# COE Special Lecture

## Socio-Environmental Aspects of Construction materials

## " Concrete Admixtures"

**Date & time** **August 12 13:00～14:30**

**Place** **Hokkaido University**

**Presented by** **Dr.T.Amaya**



## Abbreviation

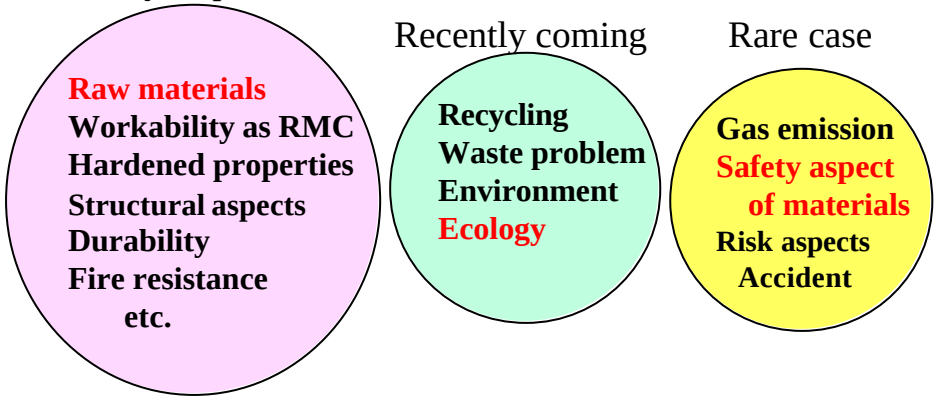
| | |
|---|---|
| RMC | Ready mixed concrete |
| AE-WR | Air entraining water reducer |
| AE-MRWR | Air entraining mid range water reducer |
| AE-HRWR | Air entraining high range water reducer |
| HRWR | High range water reducer |
| LS | Lignosulfonate |
| MS | Melaminesulfonate |
| SG | Sodium gluconate |
| PC | Polycarboxylate |



## 1. Introduction

**Most of presentations & reports on concrete can be classified into :---**

Basically important






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.

-- Total = 4,224 / Reports on concrete = 776 (1980～2003) (18.4%)

Fig-1 Number of reports on concrete

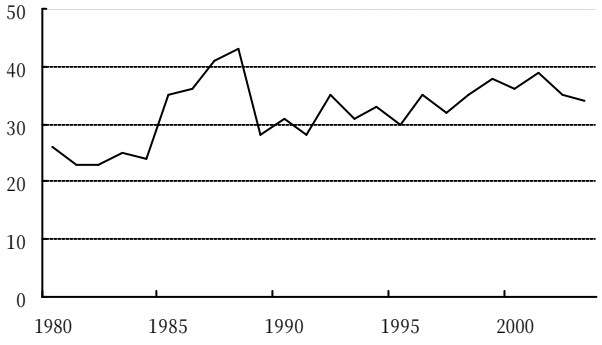



Fig-2 Reports on High Strength & High Fllowing Concrete

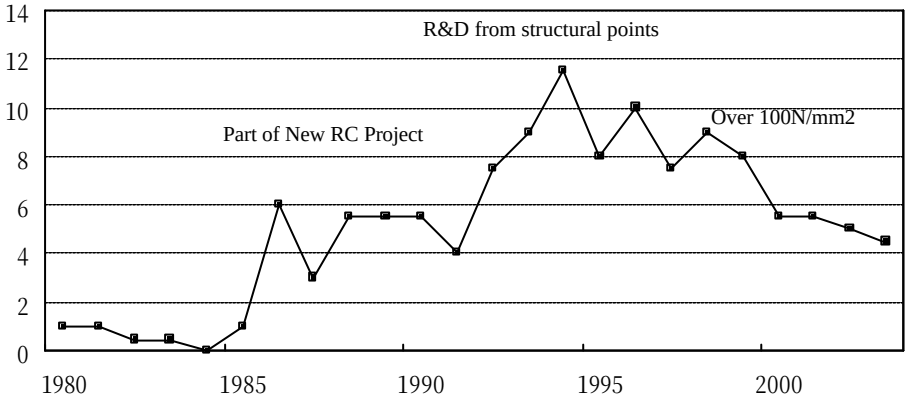
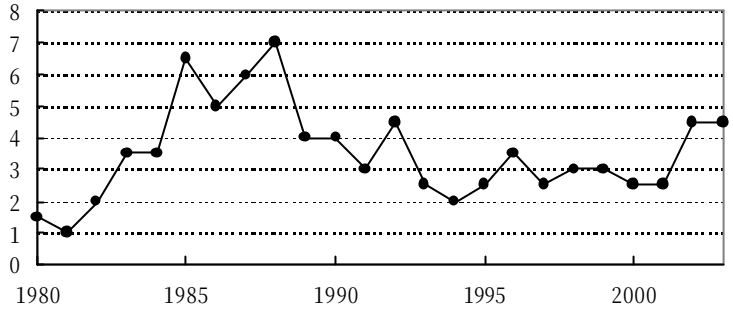




