1. Introduction
Most of presentations & reports on concrete can be classified into :---
Basically important

- Raw materials
- Workability as RMC
- Hardened properties
- Structural aspects
- Durability
- Fire resistance etc.

- Recently coming
- Recycling
- Waste problem
- Environment
- Ecology

- Rare case
- Gas emission
- Safety aspect of materials
- Risk aspects
- Accident

Ex. Reports on concrete reported by general contractors
-- Big general contractors, i.e. Taisei, Kazima, Obayashi, Shimizu, Takenaka, have published their own R&D reports.
  (18.4%)
Studies on concrete durability have been constantly done to get high quality of concrete. Ex. Alkali-silica reaction, Cl⁻ ion migration, freezing & thawing

2 Cement as main raw materials of concrete
1) History of cement
   - If concrete is defined to be composite material of lime based binder and aggregates, “Sazare-Ishi” would be the oldest concrete.
   - National anthem

   - Neolithic era, BC7000, 40 MPa of high strength concrete composed of lime (calcite) and aggregate was used in Israel.

   - BC300, Rome era, mixture of lime, aggregate and “Pozzolana” were mixed and cured in molds. Such concrete was widely used for construction in Roma.

   - Foro Romano (BC2 century)
Main cause of hardening of these concrete was carbonation of Ca(OH)$_2$.

Beginning of 19 century, hydraulic hardening minerals were invented by burning the mixture of lime and silica.

In 1824, J. Aspdin invented the basic technology of present Portland Cement.

Its color resembled to the stone in Portland Island.

Naming origin

Industrialization of cement prevailed in the world. Germany in 1850 / America in 1871 / Japan in 1875

3 Chemical admixtures

1) Introduction

Before 1960 concrete was mainly produced at job site. Around 1960 ready mixed concrete was produced by about 500 RMC plants.

Liability of concrete quality increased / Agitator truck delivery. Around 1965 almost all concrete was produced by RMC plants.

“Admixtures” are materials used for improving properties of concrete &/or mortar.

Admixtures   Improvement can be done by small amount

Chemical admixture   Improvement can be done by large amount

JIS A 6204 & Association norms

Improvement items are workability, strength development, etc.

Chemical admixture has been used to get workability with decreasing mixing water.

2) Production volume

<table>
<thead>
<tr>
<th></th>
<th>2004</th>
<th>Export 10.3 Mio.ton (14%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland cement</td>
<td>43.8 Mio.ton</td>
<td>73.9%</td>
</tr>
<tr>
<td>Blended cement</td>
<td>15.5 Mio.ton</td>
<td>26.1%</td>
</tr>
</tbody>
</table>

3) Chemical admixtures

<table>
<thead>
<tr>
<th>Example of main components</th>
<th>Use of purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-Entrainer</td>
<td>Workability / Freezing &amp; thawing</td>
</tr>
<tr>
<td>AE Water Reducer</td>
<td>Lignosulfonate / Gluconate</td>
</tr>
<tr>
<td>AE-High Range Water Reducer</td>
<td>Polycarboxylate</td>
</tr>
<tr>
<td>AE-Mid range water reducer</td>
<td>Polycarboxylate / Lignosulfonate</td>
</tr>
<tr>
<td>High Range Water Reducer</td>
<td>Melamine / Polycarboxylate</td>
</tr>
<tr>
<td>Set retarding water reducer</td>
<td>Gluconate</td>
</tr>
<tr>
<td>Set accelerating water reducer</td>
<td>Nitrite / Nitrate / Thiocyanate</td>
</tr>
<tr>
<td>Anti-freezing admixture</td>
<td>Nitrite / Nitrate / Thiocyanate</td>
</tr>
<tr>
<td>Hardening accelerator</td>
<td>Calcium chloride</td>
</tr>
<tr>
<td>Superplasticizer</td>
<td>Sulfonated naphthalene</td>
</tr>
<tr>
<td>Anti-washout admixture</td>
<td>Cellulose base &amp; Acrylic acid</td>
</tr>
<tr>
<td>Shotcrete accelerator</td>
<td>Calcium aluminate Setting time / Hardening time</td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td>Nitrite / Aminoalcohol</td>
</tr>
<tr>
<td>Shrinkage reducing admixture</td>
<td>Copolymer of Alkyleneoxido</td>
</tr>
<tr>
<td>Shrinkage compensation agent</td>
<td>CSA</td>
</tr>
<tr>
<td>Fly ash</td>
<td></td>
</tr>
<tr>
<td>Blast furnace slug powder</td>
<td></td>
</tr>
<tr>
<td>Silica fume</td>
<td></td>
</tr>
<tr>
<td>Calcite powder</td>
<td>Workability / Segregation</td>
</tr>
<tr>
<td>Cement polymer emulsion</td>
<td>Emulsion of SBR, EVA &amp; Acryl</td>
</tr>
</tbody>
</table>

