

Role of Chemicals in Modern Construction Industry

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OUTLINE

Role played by the chemicals in construction industry – in general

Relevance

Market survey

Trends and Opportunities

Role of Corrosion inhibitor and Superplasticisers in construction industry

Inhibitor and Superplasticiser Research at CSIR-SERC

Concluding remarks

Role played by chemicals in construction industry – in general

1

- **Corrosion protection**
- **Inhibitors, Protective coating for steel**

2

- **Superplasticiser – Heavy reinforcement – HPC, UHSC (RPC)**
- **Modern construction (RMC), Foam Concrete-Light weight structures- Earth quake prone area**
- **easy mix, workability, mouldability**

3

- **Adhesives and sealants**
- **water proof admixtures to seal the crack etc.**

Relevance – Chemical Admixtures



- **Mass concreting**
- **Pumping of RMC**
- **Mouldability**
- **Faster construction**
- **Minimization of labour**

World market for construction chemicals (US\$ millions)

	2009	2014	Average Annual Growth Rate, 2009-2014 (percent)
North America	4,684	5,650	3.8
Central and South America ^a	1,815	2,317	5.0
Western Europe	6,557	7,577	2.9
Central and Eastern Europe	988	1,186	3.5
Middle East and Africa ^a	1,827	2,399	5.6
Japan	3,560	3,578	0.1
China	7,868	12,106	9.0
Asia/Oceania ^a	3,400	4,339	5.0
Total	30,699	39,152	5.0%

^a Data are estimates based on percentage of GDP by construction industry, extent of informal sector and technological standards available

Trends and Opportunities

- ✓ **The global construction industry makes up about 9 percent of the world's GDP and construction is one of the main drivers of growth in almost every economy**
- ✓ **As with other areas of the specialty chemicals sector, the construction chemicals industry is directly affected by increased globalization, consolidation and significant consumption growth in rapidly developing markets**
- ✓ **The construction chemicals industry will see continued opportunities to address energy conservation and sustainability. Suppliers can benefit from government policies that require the use of specialty construction chemical products to aid in energy conservation**
- ✓ **Growing awareness of climate change will drive the demand for energy-saving materials and technologies, chemicals that increase performance and environment friendly products**

Focus from Bottom-up

- 1. Cement production – Combustion agents
- fuels -Gypsum –SET CONTROLLER**
- 2. Concrete – chemical admixture –
Superplasticiser – RMC, SCC, RPC**
- 3. Corrosion Inhibitor –accelerator –
retarder – Freeze-thaw agent**
- 4. Coating – Structural applications,
corrosion protection**
- 5. Paint - Aesthetics**



Focus from Top-down

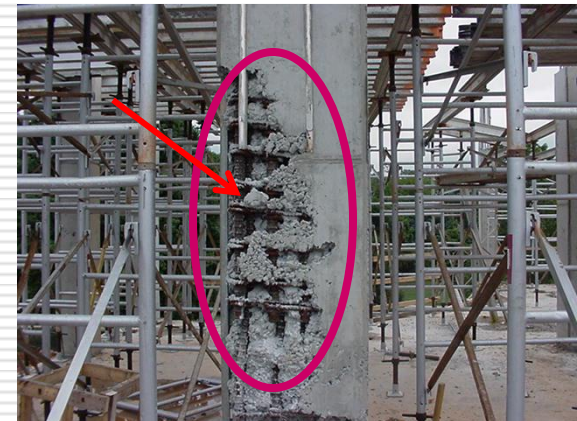
- 1. Repair and Rehabilitation- Retrofit – grouts, Fibre reinforcement, Fabric reinforced**
- 2. Chloride extraction: to control corrosion – to extract chloride – MAINLY IN MARINE ENVIRONMENT**
- 3. Corrosion Inhibitor: Migrating – High dose causes deleterious effect**



Corrosion beneath concrete



Wire Fabric



Improper use of Sp

FABcrete - Ongoing research at CSIR-SERC

- **New innovative building material with a fabric reinforcement embedded in a cementitious binder**
- **Alternate and combining component to common building materials such as steel or shot fibre reinforced concrete**
- **Made of fabric meshes of long woven, knitted or even unwoven, fibre rovings - two directions of glass, carbon or aramid that are alkali resistant and thus not vulnerable to corrosion**
- **Role of polymer modified binder for FABcrete**
 - *Combination of cementitious binder with polymer based binders*
 - *Even dispersion and penetration into the filaments in the fabrics*
 - *Used as gripping agent – adhesive property*

**CEMENT
CHEMISTRY**



**Role of Corrosion
Inhibitor in
Construction
Industry**



**Role of
Superplasticiser
in Construction
industry**

Cement Chemistry

- **Cement – hydraulic binder**
- **During calcination, the volume contracts**



- **During hydration, it swells**



Raw Materials

* Lime

* Silica

→ kiln → complex products + uncombined lime

* Alumina

* Fe_2O_3

➤ Uncombined lime

✓ No sufficient time to react

✓ State of chemical equilibrium is reached

Function of Chemical Components

- **Chemical components in portland cement → form different potential compounds**
- **Potential compounds → responsible for various physical properties**

Four Major Compounds

* C_3S

→ responsible for strength of hydrated cement paste

* C_2S

* C_3A

→ undesirable – initial reaction with SP & CI

* C_4AF

→ small quantity - does not affect the cement behaviour

Variations in Chemical Constituents

➤ Affect Cement Properties

✓ **Hardening / Hydration**

✓ **Setting Time**

✓ **Corrosion Resistance**

✓ **Color**

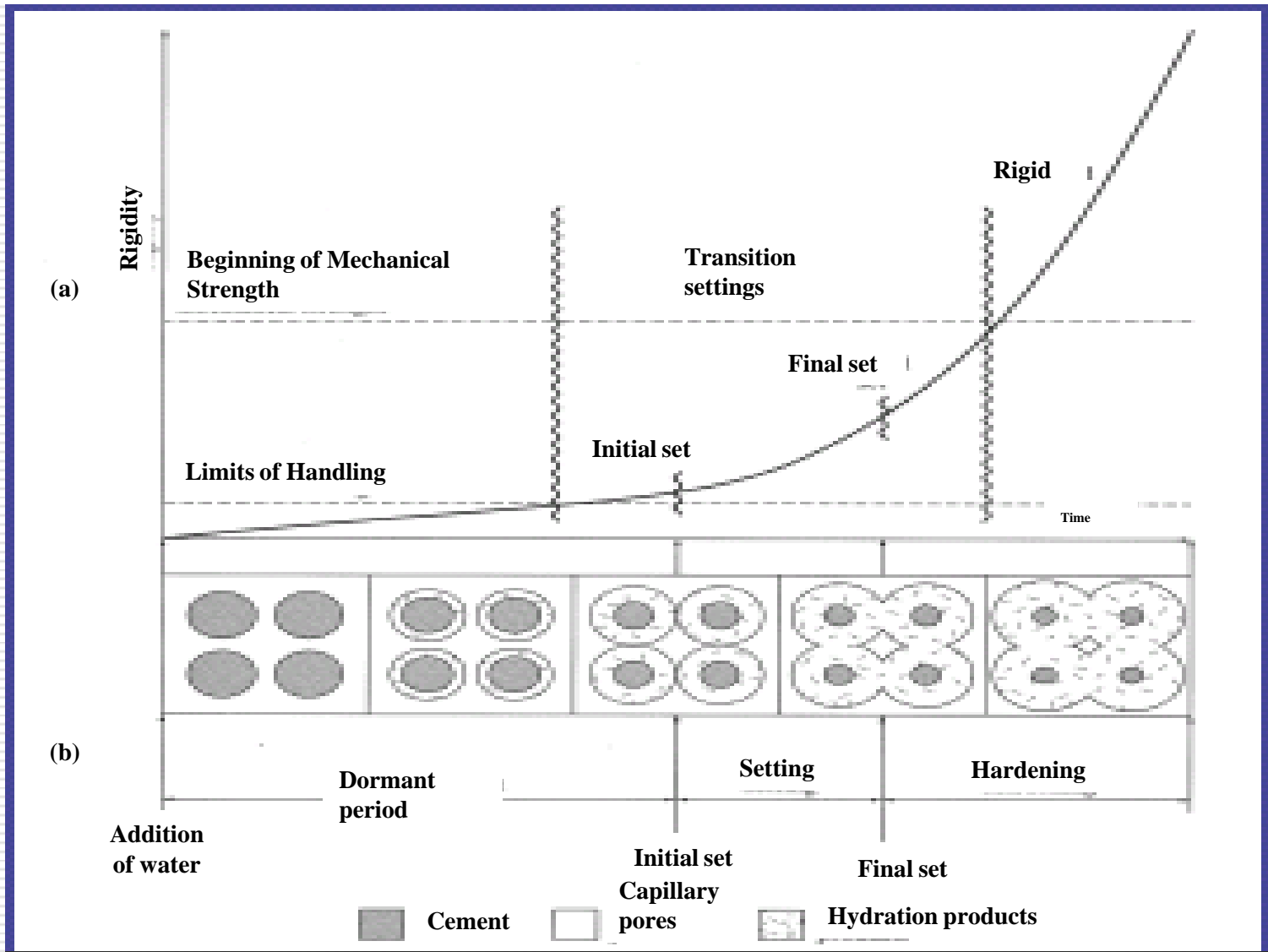
Cement Hydration

- **Reaction of cement with water**
- **Exothermic; heat released is called 'Heat of Hydration'**
- **Rate of heat evolution is faster, if the reaction is quicker**
- **Heat evolved depends on heat of hydration of individual compounds and on the clinker morphology**

Hydration Process (continued)

- **Setting – Solidification of the plastic cement paste**
- **Initial set – Beginning of solidification-Paste become unworkable - loss in consistency – not < 45 min**
- **Final set – Time taken to solidify completely – not > 375 min**
- **Hardening – Strength gain with time – after final set**

