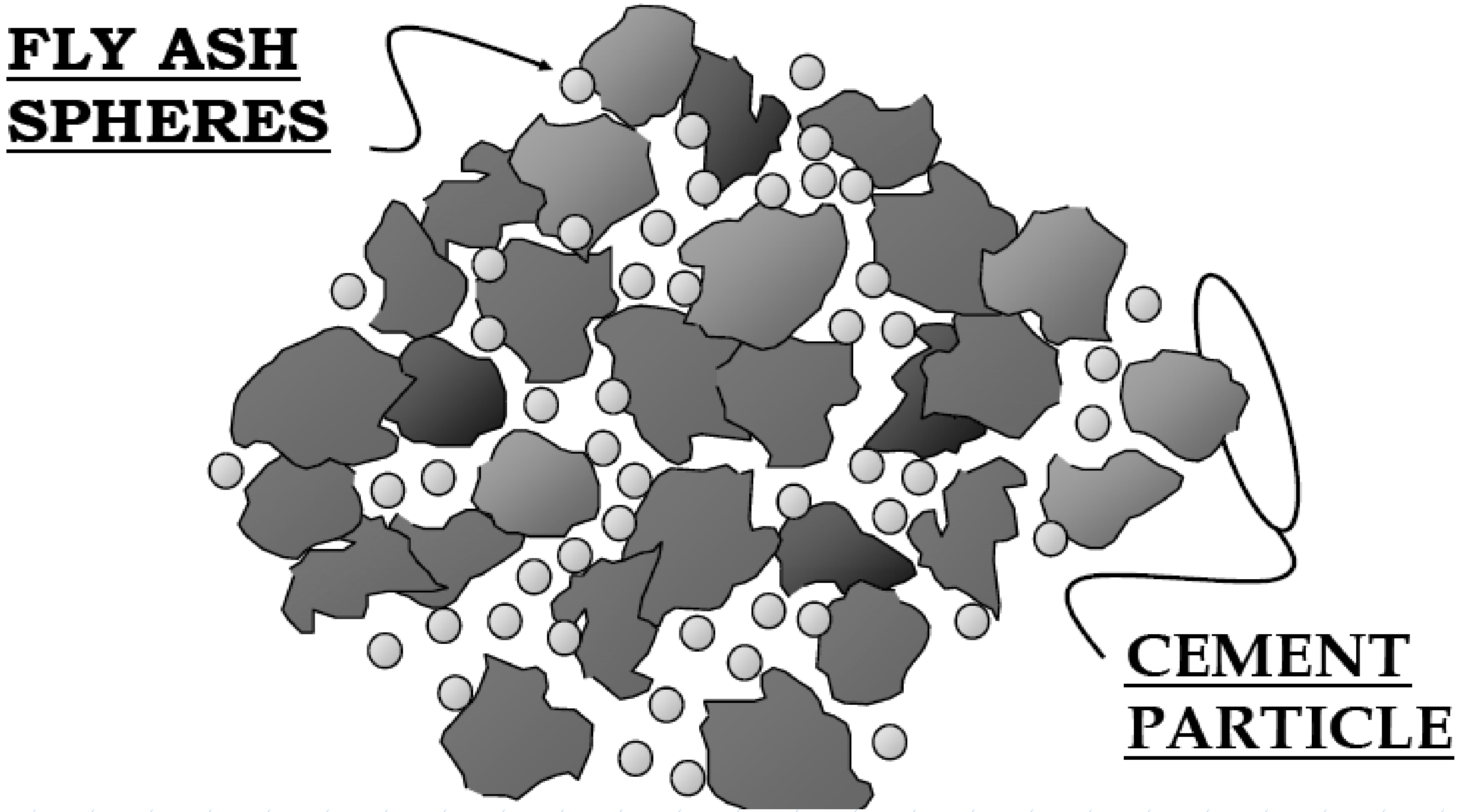
Microstructure of Fly Ash



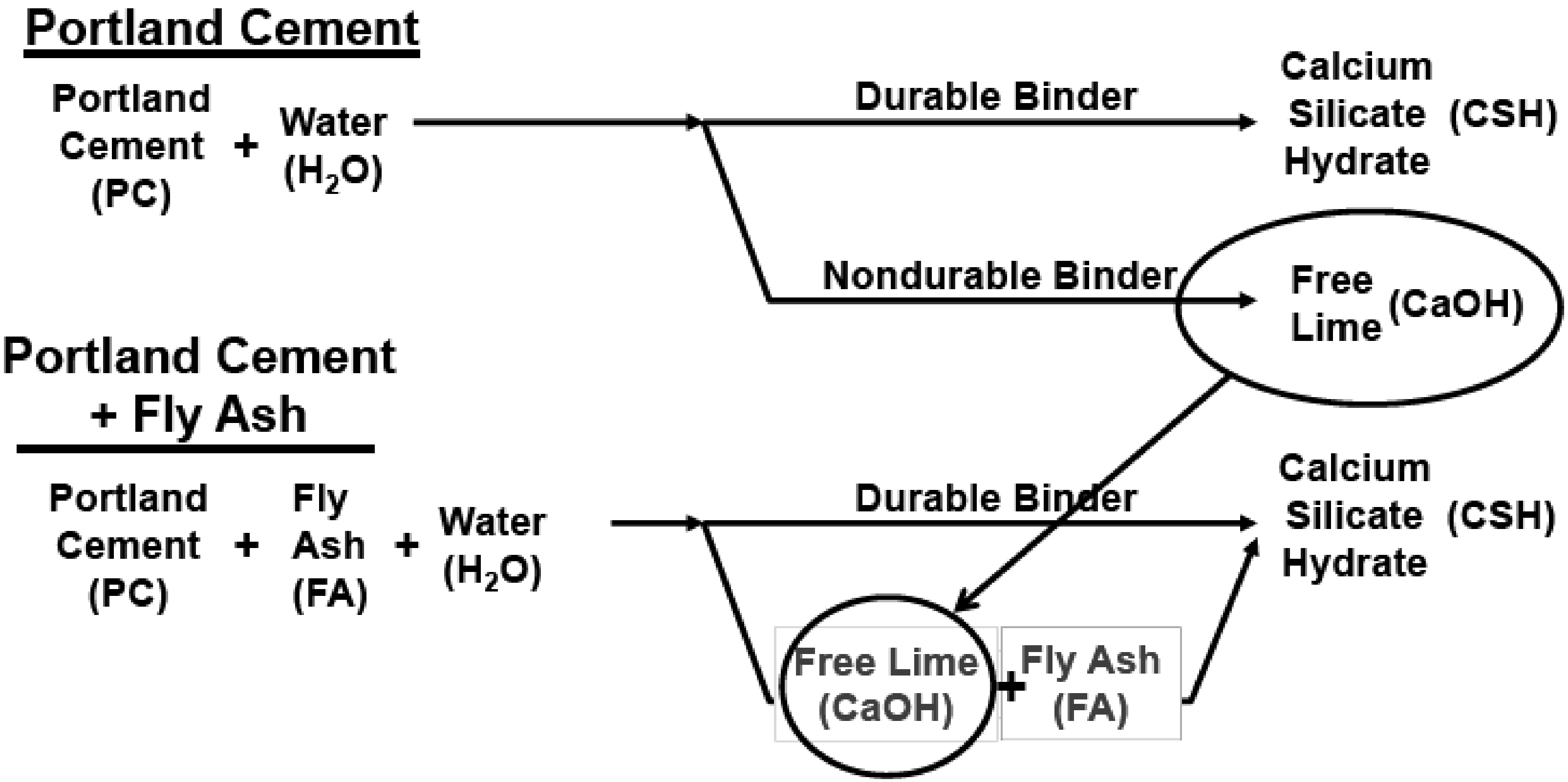


Filler effect of Fly Ash

Fly ash has a filler effect, less effective than silica fume



Hydration Products of Cementing Binders



Through Pozzolanic Activity, Fly Ash Combines with Free Lime to Produce Similar Cementitious Compounds (CSH) to those Formed by the Hydration of Portland Cement

Fineness of Fly Ash

- Finer fly ash has higher pozzolanic activity.
- Fineness determined by Blaine or BET surface area