Chemical admixtures mainly for water reduction

Other chemical admixtures

Powder type admixture Setting time / Hardening time
2) General properties of chemical admixtures

- Chemical admixture is one kind of surfactant to get
  - better workability of RMC
  - better durability of hardened concrete

- Chemical admixture can: --
  - reduce water in RMC under the same slump (flow)
  - introduce small air-bubble properly
  - extend working time of RMC, e.g. slump & flow life

- Chemical admixture react cement particles by: --
  - electrostatic repulsive force
  - chelate effect
  - steric hindrance

3) History of water reducer

<table>
<thead>
<tr>
<th>Year</th>
<th>Mechanism of effect</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1920</td>
<td>Lignosulfonate (LS)</td>
<td>By-product of pulp industry, Electrostatic repulsion</td>
</tr>
<tr>
<td>1931</td>
<td>Sodium Gluconate (SG)</td>
<td>Fermentation of glucose, Chelate of COO-</td>
</tr>
<tr>
<td>1965</td>
<td>Sulfonated naphtalene</td>
<td>Copolymerized by formaldehyde, Electrostatic repulsion</td>
</tr>
<tr>
<td>1966</td>
<td>Sulfonated melamine</td>
<td>Copolymerized by formaldehyde, Electrostatic repulsion</td>
</tr>
<tr>
<td>1982</td>
<td>Modified polycarboxylate</td>
<td>Methacrylate copolymer, Steric hindrance</td>
</tr>
<tr>
<td>1985</td>
<td>Amino sulphonated</td>
<td>Aminosulphonate copolymer, Steric hindrance</td>
</tr>
<tr>
<td>1990</td>
<td>Comb type polycarboxylate</td>
<td>Methacrylate copolymer, Steric hindrance</td>
</tr>
<tr>
<td>1998</td>
<td>Modified polycarboxylate</td>
<td>Polyamido modified aclylate, Steric hindrance</td>
</tr>
</tbody>
</table>

Market share of LS based admixture is over 50%.
Methacrylate copolymer based admixture is still under development.

The 1st use of admixture in Japan might be in 1932.
Features of chemical admixture industry

Company of chemical admixture are ‘formulators’:
-- Almost all raw materials are purchased.
-- Even main raw materials are purchased, e.g. LS, SG.

(Own production is rare case.)

Chemical admixtures are composed of:

- **Main raw material**
- **Air contents, slump, initial strength, antiseptic**
- **Water**

*Formulation confidentiality is very important.*

*Very hard to know chemicals from MSDS*

- Almost all chemical admixtures are produced by mixing the purchased raw materials, which enables **special product** by batch production. Possible to make “Tailor made product”

- **Transport cost** is important for management because of water.