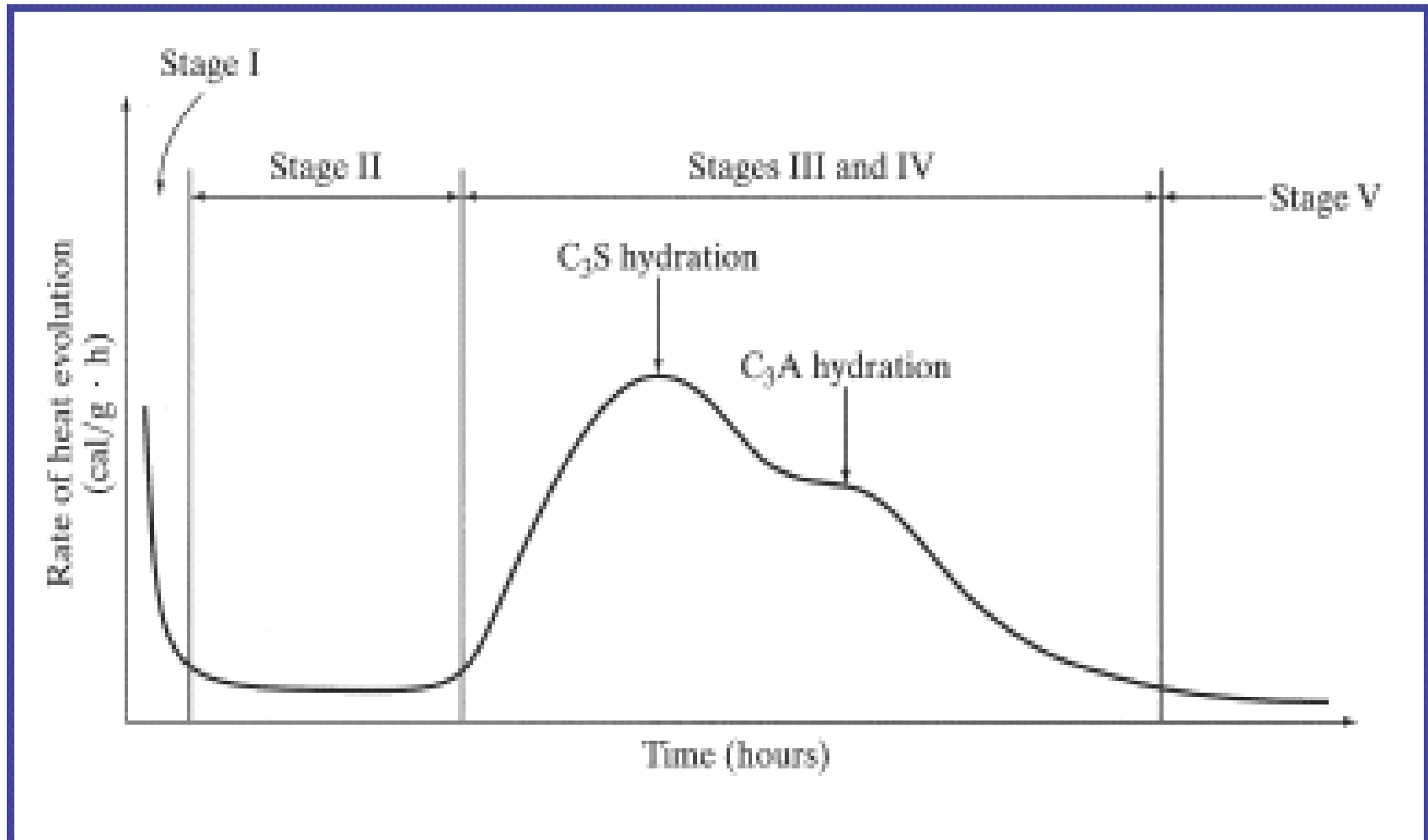
Hydration Process (continued)



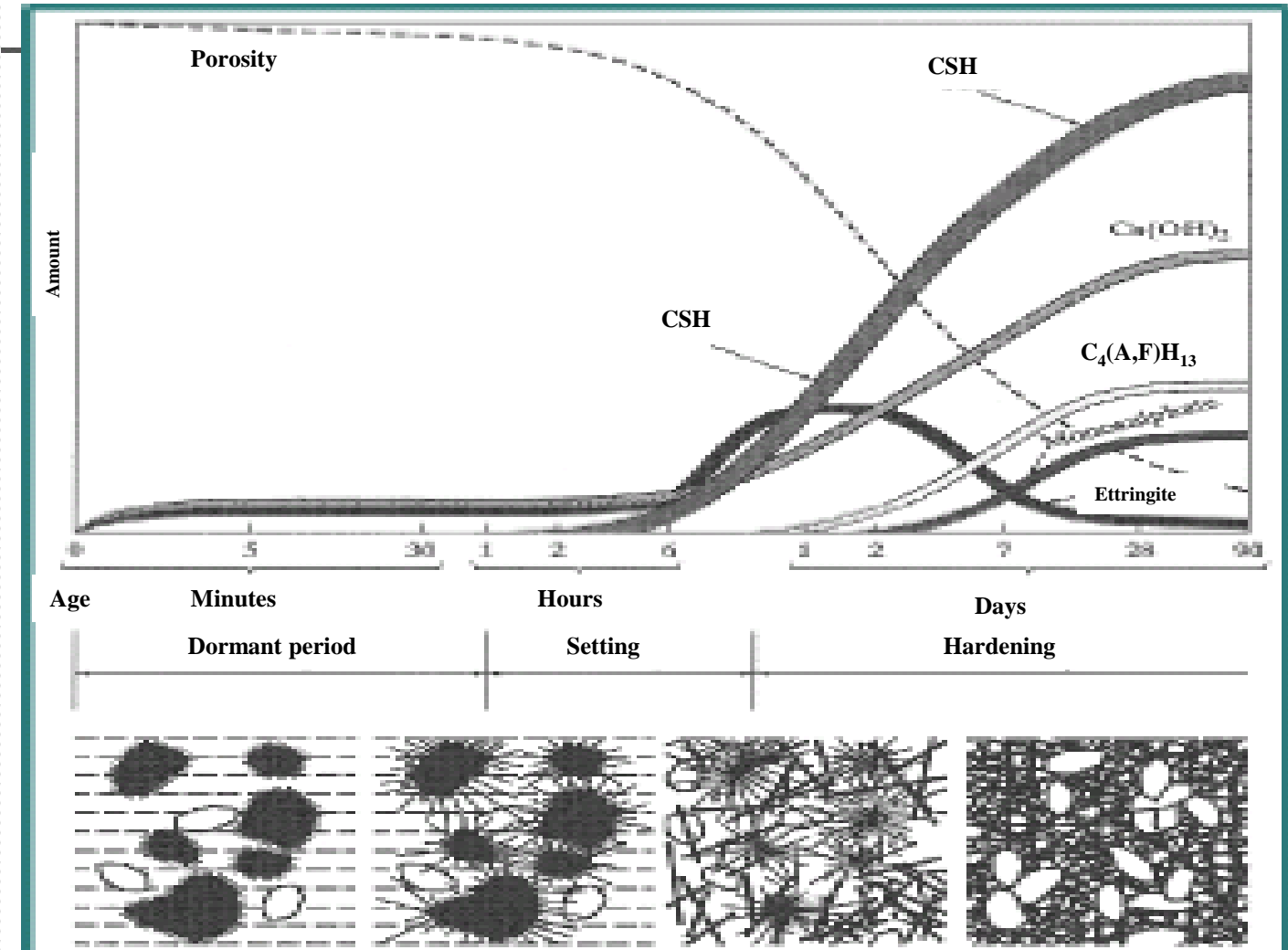
Hydration of Portland Cement (continued)

- **Sequence of overlapping chemical reactions**
- **Hydration reactions of individual clinker mineral proceed simultaneously at differing rates and influence each other**
- **Complex dissolution and precipitation process**
- **Leading to continuous paste stiffening and hardening**

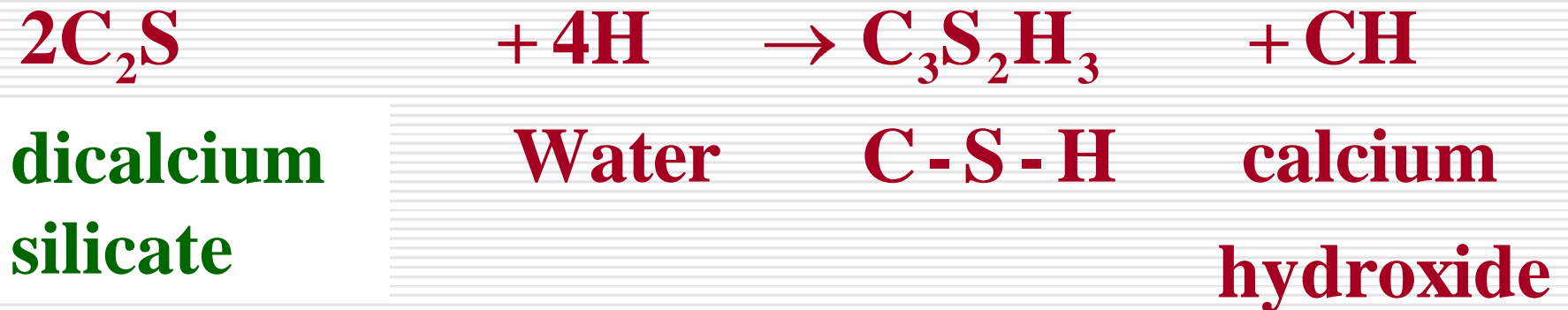
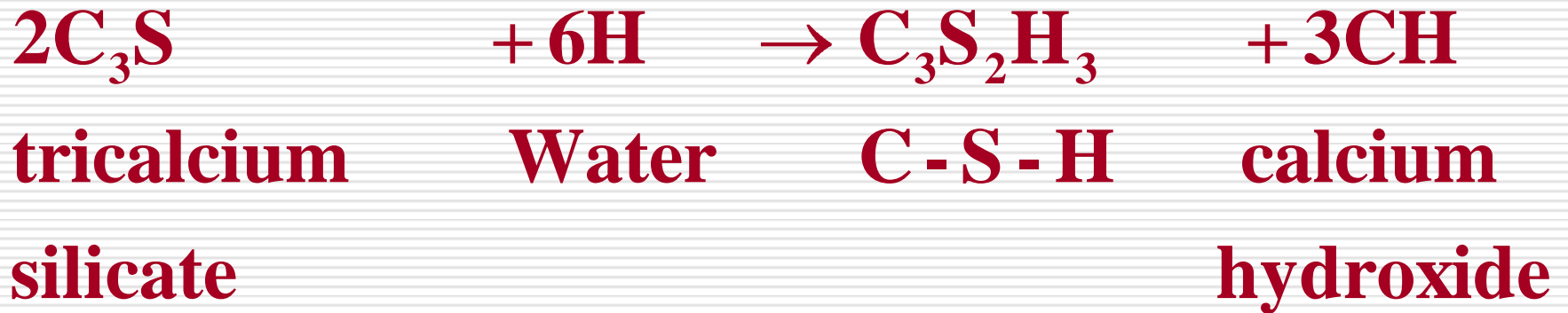
Hydration of Portland Cement (continued)



Hydration of Portland Cement (continued)



Hydration of Calcium Silicates



Hydration of Calcium Silicates (continued)

- The principal product is calcium silicate hydrate
 - Poorly crystalline material
 - Small particle (< 1mm) in any dimension
 - Composition varies over a wide range
- Calcium hydroxide is a crystalline material with a fixed composition
- Calorimetric curve – rate of heat evolution with time
- Heat flow is proportional to rate of reaction

Hydration of C_3S

➤ Stage 1

- On contact with water, calcium and hydroxide ions are released from the surface of C_3S grains
- Rapid heat evolution & pH rises over 12 within minutes
- Ceases in 15 minutes

Hydration of C_3S (continued)

➤ Stage 2

- Dormant period
- Needed to reach critical concentration of calcium and hydroxide ions
- Hydrolysis slows down in the dormant period
- Responsible for plastic state of concrete
- Lasts between 2 and 4 hours
- Then, C_3S reacts again

Hydration of C_3S (continued)

➤ Stage 3

- **Acceleration period**
- **Nuclei forms and hydration products (CH, C-S-H) begin to crystallize from solution and the reaction of C_3S proceeds rapidly**
- **CH crystallizes from solution**
- **C-S-H develops at the surfaces of the C_3S grains, developing a coating**
- **Maximum rate of heat evolution at 4 to 8 hrs**