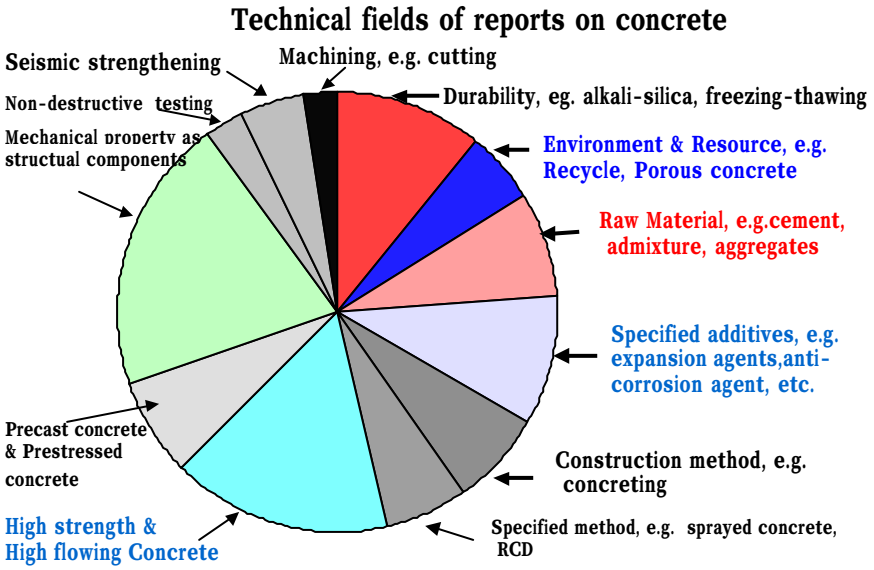

Fig-3 Number of reports on concrete durability




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

① If concrete is defined to be composite material of lime based binder and aggregates, "Sazare-Ishi" would be the oldest concrete.

→ National anthem

Natural concrete formed Before 270 million years

② Neolithic era, BC7000, 40 MPa of high strength concrete composed of lime (calcite) and aggregate was used in Israel.

③ 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)

④ Main cause of hardening of these concrete was carbonation of $Ca(OH)_2$.

⑤ 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

⑥ Industrialization of cement prevailed in the world.
Germany in 1850 / America in 1871 / Japan in 1875

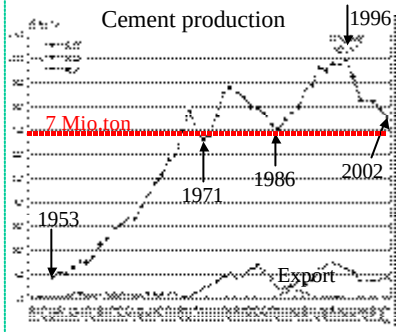


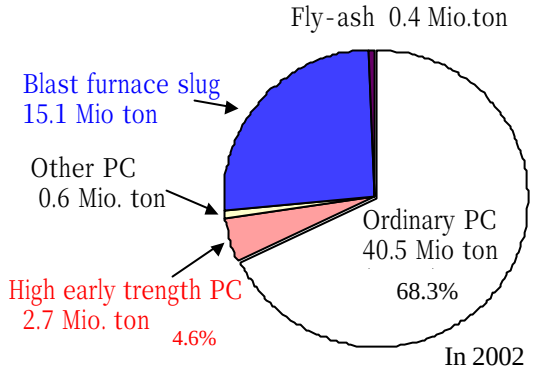
## 2) Production volume

**72.4 Mio ton** in 2004 Export 10.3 Mio.ton (14%)

Portland cement 43.8 Mio.ton 73.9%

Blended cement 15.5 Mio.ton 26.1%

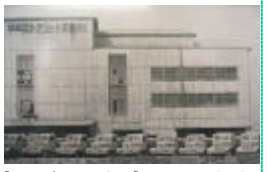





# 3 Chemical admixtures

## 1) Introduction


The 1st RMC plant in 1949

① 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.