- Fineness of Canadian fly ash varies between 1700 et 5900 cm^2/g.
- ASTM C 618 prescribes a maximum of 34% retained on the 45 μm sieve.

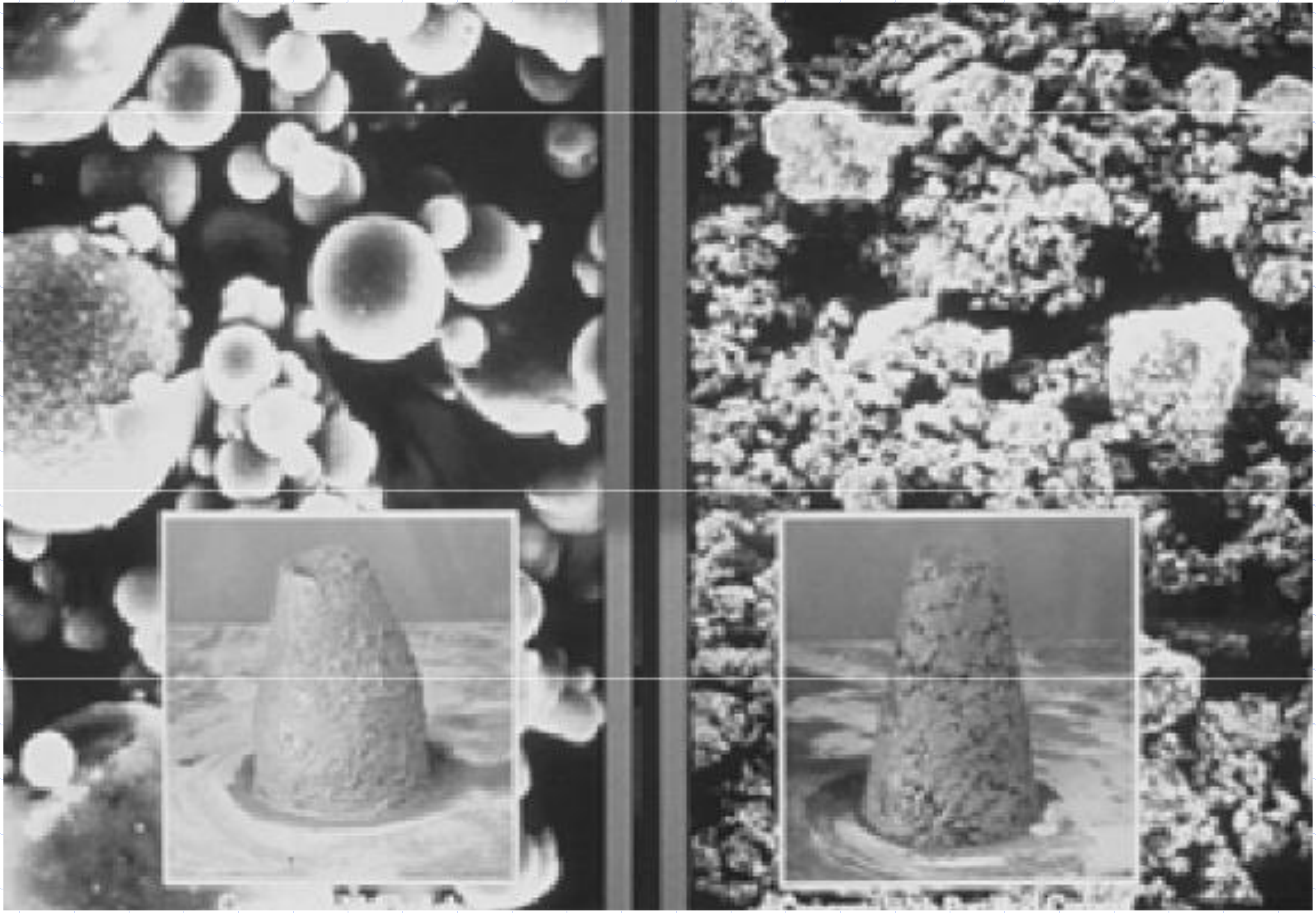
Pozzolanic Activity of Fly Ash

- Pozzolanic activity is determined in terms of a compressive strength index
- Pozzolanic activity of fly ash depends on its mineralogy, chemical composition and fineness.
- Specification: 7 & 28 days compressive strength of mortar in which 20% by mass of cement is replaced by fly ash should be at least 75% of that of an equivalent mortar made with pure portland cement