Hydration of C_3S (Alite)

(continued)

➤ Stage 4

- Rate of reaction slows down

➤ Stage 5

- Steady state within 12 to 24 hrs
- As coating of C_3S grain (hydrate layer) grows water must flow through the barrier to reach unhydrated C_3S
- Eventually water reaches unhydrated C_3S through diffusion
- Diffusion-controlled reactions are slow
- Hydration tends to reach 100% completion asymptotically

Hydration of C_2S (Belite)

- C_2S reacts in the same way as C_3S grains
- Except that the reaction is much slower

Hydration of C₃A

- C₃A reacts with sulfate ions supplied by dissolution of gypsum
- **Primary initial reaction of C₃A**
- $C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$

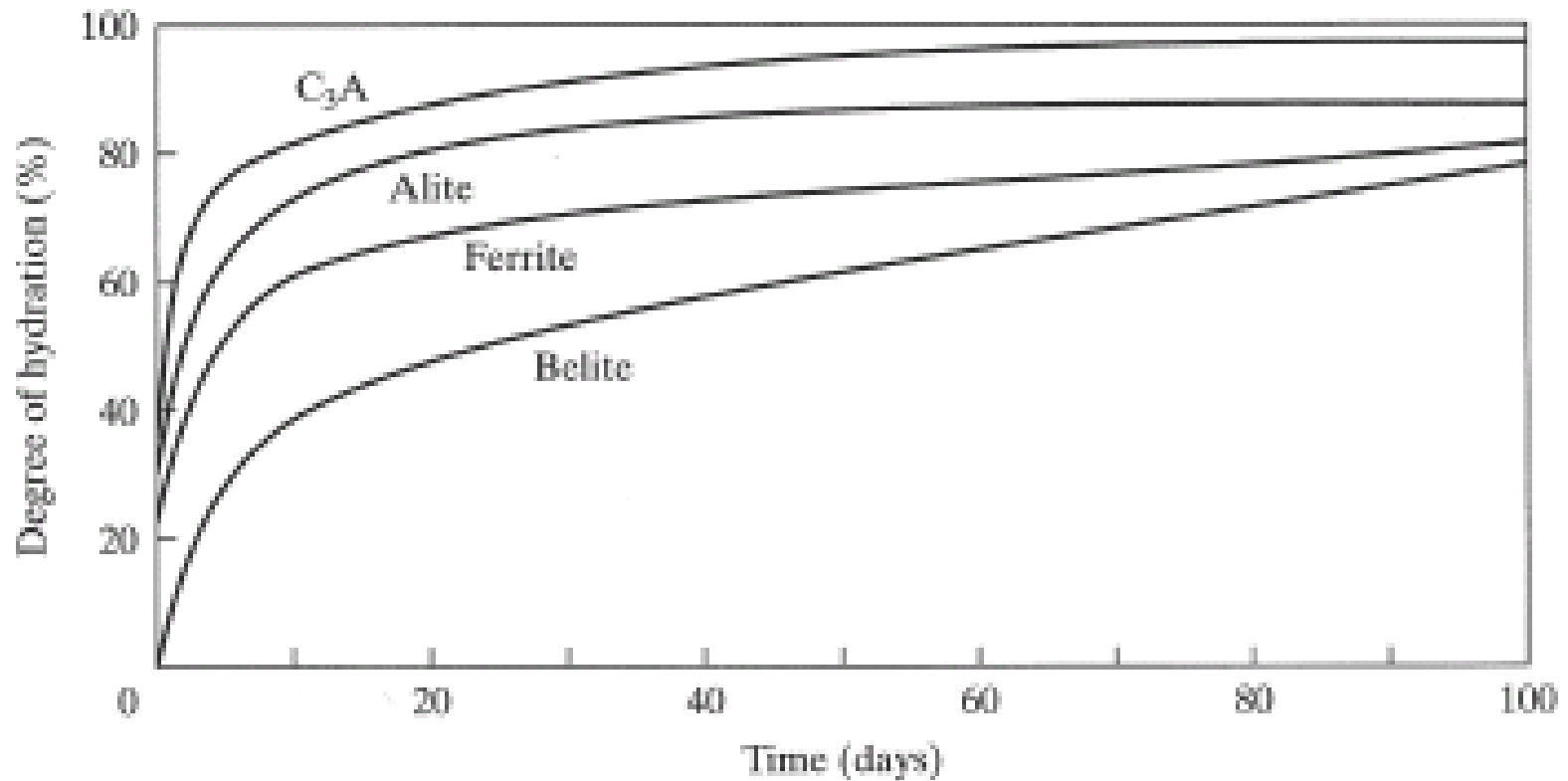
Hydration of C_3A (continued)

- Ettringite is stable only when there is an ample supply of sulfate
- If sulfate is consumed before complete hydration of C_3A , ettringite transforms into monosulfoaluminate
- $2C_3A + C_6AS_3H_{32} + 4H \rightarrow 3C_4ASH_{12}$

Hydration of C_4AF (Ferrite)

- Forms same reactions as C_3A , but to a lesser degree
- Uses small amount of gypsum
- $C_4AF + 2CH + 14H \Rightarrow C_4(A,F)H_{13} + C_2(A,F)H_3$
- Similar to monosulfoaluminate amorphous

Reaction Rate $C_3A > C_3S > C_4AF > C_2S$



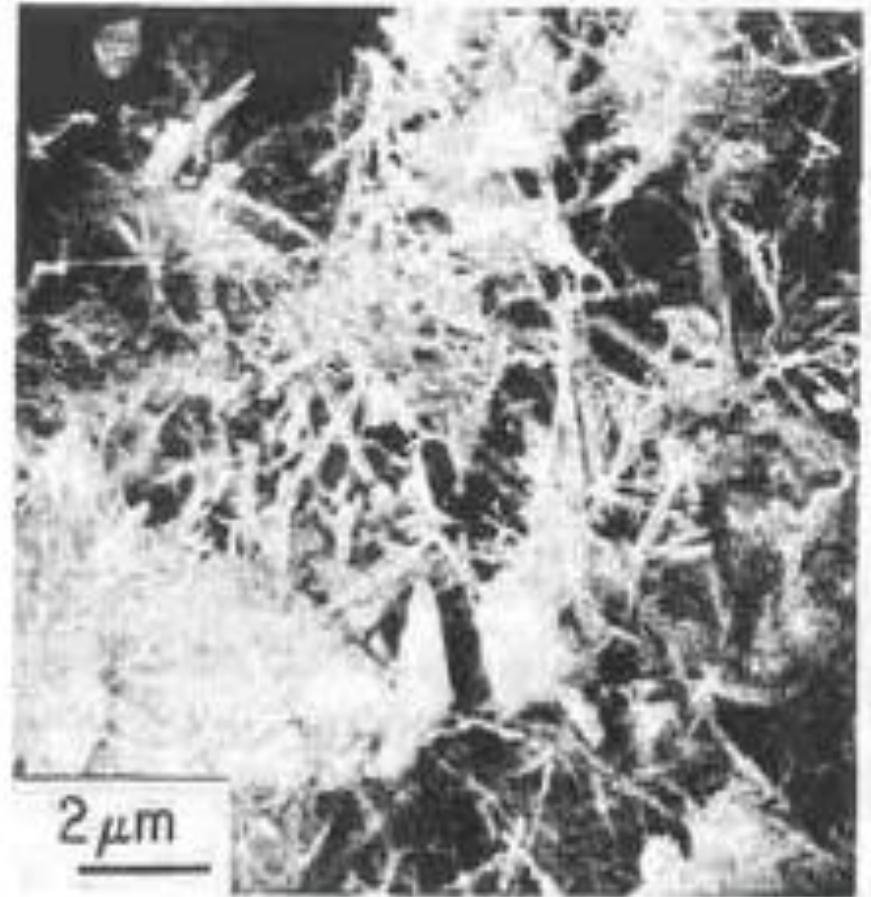
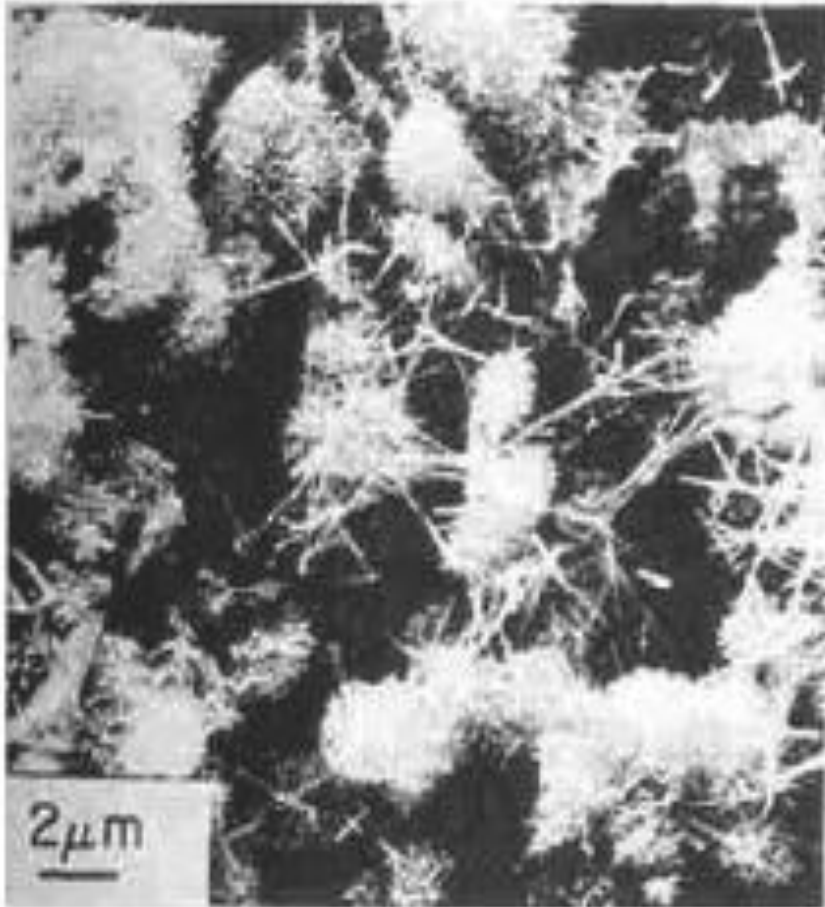
⁴(A, F) means that F substitutes for A in the formula.