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Water reducers

1. **Lignosulfonate (LS) based Water Reducer**
   - **Main use of LS**
     - (in 1997 / Solid content base)
     - 105 k ton = Admixture (67k t) + Dye disperser (8k t) + .......
     - Ca, Na, Mg base / High molecular electrolyte / Anion type
     - Molecular weight of LS: ~ 10,000 or more

   - **Long history, i.e. established technology.**
     - Less technical progress now / Mainly Delivery & Marketing
     - But, still mainly used, especially in civil engineering works.
     - In Tokyo area, demands of LS decreases because of aggregate.

   - **Cheapest raw material** as admixture raw materials

   - Cement dispersion is done by electrostatic repulsion.

   - Basically **sugar** is contained in LS raw material, which is effective for retardation.

---

LS production at pulp factory (In case of Mg salt)

- **Needle leaf tree**

- **Tip**

- **Pulp process**

- **Suction pump**

- **Filtration**

- **Reducing sugar**

- **Antiseptic** is needed from this stage.

- **Z > X > B**

- **Easy to be sulfonated**

- **Anion type**

- **Structure of LS is complicated, because lignin is natural product.**
Example of formulation of LS based admixture

a. Full season type
- Mg-LS (45% solid content) 98.2%
- TEA (80% solution) 1.6%
- Tri-butyl phosphate 0.15%
- Formalin (37% solution) 0.4% (Seasonal adjustment)
- Antiseptic* 0.035% (Seasonal adjustment)

b. Summer type
- Ca-LS (48% solid content) 98.5% (High sugar content)
- TEA (80% solution) 0.8%
- Tri-butyl phosphate 0.35%
- Formalin (37% solution) 0.5% (Seasonal adjustment)
- Antiseptic* 0.05% (Seasonal adjustment)

* Antiseptic must be changed every year because of change of Germ & bacillus.

Formaldehyde calculation
- Base Cement 300 kg/m³
- LS base AE-WR Cement x 0.5% (Contain 0.3% of 37% formalin)

300 kg/m³ x 0.5% x 0.3% x 37% = 1.7 g/m³ of formaldehyde is contained in 1m³ of ready mixed concrete.
If concrete is applied to the floor, 10 m² x 10 cm (1 m³) and if 1% of formaldehyde is emitted from concrete, ≈ 17 mg of formaldehyde.
If room height is 1.7 m ≈ 1,000 g/m³

Ventilation before use
- Guideline: 100 g/m³ 0.08 ppm

Example of formulation of SG based Water-reducing and retarding admixture

a. Basic formulation
- Sodium gluconate 31.0%
- Formalin (37% solution) 1.0%
- Water balance

b. Without formalin
- Sodium gluconate 31.0%
- Antiseptic material 0.02%
- Coloring material 0.2%
- Water balance

2) Sodium Gluconate (SG) based Water Reducer

SG is produced by fermentation of glucose.

H H OH H
HOH₂C – C – C – C – COONa
OH OH H OH

MW = 431

Reaction with cement particle:
- Water Reduction: Electrostatic force with cement grain like LS
- Retardation: Strong chelate property above pH >12
  - Gluconate ion reacts with Ca²⁺ initially released, and forms “protective layer” which causes retardation.

Advantage
- Hot season concreting
- Superior surface finish

Exposed concrete
3) Melamine sulfonates & formaldehyde condensation polymer (MS) based High Range Water Reducer (HRWR)

- MS was developed as raw material of superplasticizing HRWR in Germany in 1960.
  - At present, mainly used in precast field because of good surface finish, water reduction.
- Production of MS
  - For melamine-formaldehyde copolymer, mole ratio of Melamine : Formaldehyde = 1 : 3
    (from operation 1 : 3.3)
  - Sulfonation can be done by SO$_3$ base, e.g. pyrosulfite, sulfamic acid, sulfanilic acid.

- Recent tendency is moving to PC based admixture, because:
  - Higher water reduction / Better workability
  - No eye & skin irritation

- Formaldehyde (FA) calculation
  - Cement: 400 kg/m$^3$
  - MS base HRWR: Cement $\times$ 1.0 $\%$ (Remain 1$\%$ of free FA)
  - $400 \text{ kg/m}^3 \times 1\% \times 1\% = 40g/m^3$ of FA remains in concrete.
  - If concrete is steam-cured, almost all FA might be released.
  - But if not, FA may be released during long period.