Composition of Fly Ash

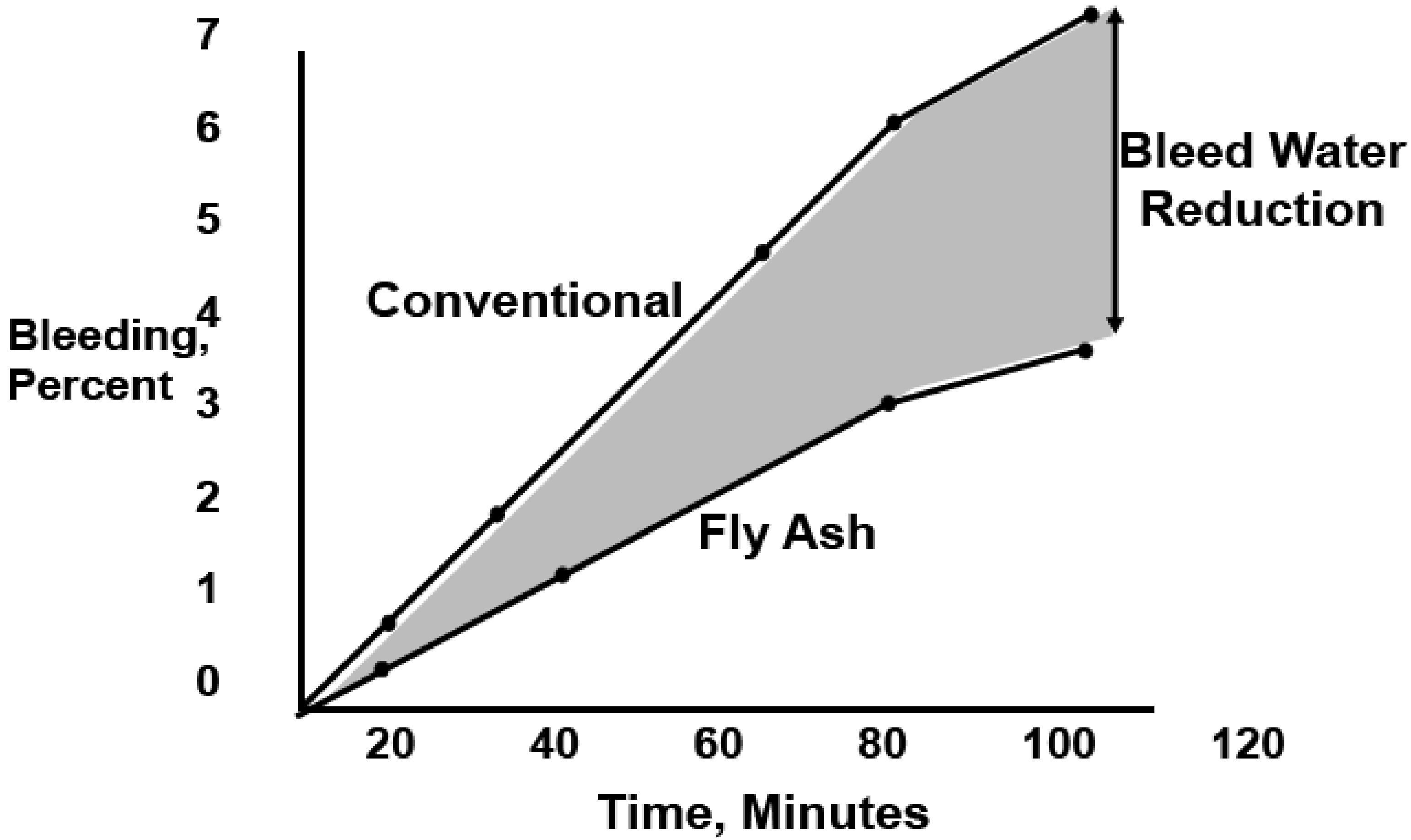
	Class F	Class C
$SiO_2+Al_2O_3+Fe_2O_3$	> 70%	> 50%
SO_3	< 5%	< 5%
Humidity	< 3%	< 3%
Unburned	< 6%	< 6%
MgO	< 5%	< 5%
Alkalis	< 1.5%	< 1.5%