Properties of Hydration Products

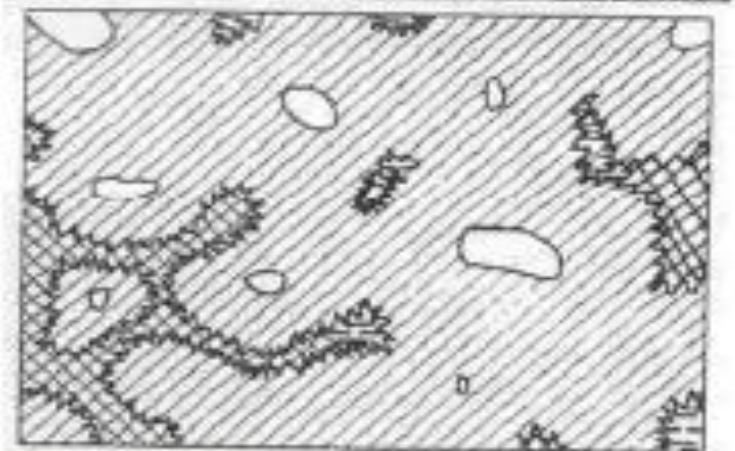
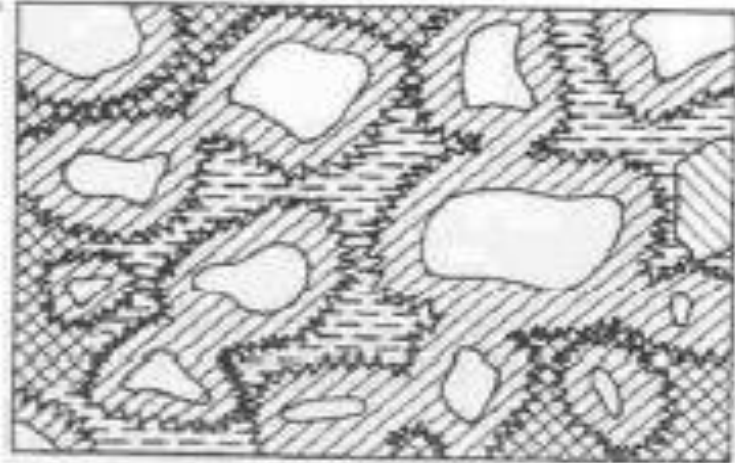
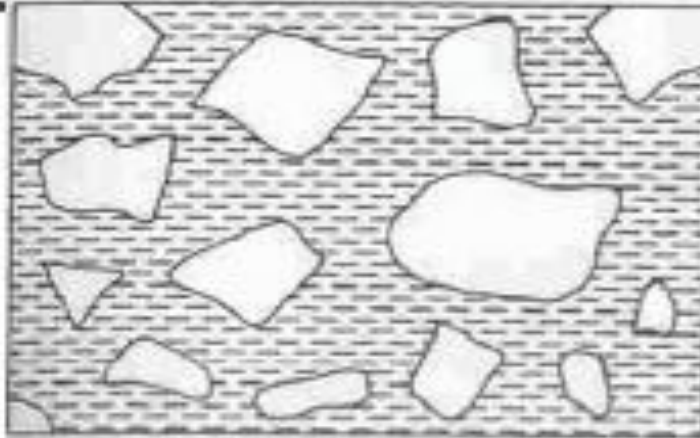
- **Calcium Silicate Hydrate (CSH)**
 - ✓ **Poor crystallinity – unresolved morphology**
- **Calcium Hydroxide (CH)**
 - ✓ **Monosulfoaluminate – well crystallized hexagonal prisms**
- **Calcium Sulfoaluminates**
 - ✓ **Ettringite – hexagonal prisms with high aspect ratio – slender needles**

Formation of CSH

SEM images



Microstructural development



Unhydrated material
Water filled capillary
pores

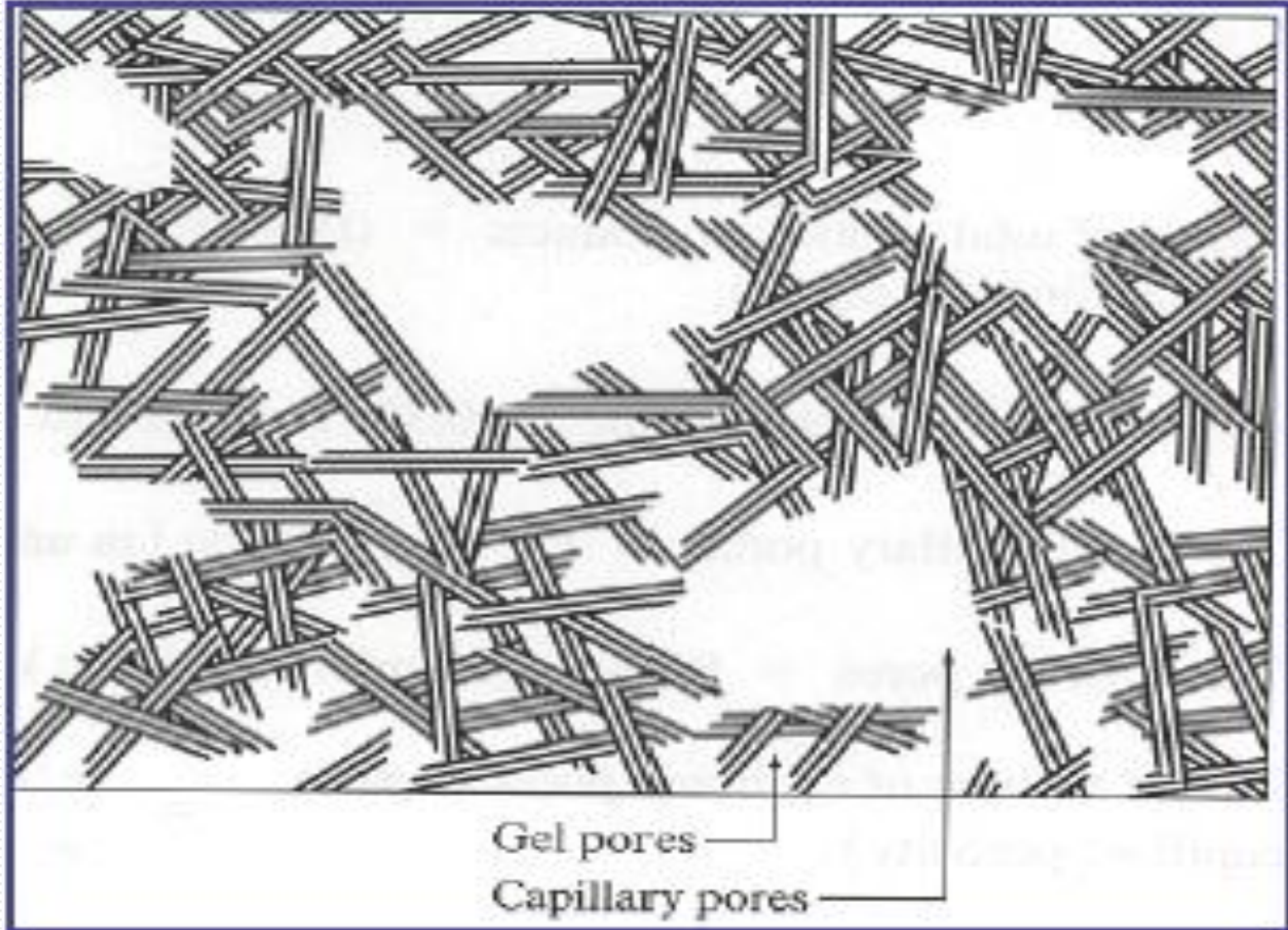


C-S-H



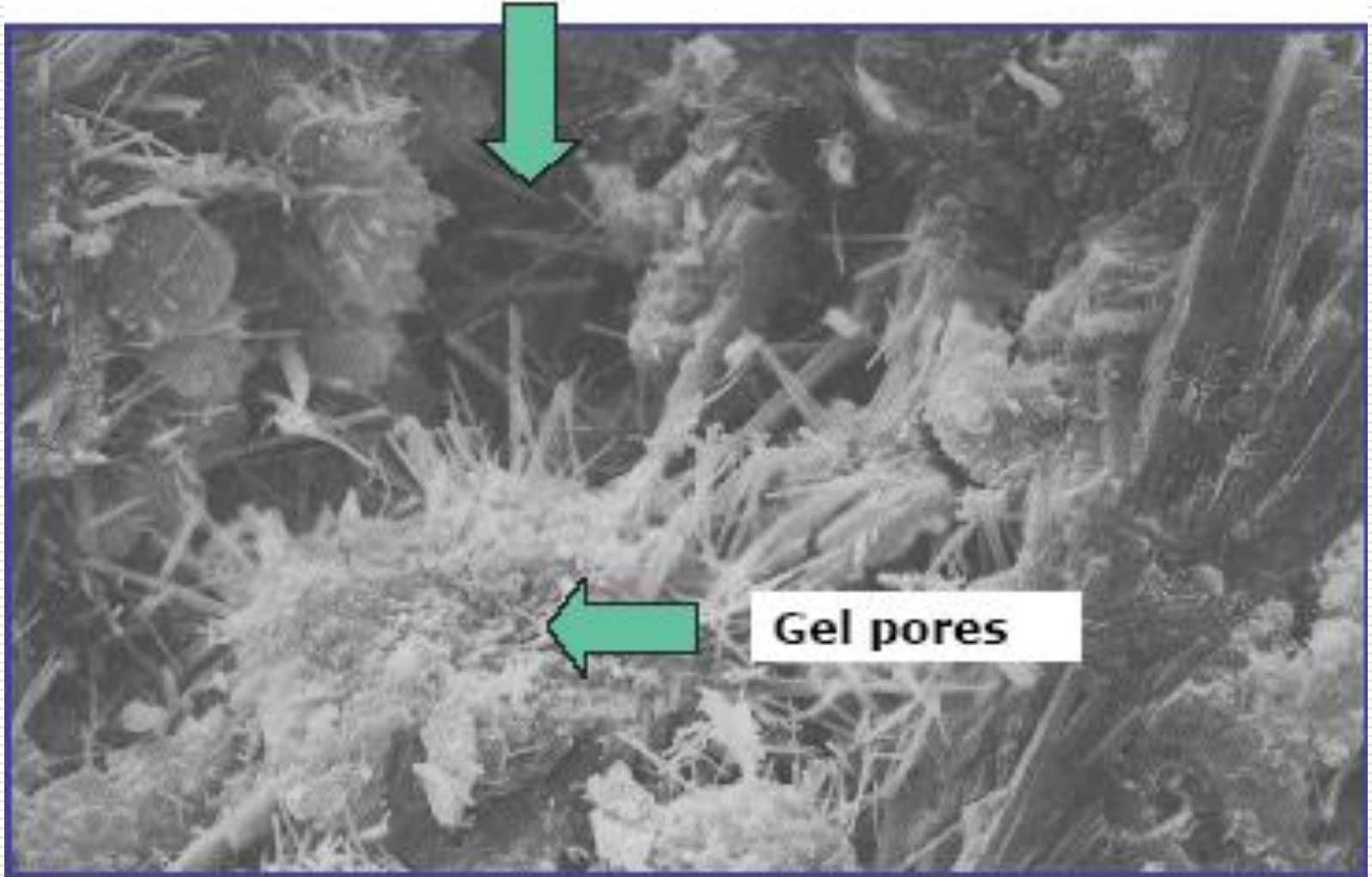
Calcium Hydroxide

Model of Porosity



Model of Porosity (continued..)