Info. Naphtalenesulfonate was developed by Dr.Hattori in 1965.

4) Polycarboxylic acid (PA) polymer based admixture.

- Background of development
  - In 1986 JASS 5 requires water content to be less than 185kg/m$^3$.
    - “New RC Project” headed by MLIT started for high strength concrete, 60N/mm$^2$.
    - (MLIT = Ministry of Land Infrastructure & Transport)
  - Although naphthalene & melamine based AE-HRWRs give high water reduction and good workability, market required much better admixtures to meet New RC Projects, i.e. future requirement.
  - To meet the requirements, many chemicals are tested, e.g. polycarboxylate ether, maleic acid co-polymer.
  - In 1984 Nippon Shokubai invented the polymer for admixture.

- Epoch-making in chemical admixture technology
Base technology of Nihon Shokubai
A Monomer of Polyalkylene glycol ester and (meth)acrylic acid
B (Meth)acrylate monomer (90~95 wt%) (90~95 wt%)
C Monomer able to copolymerize with A & B (0~50 wt%)

\[
\begin{align*}
A & : CH_2 = C-C-O-(R_2O)_n-R_3 = O \\
B & : CH_2 = C-C OOX \\
C & : R_1 : H or Methyl \quad R_2 : Alkylene \quad R_3 : H or alkyl \\
& \text{Here} \quad \text{Acrylic acid} \quad \text{Methacrylic acid} \quad \text{Glycol} \\
& \text{CH}_2=\text{C-COOH} \quad \text{CH}_2=\text{C-COOH} \quad \text{C}_n\text{H}_{2n+1}(\text{OH})_2 \\
& \text{H} \quad \text{CH}_3
\end{align*}
\]

Patent claims copolymer composed of 3 monomers, A, B & C. ACBABB AACA

Example of formulation (wt. %)

<table>
<thead>
<tr>
<th>Product name</th>
<th>80N</th>
<th>80S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer-600</td>
<td>37.1</td>
<td>22.3</td>
</tr>
<tr>
<td>Polymer-700</td>
<td>-----</td>
<td>29.7</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>TEA</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Coloring</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Water</td>
<td>59.4</td>
<td>44.6</td>
</tr>
<tr>
<td>AE agent</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>AF agent</td>
<td>1.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>

High flowing & high strength concrete

a Basically polymer’s function as admixture is done by adsorption of carboxylic ion to hydrated cement grain by hindering cement grain coagulation by graft (side chain)
b AE-HRWRs would be formulated by formulating 2-3 kinds of polymers to meet requirements, e.g. SP-80N & SP-80S.
c These polymers showed the big possibility of high strength & high flowing concrete as shown later.
d Almost all polymer are produced by a few chemical companies, because polymerization process needs know-how of high molecular synthesis including safety items.
e This kind of polymer is still under development and their details are closed, which causes strong confidentiality even to MSDS.
Example of polymer synthesis: Radical chain reaction

Vinyl acetate monomer

Example of polymer synthesis --- Modified Nihon Shokubai

3 intermediates co-polymerize, in the case of 715M polymer

Main polymer

Intermediates and others

Composed of many kinds of Polymers !!
5) Mid range AE-Water Reducers

- Mid range AE-WR → AE-WR → AE-HRWR
- Water reduction: Over 10% → Bigger
- Slump keeping: Over 18% → Better
- Price: ~50 ¥/kg → 65~80 ¥/kg → > 160 ¥/kg
- Strength level: < 25 N/mm² → 20-30 N/mm² → > 30 N/mm²

- On the point of durability JASS 5 requires water content must be less than 185 kg/m³, preferably <180 kg/m³
  - Very hard to attain using present AE-WR with recent low quality of sand, especially west part of Tokyo & Osaka area.
  - Especialy 20-30 N/mm² concrete
  - Water content is checked at job site.
- Then requirements are just between AE-WR & AE-HRWR regarding water reduction, slump keeping & price.