Effect of Fly Ash on Workability

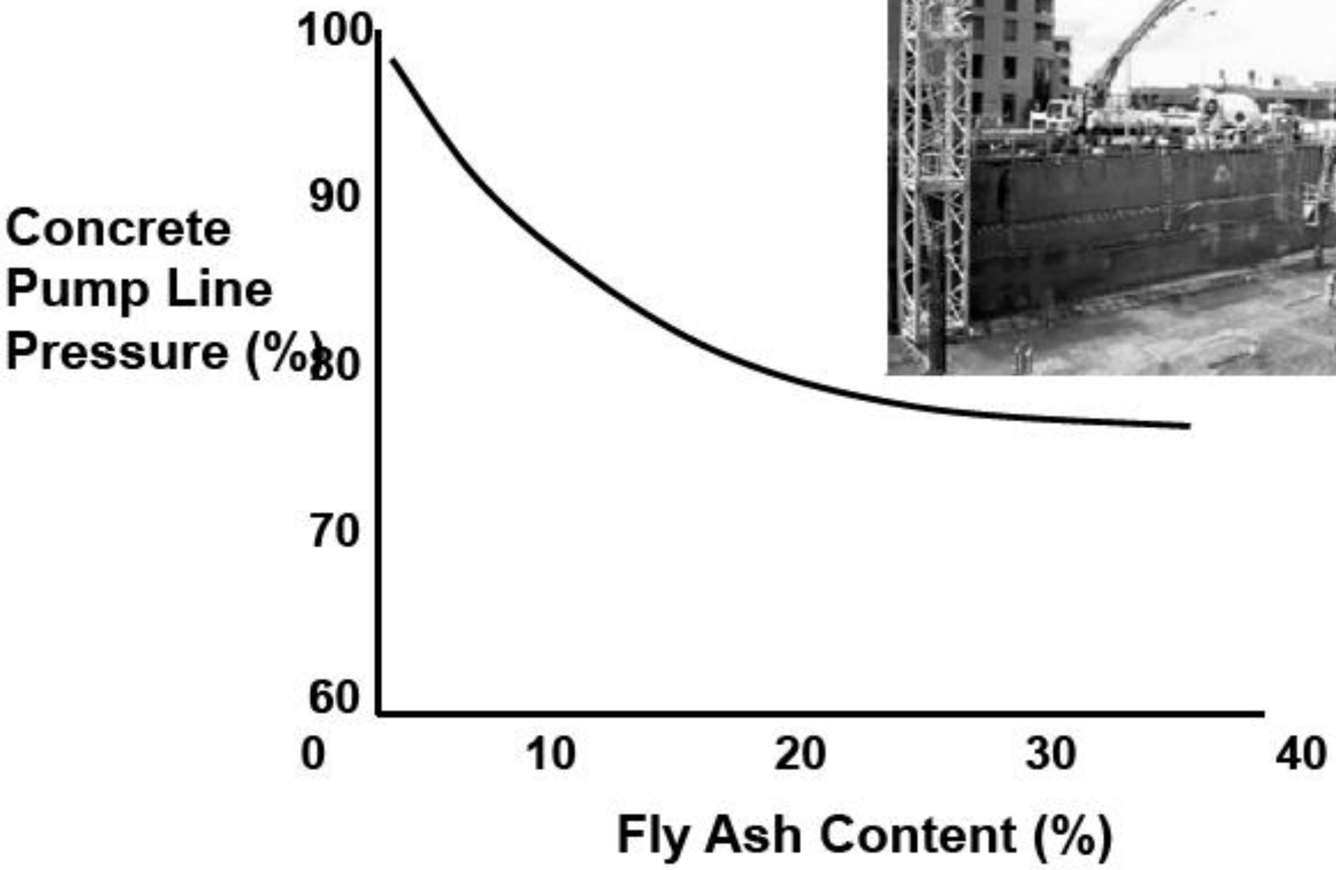


Typical Concrete Bleeding Curve

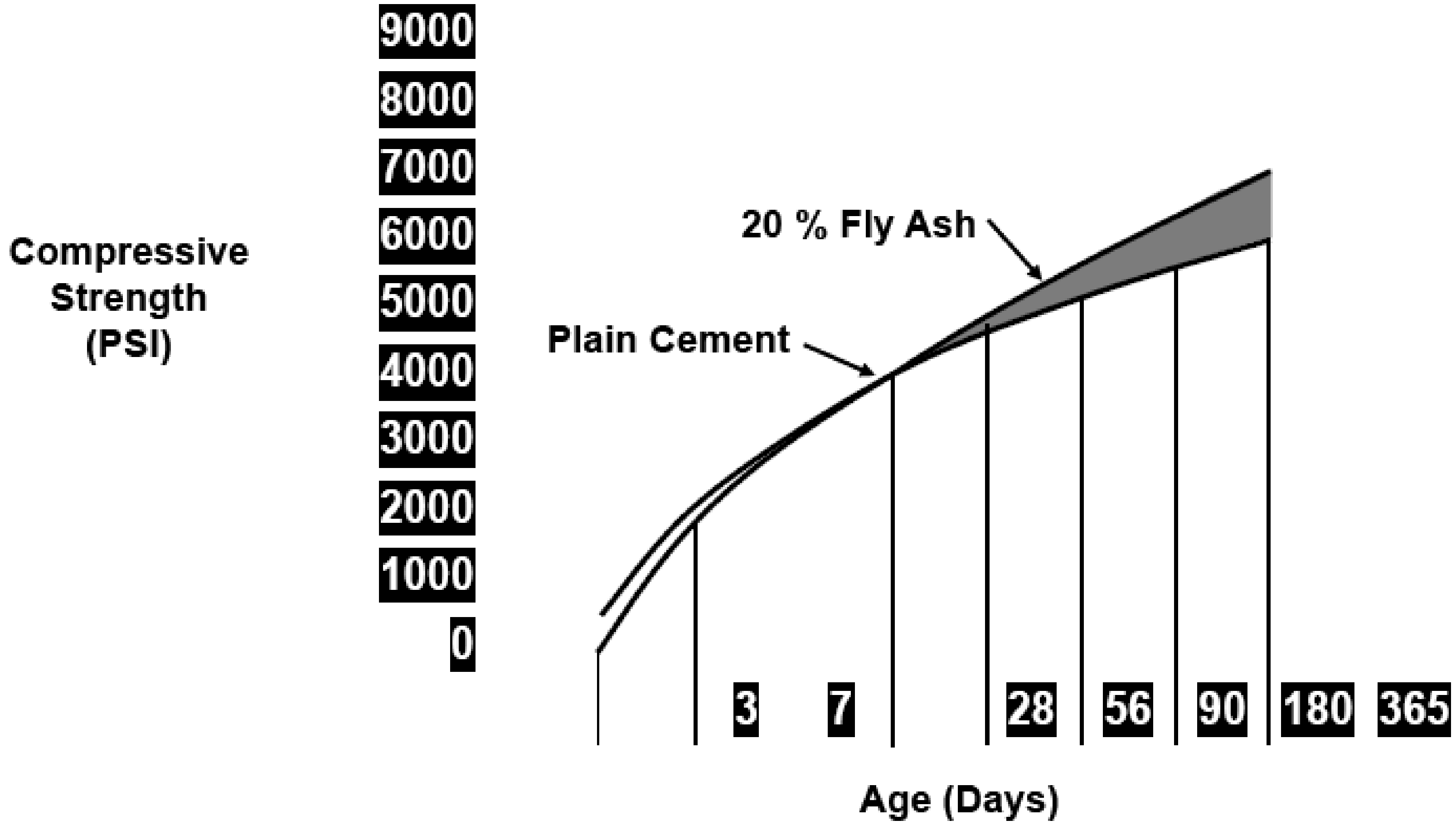
(fly ash usually reduces bleeding water)