Capillary pores

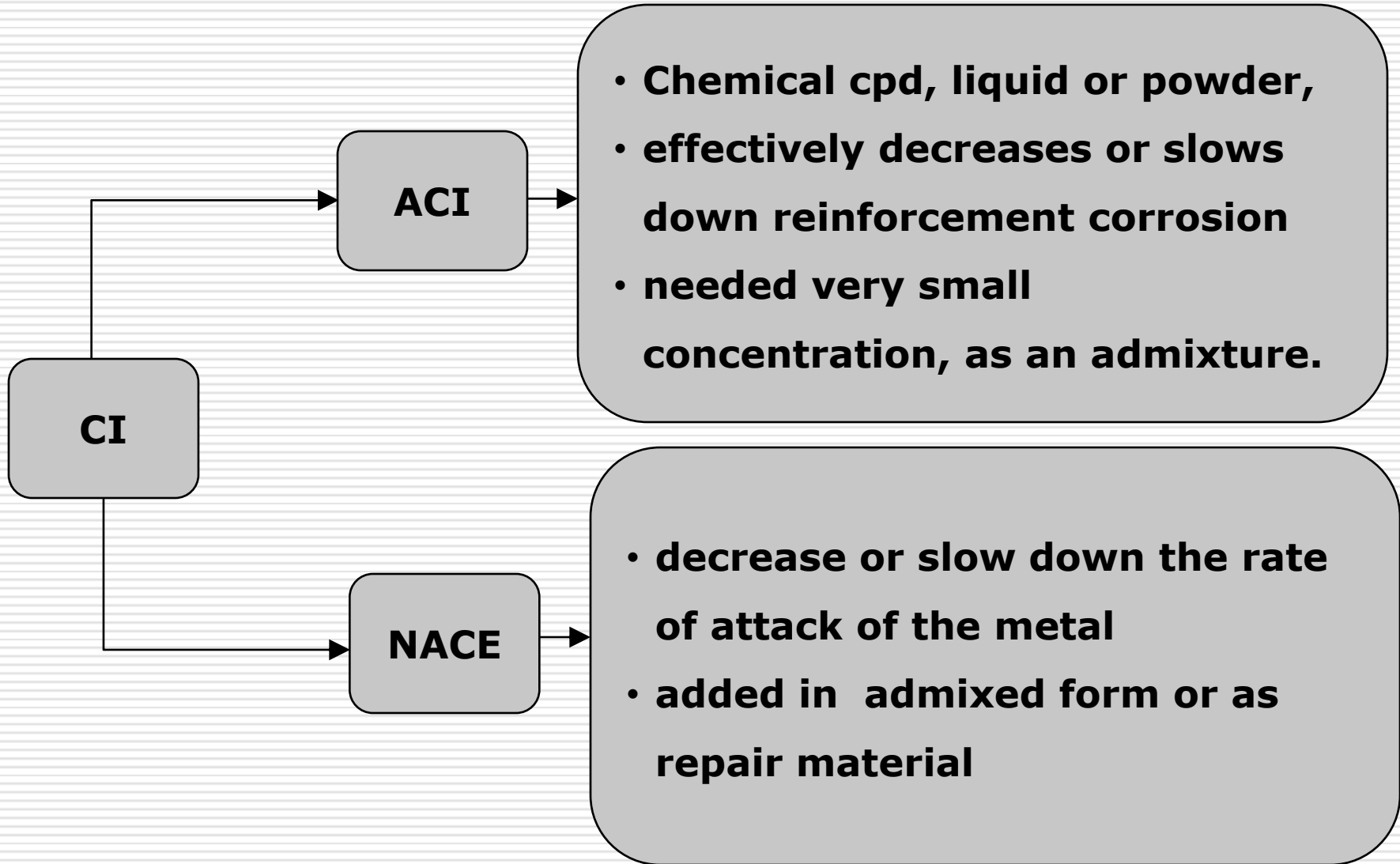


Techniques for Determination of composition

- **Chemical analysis**
 - **X-ray diffraction**
 - **X-ray Fluorescence**
 - **Optical microscopy**
 - **Scanning electron microscopy with energy dispersive X-ray analysis**
 - **Electron microprobe analysis**
 - **Selective dissolution**
 - **Thermal analysis**
-

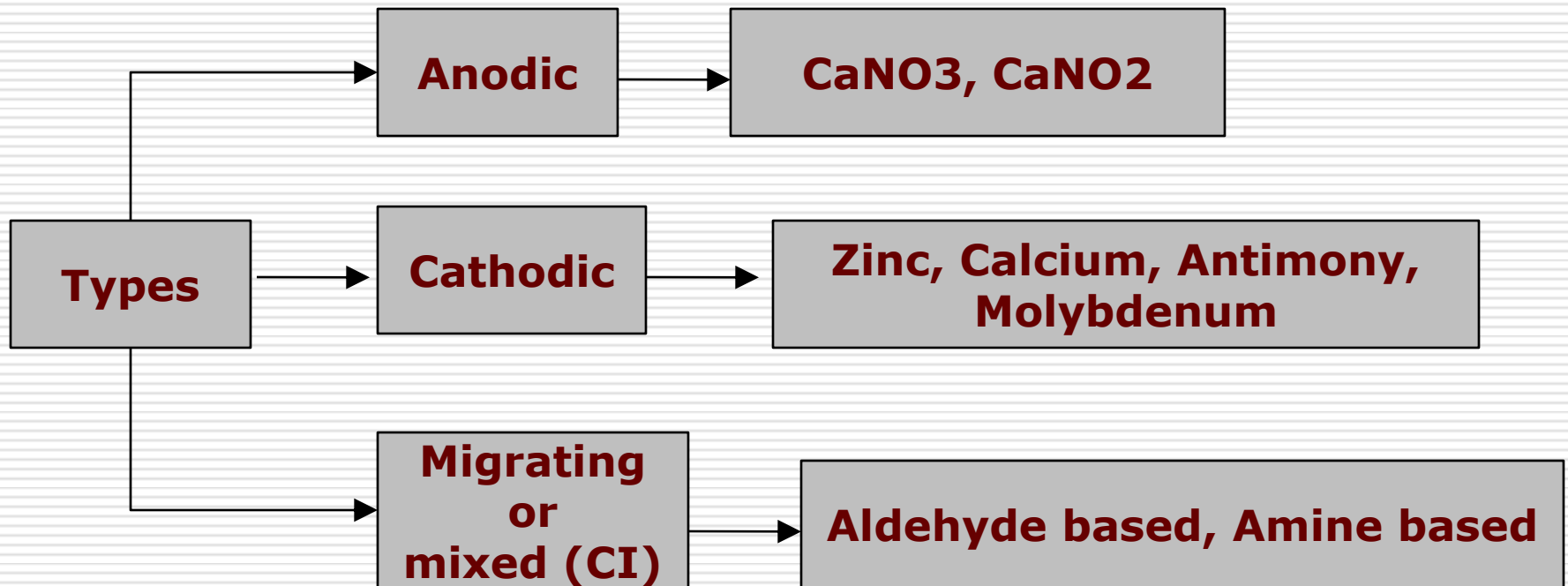
Role of Corrosion Inhibitors (CI) in Construction Industry

Corrosion Inhibitors (CI)



Corrosion inhibitor (CI) – at a glance

Should be viewed as an additional protective measure – not as an alternative to the design specifications for durable concrete



Corrosion inhibitor (CI) – at a glance

- **Essentiality of CI- corrosion protection demanded**
- **Advantages: To provide corrosion protection**
- **Uniformly mixed throughout the concrete matrix**
- **Protecting the entire steel surface**
- **Concrete's low permeability – protects inhibitor leaching**
- **Features of ideal CI**
 - **adequate amount to prevent corrosion of embedded steel**
 - **no adverse effect on properties of fresh & hardened concrete**

Requirement - To mitigate reinforcement corrosion

Formation of barrier layers

Oxidation by passivation of the surface

Influencing the environment in contact with the metal

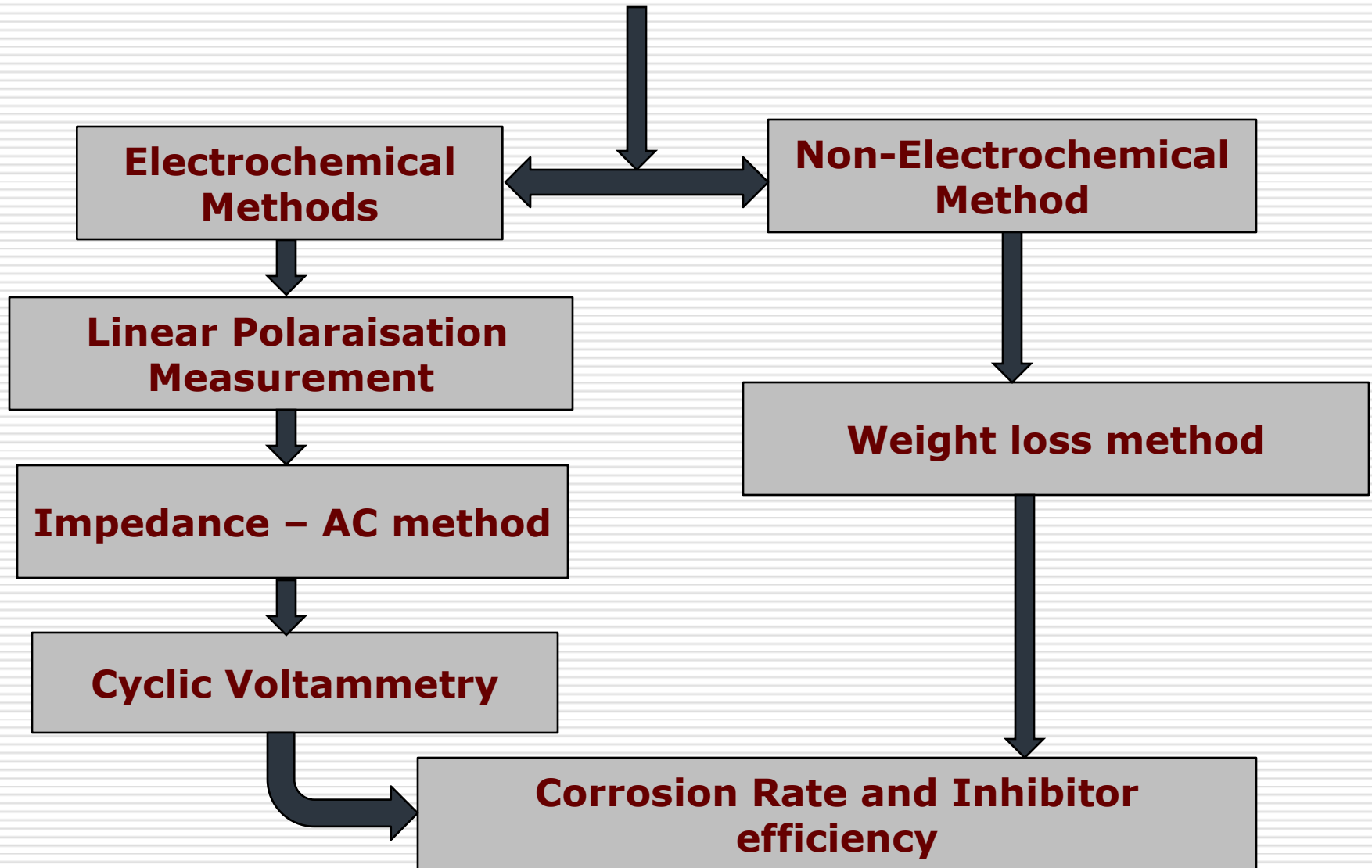
To be an effective CI

- **possess strong electron acceptor or donor properties or both**
- **solubility be such that rapid saturation of the corroding surface occurs without being readily leached out**
- **Induce polarization of the respective electrodes at relatively low current values**
- **Compatible with the intended system without adverse effects**
- **Effective at the pH and temperature of the system environment**