6) High range water reducer (HRWR)

- HRWR has been mainly used for PCa & PC, not for RMC factory.
- Main requirements of PCa & PC are:
  - Water reduction & easy to cast
  - Good surface finish after curing
  - Slump life is not required, i.e. half or less of RMC plant use.

- Main raw materials of HRWR are:
  - Melamine sulfonate & formaldehyde condensation polymer (MS)
  - Naphthalene sulfonate & formaldehyde condensation polymer (NS)

- Polycarboxylate (PA) polymer based admixture has gradually been used, because of better water reduction.
  - Utilize the technology of PC based admixture

- Idea of formulation
  - a Based on AE-HRWR
  - Dilution → Quality of AE-HRWR is possible by excess dosage.
    - Since 1996 this type has been major products.
    - Ex) Existing AE-HRWR 55.0 wt%
    - Existing LS based AE-WR 5.0 wt%
    - Sodium gluconate 4.5 wt%
    - Water Balance
  - Mix with cheaper & compatible material
  - b Use of cheaper & lower quality of PC polymers, which are not acceptable as AE-HRWR.
  - c Add PC polymers into AE-WR

- Site PC ---- New trend at job sites
  - Beam, floor slab, balcony, etc. are produced at job site to reduce construction period, etc.
  - Job site of MM Towers
  - Site PC office
  - Bar arrangement
  - Concrete High strength concrete 60N/mm²
  - Demold next day and lifting up by crane
  - Something will happen in PCa industry?
  - Demand of admixture for high strength concrete
7) Hardening accelerator
- After setting of cement, strength development starts.
- Hardening accelerator is used for:
  - Getting initial strength during concreting in cold season
  - Getting efficiency of mold-cycle at precast factory
  - Getting initial strength for AE-WRs & AE-HRWRs
- Chemicals used for hardening accelerator effects on setting a little, followings are famous raw materials:
  - Ca-nitrite, Ca-thiocyanate, Ca-formate, TEA
  - CaCl₂ was used for this purpose, but stopped.
- Example of formulation (wt. %)
  - Lactic acid: 5.0
  - Ca-nitrite: 13.5
  - Methylene diethanolamine: 6.5
  - Water: Balance

8) Anti-freezing admixture
- When concrete is applied in intense cold season, initial strength development is essential factor to avoid damage of freezing.
  - Use of high early Portland cement, &/or anti-freezing admixture, proper curing to avoid concrete freezing, etc.
- Technical bases of anti-freezing admixture are:
  - Accelerating the initial hydration of cement
  - Lowering freezing point
- Generally it is formulated by combining the materials
  - Hydration-accelerator: Ca-(Na-) nitrite, nitrate, thiocyanate
  - Tri-ethanol amine
  - Anti-freezing material: Ethylene glycol
  - Water reducer: Lignosulfonate, Melaminesulfonate

9) Quick setting admixture
- Quick setting admixture is used to get very short setting time and very fast strength development.
  - Ex. In case of JSCE’s norm on NATM
    - Initial setting < 5 min
    - Final setting < 15 min
    - 12 hours strength > 1.0 N/mm²
- Before 1980, sodium aluminate was used, but stopped because of alkali problem.
  - Then safety and ecological concerns have been dominant in the sprayed concrete accelerator market.
- As non-alkali type, Ca-aluminate, Ca-sulfoaluminate and aluminum sulfate are gradually used.
Non-alkali quick setting admixture is used for other applications, e.g. steel segment, bolt box of concrete segment, using shotcrete technology, e.g. mortar mixing, spraying machine.