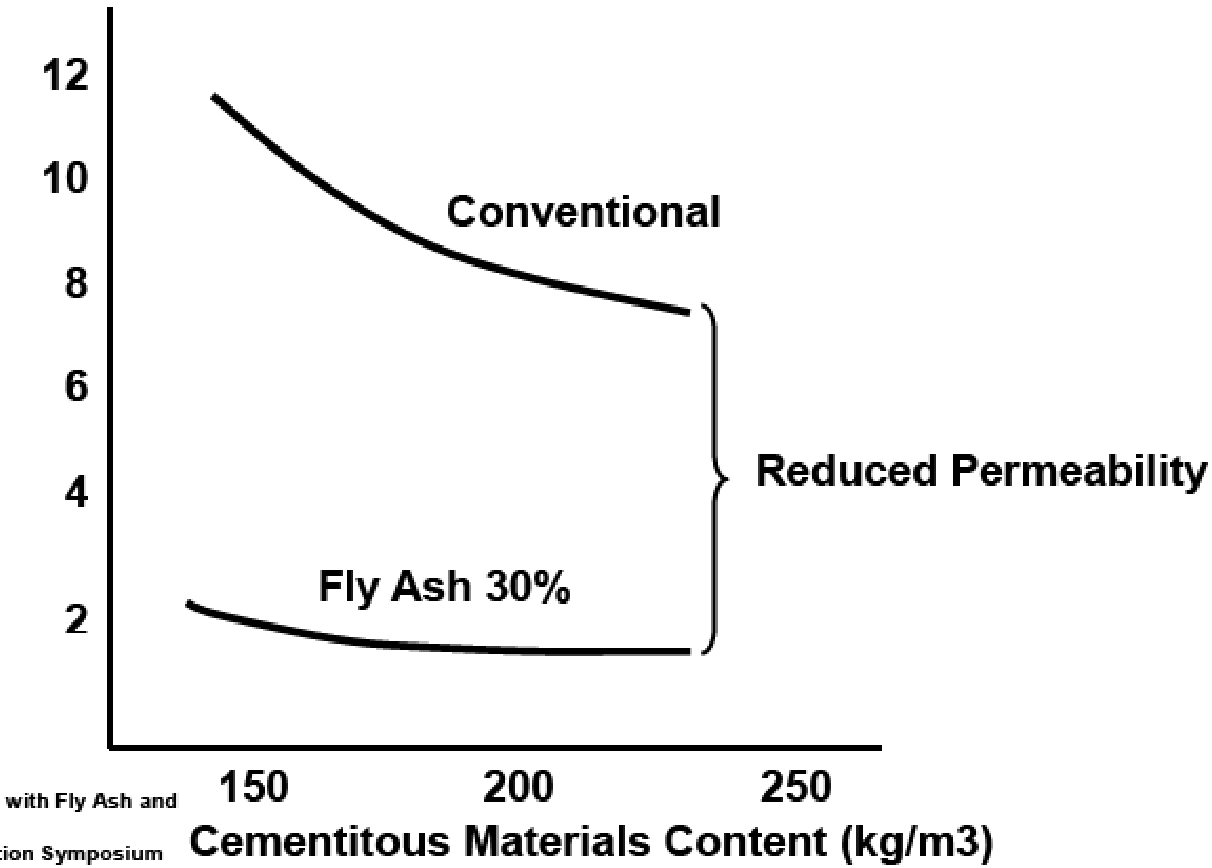
Effect of Fly Ash on Pumpability



Effect of Fly Ash on Compressive Strength



Permeability with Fly Ash



Source: "Bureau of Reclamation Experience with Fly Ash and Other Pozzolans", Elfert, Ralph J. Jr.
Proceedings: Third International Ash Utilization Symposium
Bureau of Mines Circular 1974 March 1973

Chloride Diffusion with Fly Ash

MIX	COULOMB	COULOMB RANGE	CHLORIDE PERM.	TYPICAL OF
658 / 0	4509	> 4000	HIGH	W/C > 0.6 PCC
658 / 75	2404	2000 - 4000	MODERATE	W/C 0.4 - 0.5 PCC
530 / 130	1497	1000 - 2000	LOW	W/C < 0.4 PCC
530 / 260	797	100 - 1000	VERY LOW	SILICA FUME
611 / 275	639	100 - 1000	VERY LOW	SILICA FUME

Cement/fly ash

Improved Durability Properties

- "The quantity of fly ash necessary to prevent expansive damage due to alkali-aggregate reaction may be greater than the amount necessary for strength and workability properties of concrete."
- "Class F fly ash may be used at 20-25 percent or higher mass replacement as a general preventive measure."

  - "As a general rule, Class F fly ash (low CaO content) can improve the sulfate resistance of concrete mixtures."
  - Generally, …fly ashes with less than 15 % CaO content will improve the sulfate resistance of concrete.

Slag

- Slags are by products of the metallurgical industry
- The most used in cement is iron blast furnace slag
- Hydraulic slags give similar hydration products to OPC but react slowly with water
- Can be activated chemically with lime or sulfates, physically by finer grinding, and thermally
- They give comparable strength to OPC at 28 days
- They are low-heat of hydration cements.

Ground Granulated Blast Furnace Slag

- Granulated blast furnace slag is a glassy granular material that varies, depending on the chemical composition and method of production, from a coarse, popcorn-like friable structure greater than 4.75 mm (No. 4 sieve) in diameter to dense, sand-size grains passing a 4.75 mm (No. 4) sieve. Grinding reduces the particle size to cement fineness, allowing its use as a supplementary cementitious material in portland cement concrete.