Inhibitor - Mechanism

- **forming a film on the metallic surface by adsorption**
- **Complex formation with cement or cementitious material**
- **Inhibitors slow corrosion process - (Electrochemical evaluation)**
- **Increasing the anodic or cathodic polarization behavior (Tafel slopes)**
- **Reducing the movement or diffusion of ions to the metallic surface**
- **Increasing the electrical resistance to the metallic surface**

Techniques to assess inhibitor efficiency



Potential-dynamic polarization method

- The inhibition efficiency can be calculated from the value of I_{corr} by using the formula,
- Inhibition efficiency (%) =
$$\frac{I_{\text{corr}}(\text{blank}) - I_{\text{corr}}(\text{inh})}{I_{\text{corr}}(\text{blank})} \times 100$$
- where $I_{\text{corr}}(\text{blank})$ is the corrosion current in the absence of inhibitor and $I_{\text{corr}}(\text{inh})$ is the corrosion current in the presence of inhibitor

AC impedance method

- The inhibition efficiency can be calculated by using the formula,
- Inhibition efficiency (%) =
$$\frac{R_t(\text{inh}) - R_t(\text{blank})}{R_t(\text{inh})} \times 100$$
- Where the $R_t(\text{inh})$ is the charge transfer resistance in the presence of inhibitor
 $R_t(\text{blank})$ is the charge transfer resistance in the absence of inhibitor

Techniques to assess corrosion in reinforced concrete structures

- **Half cell potential (ASTM C876) : electrochemical technique**
survey of the condition is the first step towards its rehabilitation
- **Rapid, cost effective and non-destructive survey offers key information on the evaluation of corrosion and aids in the quality assurance of concrete rehabilitation and in the prediction of remaining service life**
- **Assess the severity of steel corrosion to measure the corrosion potential, since it is qualitatively associated with corrosion rate**

Probability of corrosion according to half-cell readings

Half-cell potential reading vs Cu/CuSO₄	Corrosion activity
Less negative than -0.200 V	90% probability of no corrosion
Between -0.200 V and -0.350 V	An increasing probability of corrosion
More negative than -0.350V	90% probability of corrosion
<-500 mV	Severe corrosion

Measurement of Electrical conductivity of concrete

Rapid chloride permeability system – RCPT

(ASTM C1202 or AASHTO T277)

- Specifies the rating of chloride permeability of concrete based on the charge passed through the specimen during six hours of testing period
- ASTM C1202 recognizes that a correlation between the rapid chloride permeability test and the **90 day ponding test results is necessary**, while AASHTO T277 does not require this correlation

NDT – IR, Laser, UPV, Electrical measurement, etc.

Prerequisites for Repairing

- **Pores are responsible for transport of aggressive substances such as chloride, oxygen and moisture, which can cause deterioration**
- **Pore solution, its chemistry and types present in the concrete should be analysed**
- **Compatibility of repair system**

Do and Don't in Use of CI

```
graph TD; A[Do and Don't in Use of CI] --> B[Do's]; A --> C[Dont's]; B <--> C; B --> D["• Required Dosage optimisation (electrochemical and Non electrochemical)  
• Compatibility studies between CI and Cementious materials such as hydration, setting Time, Leach out study  
• Durability aspects"]; C --> E["• Improper Dosage results in adverse effects  
• inconsistent corrosion rate  
• Unprecedented hydration and offset setting time  
• Use of expired CI  
• Use of different CI for a particular work"];
```

Do's

- **Required Dosage optimisation (electrochemical and Non electrochemical)**
- **Compatibility studies between CI and Cementious materials such as hydration, setting Time, Leach out study**
- **Durability aspects**

Dont's

- **Improper Dosage results in adverse effects**
 - **inconsistent corrosion rate**
 - **Unprecedented hydration and offset setting time**
- **Use of expired CI**
- **Use of different CI for a particular work**

Corrosion inhibitor research at CSIR-SERC

Synthesis of polymer based inhibitor towards reinforcement corrosion

- Presently used Inhibitors: inorganic based-Calcium nitrate, Calcium nitrite
- Organic based – MCI – amines, ester based
- Current research: synthesis of di-aniline based CI
- Electrochemical evaluation – simulated pore solution
- Results are compared with already available CI's
- High efficiency, even with very small concentration
- Mechanism – study is under progress
- Long term effect is also in progress

Role of Superplasticiser (SP) in Construction Industry

Chemical Admixture - Introduction

- **Chemical Admixture - Additive to concrete mixture – to enhance concrete properties – fresh or hardened stage**
 - **ex: Superplasticisers, Corrosion Inhibitors, Set Retarders, Set Accelerators, Alkali-Silica Mitigating Inhibitors, Air-entraining agents, etc.,**

Superplasticisers

- **Organic compounds of high molecular weight - Synthetic**
- **Technically - an admixture, which when added to concrete either**
 - **imparts extreme workability without the addition of extra water, to produce ‘flowing concrete’, or**
 - **Allows large reduction of the water content to be made without loss of workability; or**
 - **permits simultaneous increase in both workability and strength without incurring substantial extra cost**

How super are superplasticiser

SP

- When used to produce easily placed concrete, it can transform a 2-inch slump conventional mix into an 8-inch-slump flowing mix

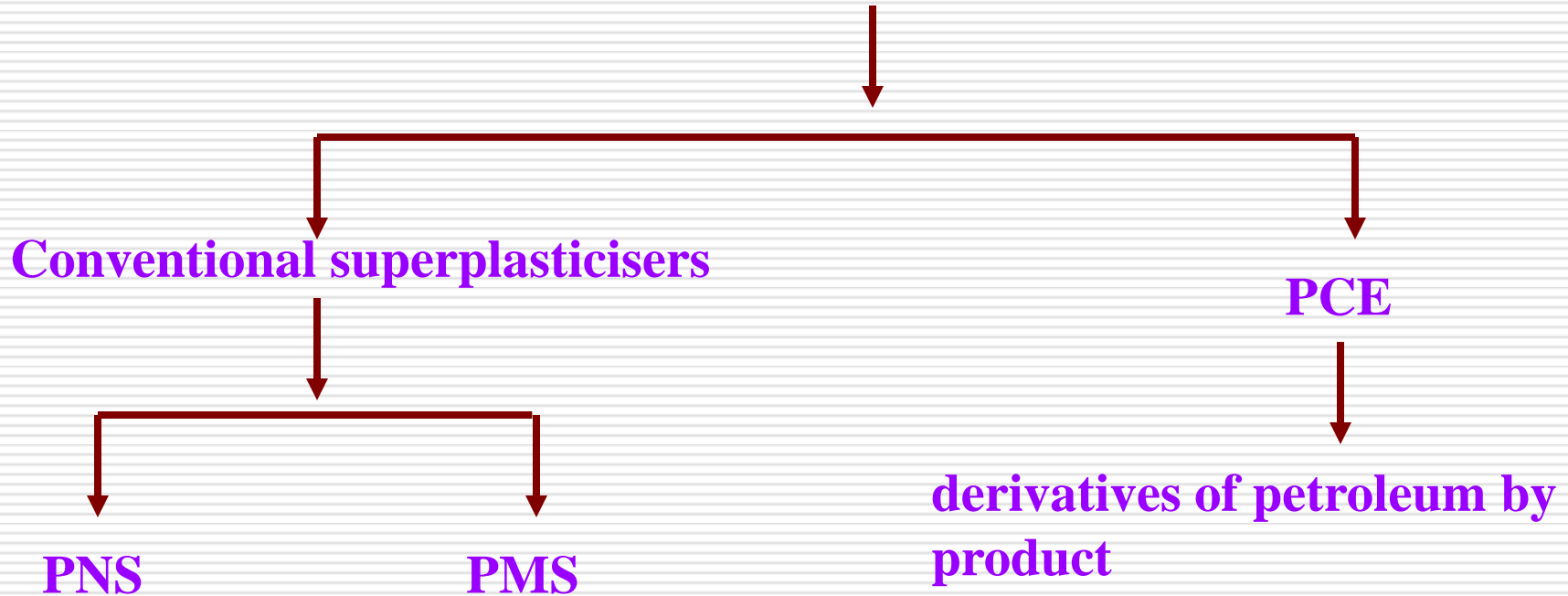
SP

- When used as a water-reducing agent, it permits 20 to 30 percent of the water in a normal mix to be eliminated without losing slump or workability

SP

- If it is used as cement savers, **10 to 15 percent reduction in cement is possible**, while maintaining the same strength of concrete

Types of Superplasticisers

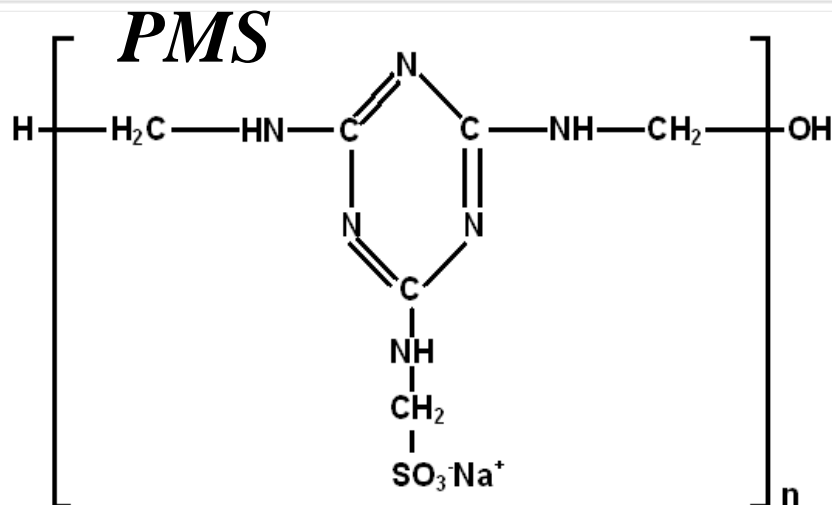


PNS – Poly naphthalene Sulfonated Formaldehyde

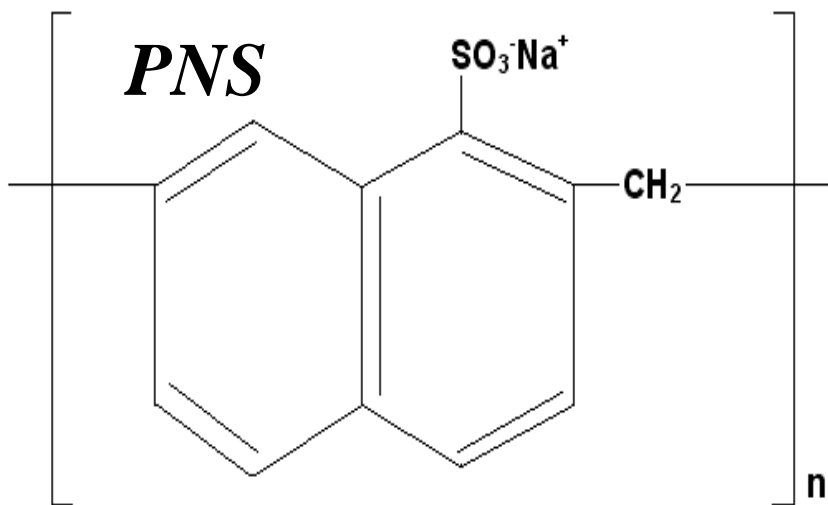
PMS – Poly Melamine Sulfonate Formaldehyde