Example of steel segment

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>1000 kg</td>
</tr>
<tr>
<td>Acryl emulsion (44% solid)</td>
<td>160 kg</td>
</tr>
<tr>
<td>Water</td>
<td>380 kg</td>
</tr>
<tr>
<td>Crashed glass sand</td>
<td>500 kg</td>
</tr>
<tr>
<td>Admixture (45% $\text{Al}_2\text{(SO}_4)_3$)</td>
<td>60 kg</td>
</tr>
</tbody>
</table>

Spray = 1 $\text{m}^3/\text{h}$  
No dust / Easy to trowel / Good adhesion

From norms on anti-washout admixture

Guideline of underwater concrete is described in JSCE’s norm. Japan Society of Civil Engineers

<table>
<thead>
<tr>
<th>Water</th>
<th>Cement</th>
<th>Sand</th>
<th>Gravel</th>
<th>Viscous</th>
<th>HRWR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Cement</td>
<td>Sand</td>
<td>Gravel</td>
<td>Viscous</td>
<td>HRWR</td>
</tr>
</tbody>
</table>

Viscous material is cellulose derivatives. Melamine based high range water reducer(HRWR)

Separation factor in water, i.e. amount of suspended substance, is 12 mg/L. (Norm: less than 50 mg/L)
Flowing concrete / Self-leveling / Much less turbidity
Less strength drop ( $\frac{\text{water}}{\text{air}} = 90\%$ )

10) Anti-washout admixture for underwater concrete

In case of underwater concreting, e.g. revetment, pier, segregation of cement-paste and aggregate must be avoided, even though tremie-tube is used.

How to solve?

Turbidity by suspended particles

Self leveling

How to minimize environmental impact of cement washout?

Viscous admixture

Main component; Water soluble polymer, such as Cellulose base & Acrylic acid base
Other components; Anti foam agent, (AE)Water reducer, etc.

11) Corrosion inhibitor admixture

Formulated to protect embedded reinforcing steel from corrosion, and to provide an effective means for extending the service life of concrete structures.

Basically surface of steel in high alkali is protected from corrosion because of being covered by hydrophobic thin layer, $20\sim60\mu$, of $\text{Fe}_2\text{O}_3$.

By carbonation &/or chloride ion migration in concrete, steel corrosion starts, and then cracks are formed. (Volume of $\text{Fe}_2\text{O}_3$ is 1.5 times larger than that of steel.)

Once crack forms, corrosion speed is enhanced.
Two types of corrosion inhibitor

a Anode action type : NO⁻ ion / JIS A 6205
Depresses oxidation of steel & forms Fe₂O₃ inhibitive film
Major product in Japan
Toxicity : Nitrite salts are listed toxicity class 2 in CH.

b Dual action type : Amino-alcohol (AMA)
Film forming, protecting both cathode & anode parts
Non-hazardous

c Mechanism of anti-corrosion of AMA
AMA is absorbed on steel in a layer of about 20 nm thickness
Hydroxide at steel surface are replaced by AMA
AMA can displace Cl⁻ ions from steel surface

After immersing Pt foil in dimethylethanolamine,
surface material was checked by SIMS.
Mass 58 → (CH₃)₂NCH₂⁺ ion
Mass 72 → (CH₃)₂NCH₂CH₂⁺ ion

Chlorine part of XPS spectrum

12) Surface retarding agent
Using properties of retardation, SG is used for placing joint admixture, i.e. being formulated to retard the set of surface mortars in concrete to enable the aggregate to be exposed.

Example of formulation of placing joint admixture
Sodium gluconate 11.0 %
Antiseptic material 0.07 %
Coloring material 0.10 %
Water balance

4 Conclusion
1) Concrete is essential material in our life.
   If properly applied, long & high quality service can be expected.
   Proper mix-proportion & dense filling
   Exposed concrete in
   Otaru North Break Water
   Charles de Gaulle Airport

2) Cement industry plays a role of disposal facility in our society as raw material, fuel & powder admixture.

3) Chemical admixture can improve concrete quality by its performances, e.g. water reduction.

4) Message to young researchers
Doesn't Chemical admixture have disadvantage?