Specification and Grade of Slag

ASTM C 989 (AASHTO M 302)

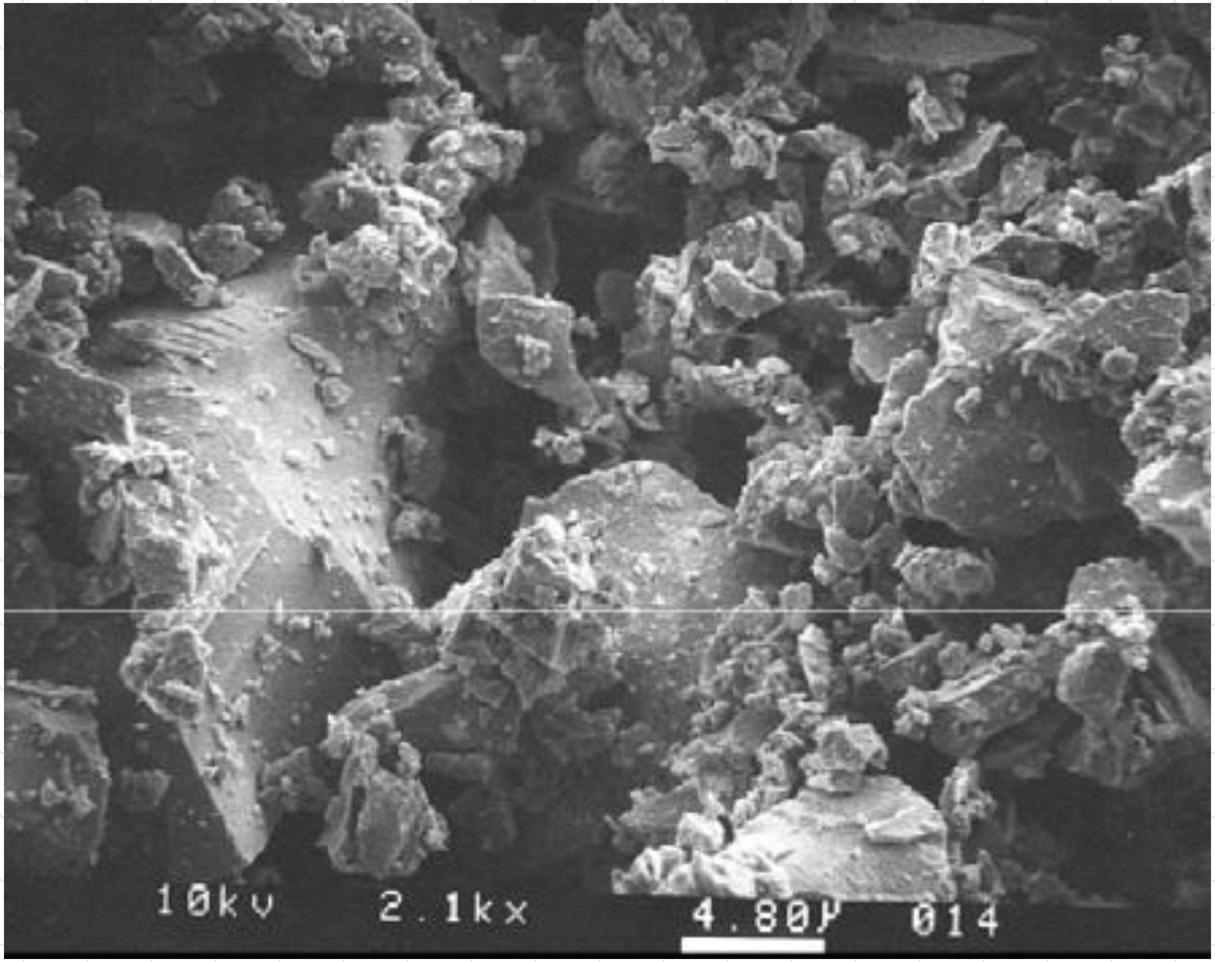
- Grade 80

  Slags with a low activity index
- Grade 100

  Slags with a moderate activity index
- Grade 120

  Slags with a high activity index

SEM image of Slag



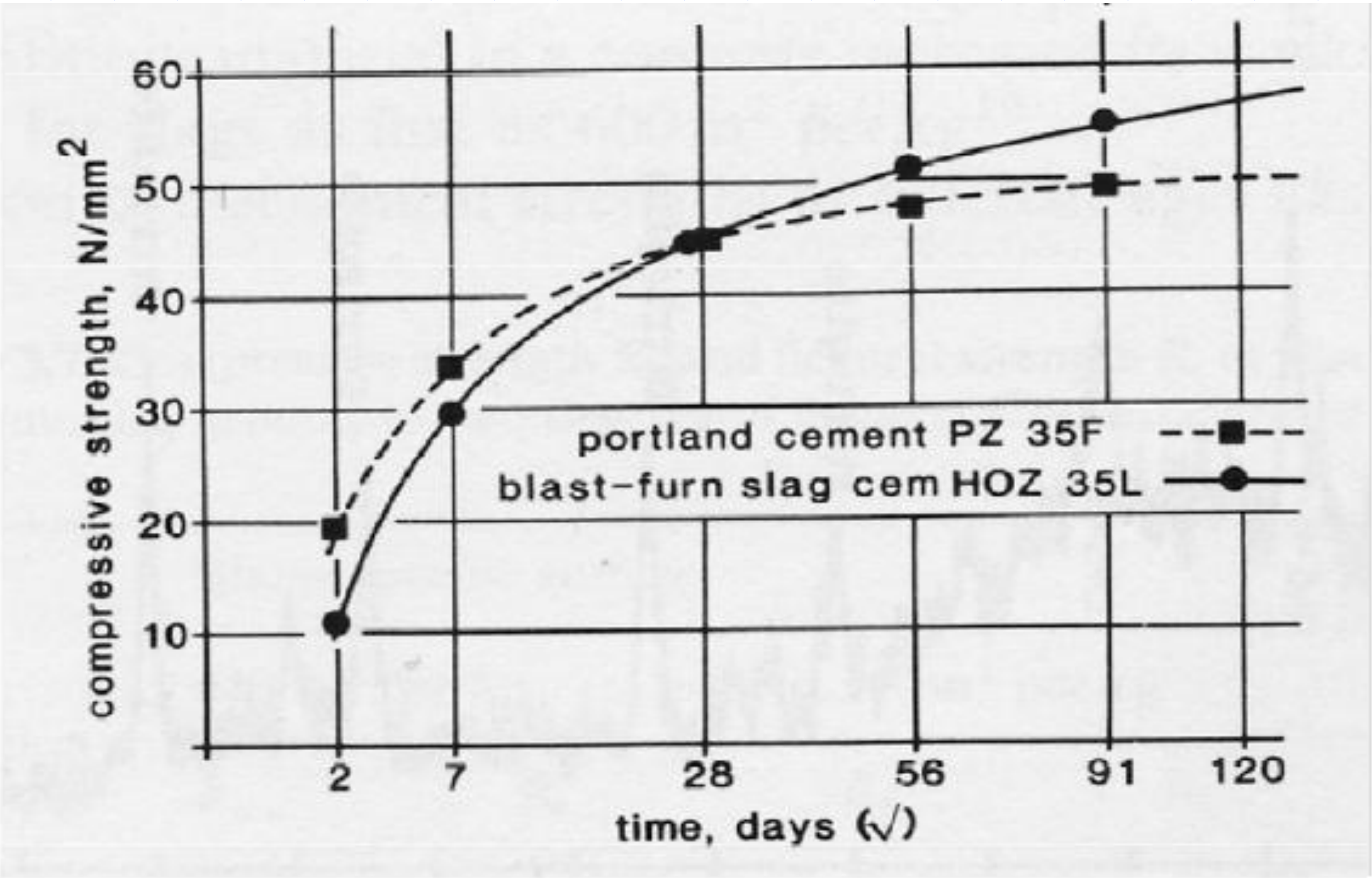
Effect of Slag on Workability

- GBFS is product of grinding, angular particles like cement, but smoother. Also, its density (2.9) is lower than that of cement (3.1). **Replacement by weight leads to higher paste volume and better workability**
- **Water requirement** for same cohesion is reduced.
- **Setting time** is **increased** (slower hydration of GBFS) at low temperature, no clear effect at high temperatures

Mechanical Properties using Slag

- **Strength** development of slag cement is slower at early age than that of OPC but faster at later ages.
- At one year slag cement achieves significantly higher strength.