PCE – Poly Carboxylic Ester

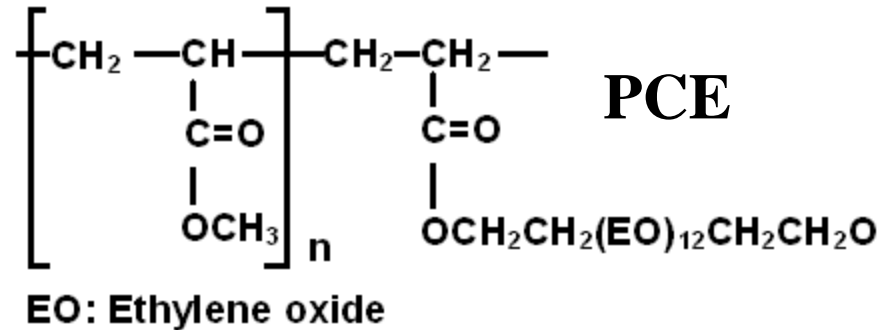
Chemical Structure of PMS & PNS



- **n = condensation number (50-60) given mol. wt in the range of 20,000**
- **Form of sodium salt –soluble in water – due to the presence of sulphonate groups on the side chains**



- **Similar in many ways to PMS category – with simple repeating unit**
- **n = 5 -10 giving mol. wt in the order of 2000**



- Allow 40% reduction of water – due to their chemical structure, which enables good particle dispersion
- Mainly composed by a methyl-polyethylene glycol copolymer (side chain) grafted with methacrylic copolymer (main chain)
- PEO group affords a non uniform distribution of electron cloud, which gives chemical polarity to the side chains
- Number of length of side chains are flexible parameters- easy to change
- Side chains have a huge amount of PEO units, lower with higher molar mass w.r. to charge density of polymer – enables poor performance on cement suspensions
- To have both parameters at the same time – long side chain and high charge density – keep no. of main chain units much higher than no. of side chains units

Mode of Action

PNS, PMS – Electrostatic repulsion

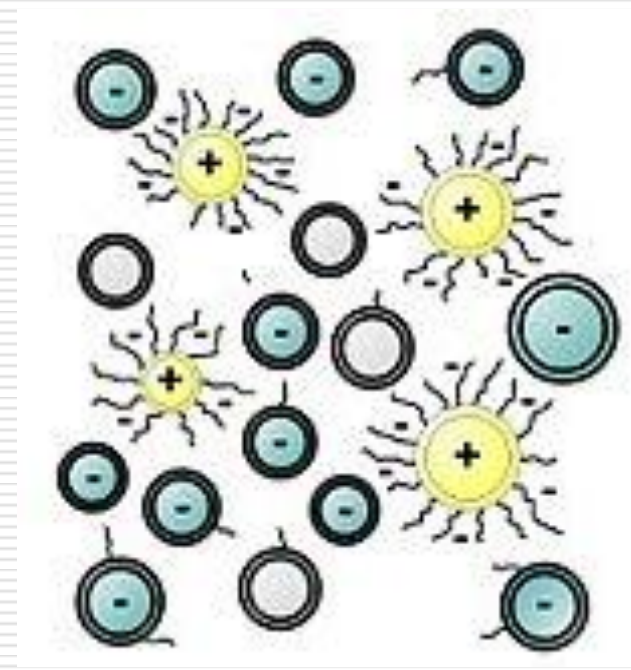
PCE – Steric stabilization – due to the presence of bulky group

Mechanism of PNS and PMS

- **Very large molecules (colloidal size) – dissolves in water to give ions with a very high negative charge (anions)**
- **Configuration of anions not known – sulphonated groups (anions) oriented outwards into the water**
- **Anions – attracted to the surface of cement grains – at the normal levels of admixture usage**
- **Adsorbed in sufficient numbers form a complete monolayer around them**
- **Combination of electrostatic repulsion and large ionic size (provide physical separation) brings about rapid dispersion of the individual cement grains**
- **Water trapped within the original floccs is released and contribute to the mobility of the cement paste – hence increases the workability of concrete**
- **Not much reduction in the surface tension of water – little tendency to excessive air entrainment even at high dosage**

Mechanism of PCE

- **Backbone - Negatively charged-** permits adsorption on the positively charged colloidal particles
- **As a consequence of adsorption – changes in zeta potential of suspended particles – due to adhesion of the polymer on the particle surfaces – ensures to the side chains possibility to exert repulsion forces, which disperse suspended particles and avoid friction**
- **Forces directly detected using Atomic Force Microscope – liquid environment (model substances)**



How to use SPs?

- ❑ **Laboratory trial mixes must be needed – absence of accumulated experience with SPs – function by dispersing cement particles – efficiently in concrete rich in cement and other cementitious materials**
- ❑ **Reproportion of mix (to make cement-sand paste thicker and less soupy) – must for conventionally proportioned mixes for high slump –to prevent bleeding**

How to control the negative effect?

- ❑ **Major effect- bleeding – to control - add fines (by absorbing water)**
- ❑ **Smaller size coarse aggregate – inhibits segregations – less buoyant - Pozzolans addition – 4 to 5 % more of finer fractions of sand-to prevent segregation**
- ❑ **Maximum dosage of SPs beyond which segregation is inevitable**
- ❑ **Selection of coarse fine aggregate – improve workability and finishability, even with low slump**

Do and Don't in Use of SP

Do's

- **Required Dosage optimisation (slump, Marsh cone, flowability desirable for particular mix grade)**
- **Compatibility studies between SP and Cementious materials (Zeta potential, hydration, setting Time, Leach out study)**
- **Durability aspects**

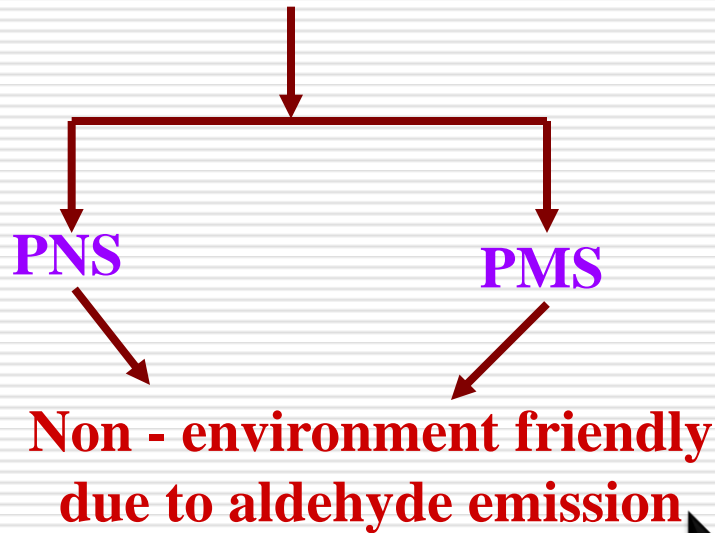
Dont's

- **Improper Dosage results in adverse effects**
 - **Inconsistent setting time**
 - **Unprecedented hydration**
- **Use of expired SP**
- **Use of different SP for a particular work**

Emergence of Alternate SP

Weakness of available sps

Conventional superplasticisers



PCE

derivatives of petroleum by product

- Scarcity due to demand of petroleum derivatives
- Non-biodegradable

Strength -
Emergence of new
alternate

Environment friendly
superplasticiser

Bio-polymer

- **EMPOWER Project : Bottom up approach for the synthesis of multifunctional admixtures towards green construction**
- **Survey - Most abundant bio-renewable and major biopolymer on earth – Cellulose - Major constituent: cotton, wood, baggase and biomass**
- **Poly dispersed linear glucose polymer chains – form hydrogen bonded supramolecular structures**
- **Future Work : planned based on the literature survey conducted – availability of resources, green solvent**

**Separation of
Cellulose from
Biomass**

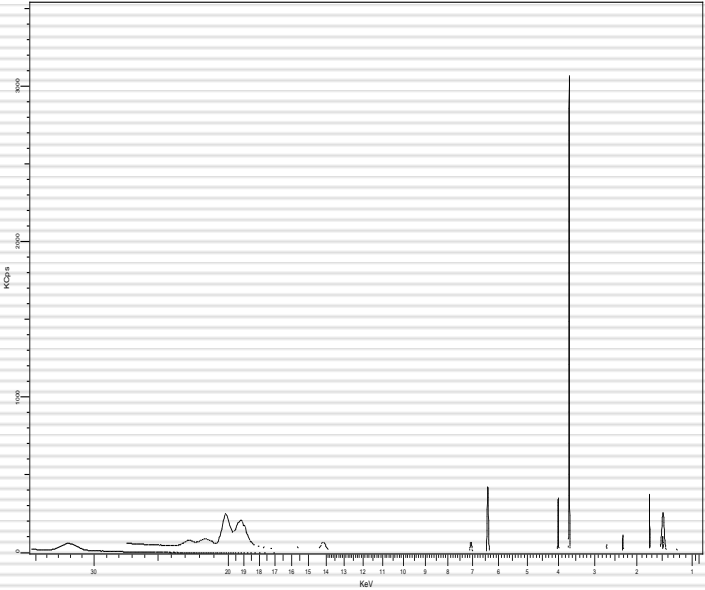
**Extraction of
Cellulose -
using different
types of solvent
system**

**Characterization
of Precursor
materials**

Characterization of Cement

XRF – X-ray fluorescence: Constituents of cement

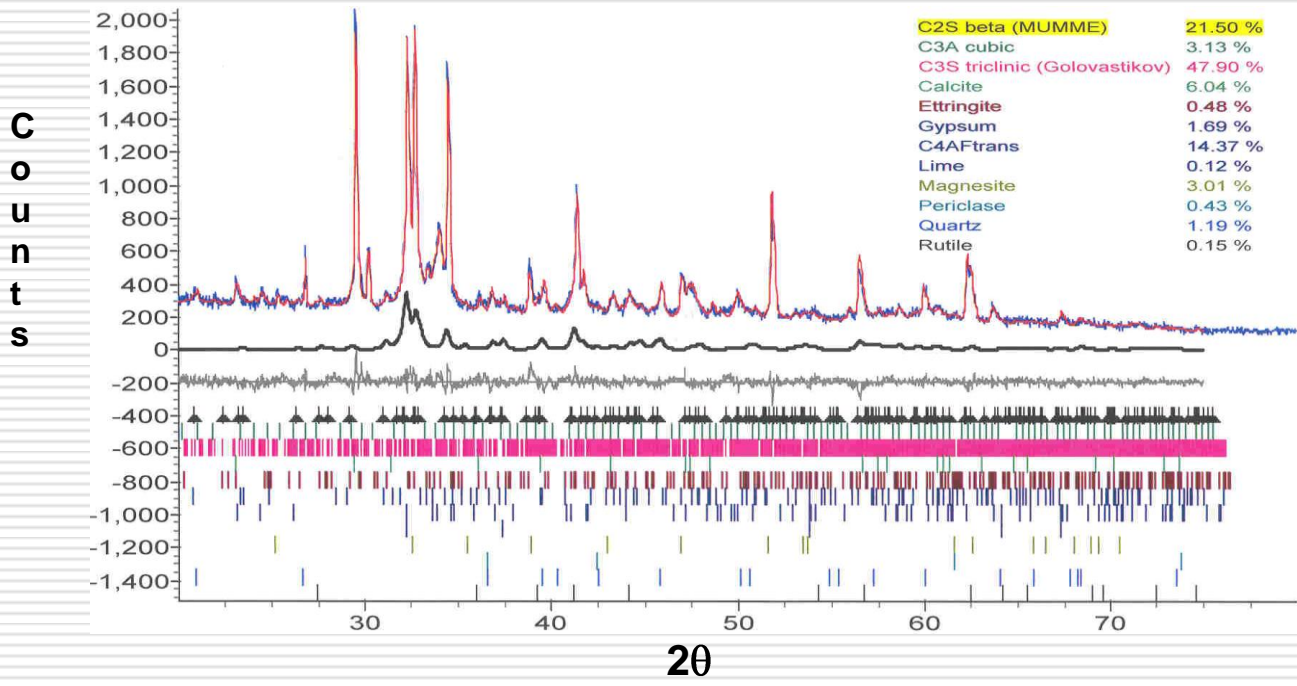
Oxides	Percentage (%)
Al_2O_3	5.6
BaO	0.8
CaO	63.4
Fe_2O_3	4.0
K_2O	0.5
MgO	0.8
MnO	0.04
Na_2O	0.2
P_2O_5	0.3
SiO_2	20.2
SO_3	3.4
SrO	0.1
TiO_2	0.4
ZrO_2	0.01



XRF spectrum

Characterization of Cement

XRD – X-ray diffraction: Bogues compounds : Phases of cement

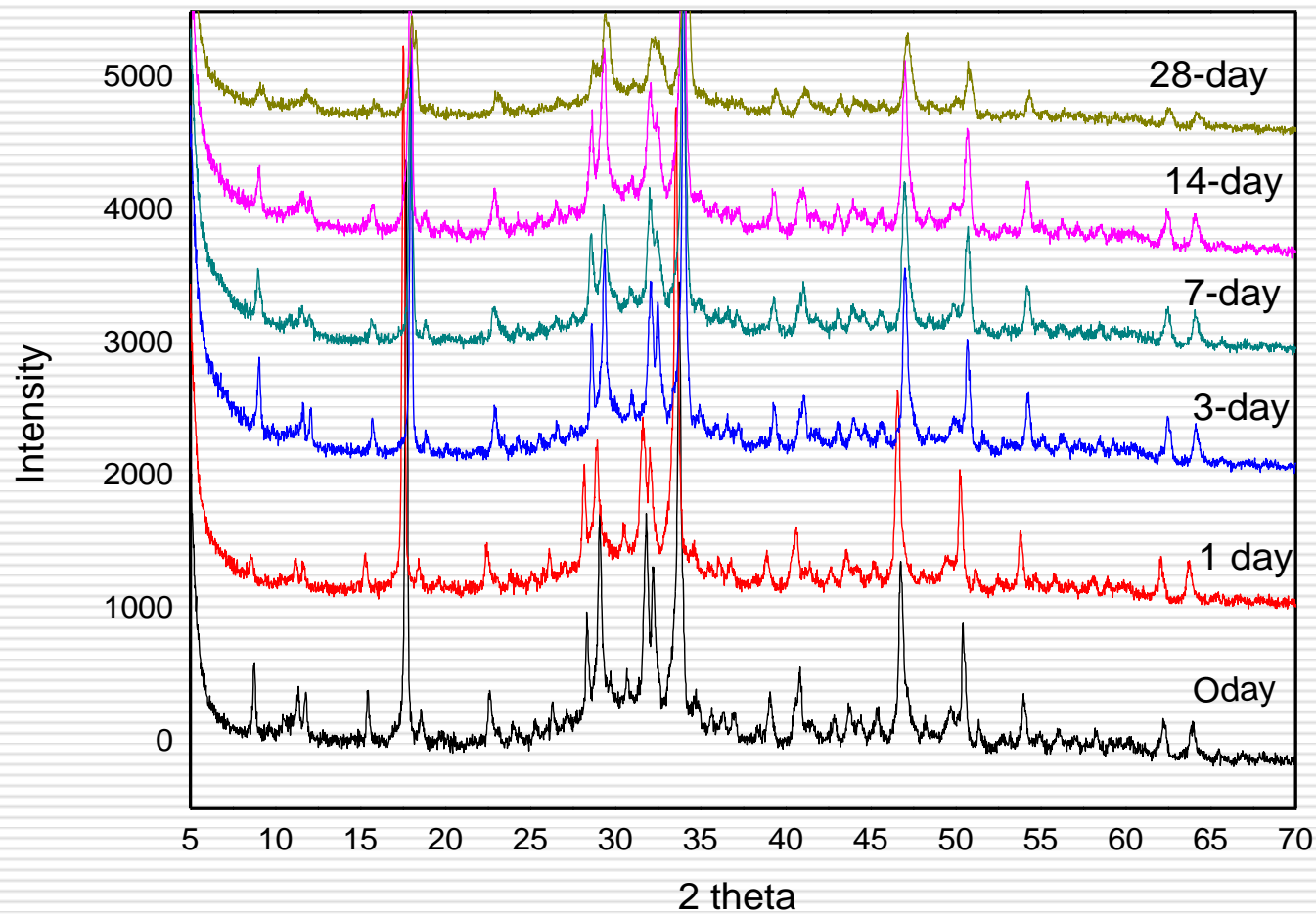


- C3S : 47.90%
- C2S : 21.50%
- C3A : 3.13%
- C4AF: 14.37%

XRD spectrum

Hydration study of cement with cellulose superplasticizer

XRD – X-ray diffraction: Bogues compounds : Phases of cement



XRD spectrum

Consistency and Setting time of Cement- SPs

Name of the Super Plasticizer	w/c	Consistency (mm)	Initial Setting Time	Final Setting Time
Control	0.31	13	2 hrs 20 min	5 hrs 20 min
Control	0.32	23	2 hrs 15 min	5 hrs
Cellulose SP (0.5%)	0.28	19	3 hrs	5 hrs
PC SP (0.5%)	0.25	19	3 hrs 20 min	7 hrs
PNF SP (0.5%)	0.25	21	1 hrs 40 min	36 hrs

Future Programme of Work

Structural Modifications – Changes in Chemical Functionalities



Multi Functional Properties – Retarders, Corrosion inhibitor, Internal moist curing – controlled release - mechanism etc

*How to adopt
multifunctional
characteristics*

*Bio-Inspired
Material*

NANO CELLULOSE – NATURE NANO

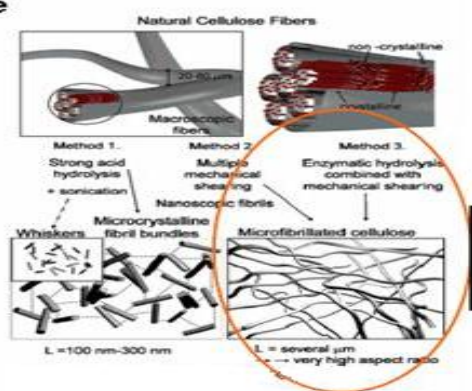
"Bottom-up approach towards green construction"

- Developing technology for sustainable construction materials
- Synthesis of superplasticisers using biopolymer
- Synthesizing Corrosion Inhibitor - Self - healing mechanism
- Autogenic healing of cracks at nano level - Crystal growth mechanism

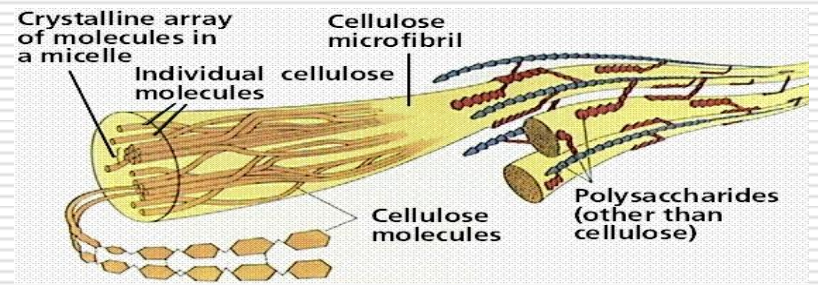
Treatment Methods

Micro/nanofibrillated cellulose

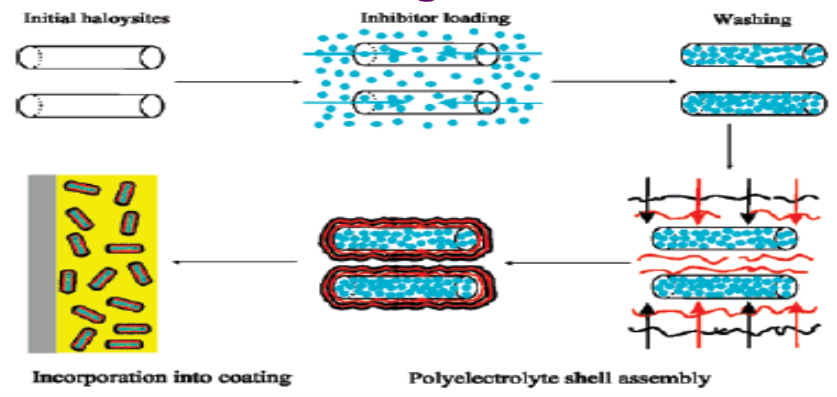
- Chemical pre-treatments
 - ✓ Controlled acid hydrolysis
 - ✓ Alkaline swelling and/or hydrolysis
 - ✓ Surface cellulose chemical modifications
- Enzymatic pre-treatments
 - ✓ Cellulases
 - ✓ Hemicellulases
- Mechanical treatments
 - ✓ Fibers refining/beating/grinding
 - ✓ "Homogenizers"



Crystalline array



Inhibitor loading



Concluding Remarks

- ✓ **Importance of corrosion inhibitors and superplasticisers in construction industry**
- ✓ **Mechanisms**
- ✓ **Proper usage – do's & dont's**
- ✓ **R&D at CSIR-SERC**

Concluding Remarks (continued)

- ♣ **Increased urbanization, especially in emerging countries, will drive public infrastructure and housing projects**
- ♣ **Safety, Durability, Aesthetics of structures are mainly brought by the chemicals**
- ♣ **Working together - chemical and construction industries can continue to build a better, safer and more sustainable world – Homogeneous solution for Heterogeneous problem**

***"Greener" approach results
in Modern and Sustainable
Building***



Thanks for your kind attention