- Rate of strength gain depends on type of slag, cement replacement rate, temperature, activation technique used, etc.
- For the same compressive strength, slag cement tends to have around 20% **higher tensile strength** (due to difference in hydrate structure).
- On the basis of same strength, addition of slag also seems to lead to somewhat **higher modulus of elasticity**.

Strength development with Slag



Strength development in concrete with OPC and with 65% slag

Natural Pozzolans

- Have been in use for many centuries. Overshadowed by more popular recycled pozzolans (fly ash, silica fume, slag, etc.)
- Name originates from town of Pozzuoli near Naples in Italy (Roman time).
- From volcanic origin
- Viable deposits and use: Italy, Greece, Germany, Canary Islands, Canada, New Zealand, Indonesia, France, Western USA.

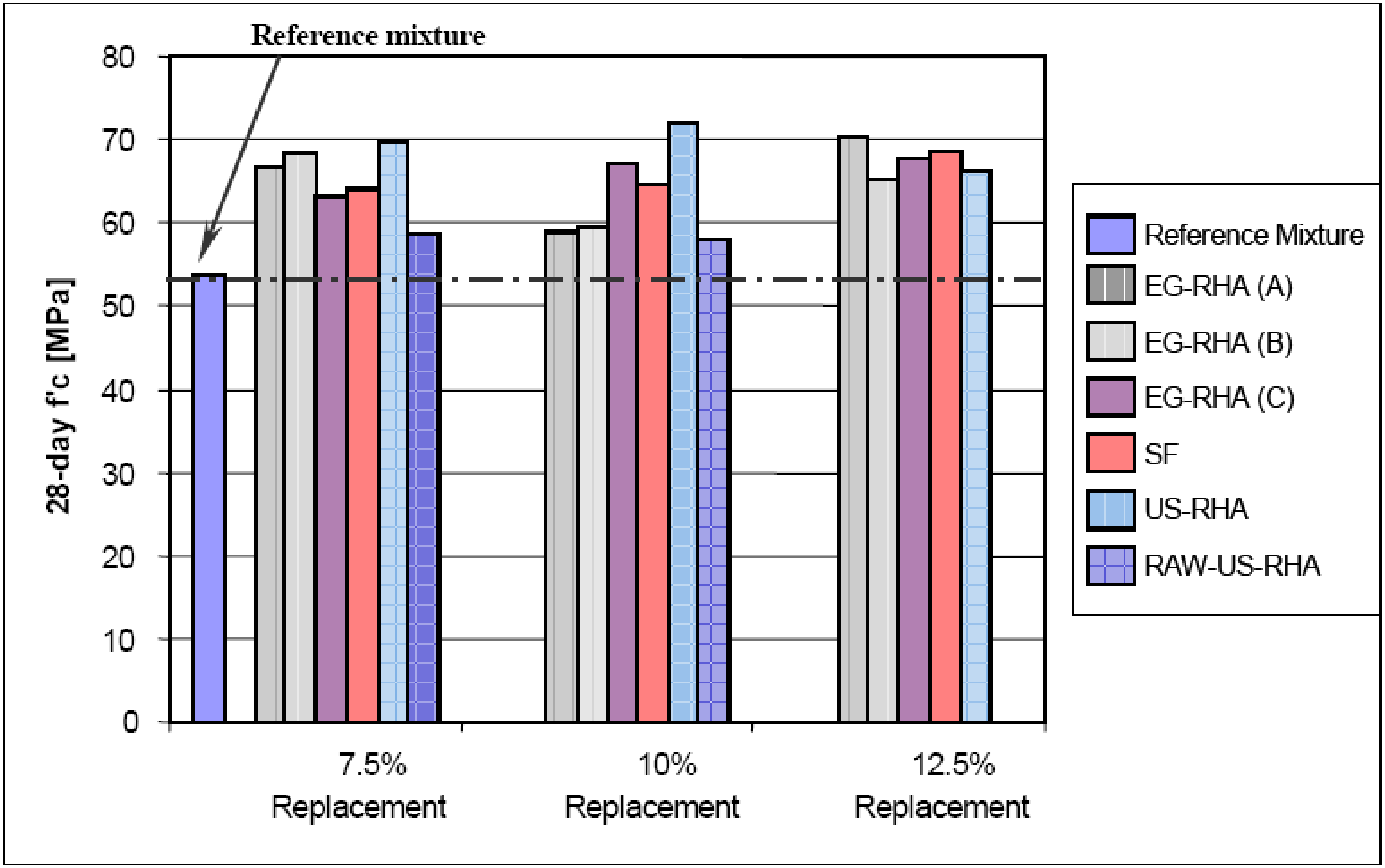
Natural Pozzolans

Natural Pozzolans – Example Ash from volcanic eruptions is a source of natural pozzolans.

Natural Pozzolans: Rice Husk Ash (RHA)

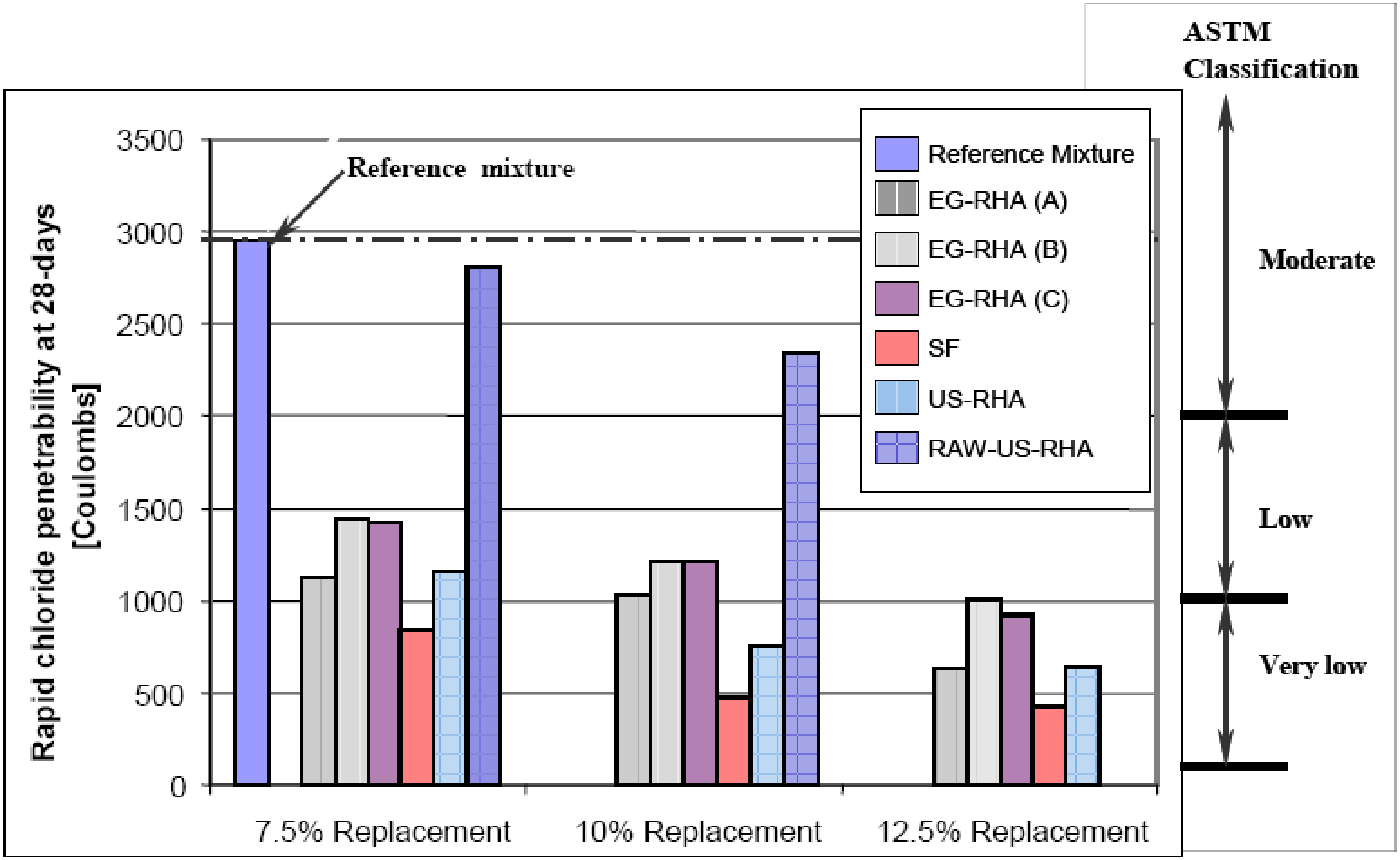
- Each ton of rice produced leads to 200 kg of rice husk byproduct. Total of 100 million tons of rice husk worldwide
- Combustion of 1-ton of rice husk produces energy = ½ ton of coal + 20% ash containing more than 90% silica.
- Under controlled combustion conditions silica is amorphous. Also high surface area, highly reactive like silica fume when finely ground.

Effect of RHA on Strength



Effect on 28-day strength

Effect of RHA on Chloride Penetration



Effect on chloride diffusion

Chemical Analysis of Supplementary Materials

	Class F fly ash	Class C fly ash	Ground slag	Silica fume	Calcined clay	Calcined shale	Meta-kaolin
SiO_2, %	52	35	35	90	58	50	53
Al_2O_3, %	23	18	12	0.4	29	20	43
Fe_2O_3, %	11	6	1	0.4	4	8	0.5
CaO, %	5	21	40	1.6	1	8	0.1
SO_3, %	0.8	4.1	9	0.4	0.5	0.4	0.1
Na_2O, %	1.0	5.8	0.3	0.5	0.2	—	0.05
K_2O, %	2.0	0.7	0.4	2.2	2	—	0.4
Total Na eq. alk, %	2.2	6.3	0.6	1.9	1.5	—	0.3

Questions and Assignments

- Discuss various types of supplementary materials available in Pakistan and its Characteristics. (*Note*: *Put colour pictures*)
- Discuss rice husk effects on concrete
- Report and Power point Presentation
- Need to submit in Group