② "**Admixtures**" are materials used for improving properties of concrete &/or mortar.
(Powdery) Admixture Improvement can be done by large amount.
Chemical admixture Improvement can be done by small amount
⇨ JIS A 6204 & Association norms

③ Improvement items are workability, strength development, etc.

④ Chemical admixture has been used to get workability with decreasing mixing water.



| | Admixtures | Example of main components | Use of purpose |
|---|---|---|---|
| **Chemical admixtures mainly for water reduction** | | | |
| 1 | Air-Entrainer | Nonion type surfactant | Workability / Freezing & thawing |
| 2 | AE Water Reducer | Lignosulfonate / Gluconate | |
| 3 | AE-High Range Water Reducer | Polycarboxylate | Workability / Higher strength etc. |
| 4 | AE-Mid range water reducer | Polycarboxylate / Lignosulfonate | |
| 5 | High Range Water Reducer | Melamine / Polycarboxylate | Strenth development / Workability |
| 6 | Set retarding water reducer | Gluconate | |
| 7 | Set accelerating water reducer | Nitrite / Nitrate / Thiocyanate | Setting time / Hardening time |
| 8 | Anti-freezing admixture | Nitrite / Nitrate / Thiocyanate | |
| 9 | Hardening accelerator | Calcium chloride | |
| 10 | Superplasticizer | Sulfonated naphthalene | Workability / Job-site addition |
| 11 | Anti-washout admixture | Cellulose base & Acrylic acid | Underwater concrete |
| **Other chemical admixtures** | | | |
| 12 | Shotcrete accelerator | Calcium aluminate | Setting time / Hardening time |
| 13 | Corrosion Inhibitor | Nitrite / Aminoalcohol | Corrosion |
| 14 | Shrinkage reducing admixture | Copolymer of Alkyleneoxido | Surface tension |
| **Powder type admixture** | | | |
| 15 | Shrinkage compensation agent | CSA | Introduce chemical prestress |
| 16 | Fly ash | | Durability / Long term strength |
| 17 | Blast furnace slug powder | | |
| 18 | Silica fume | | |
| 19 | Calcite powder | | Workability / Segregation |
| 20 | Cement polymer emulsion | Emulsion of SBR, EVA & Acryl | Workability /Durability / Adhesion |

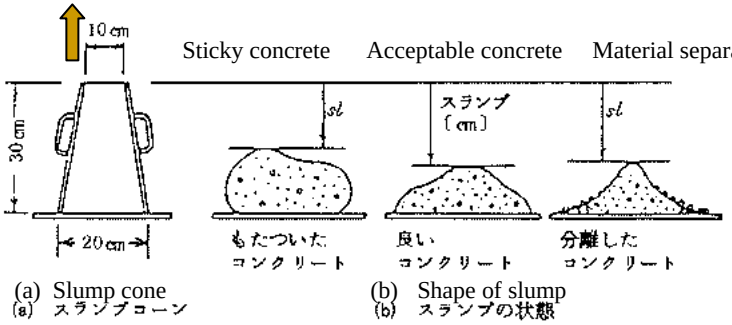
## 2) General properties of chemical admixtures

① Chemical admixture is one kind of surfactant to get
- -- better workability of RMC
- -- better durability of hardened concrete

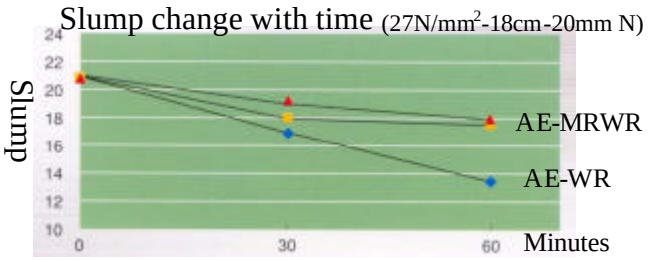
② Chemical admixture can :--
- -- reduce water in RMC under the same slump (flow)
- -- introduce small air-bubble properly
- -- extend working time of RMC, e.g. slump & flow life

③ Chemical admixture react cement particles by :--
- -- electrostatic repulsive force
- -- chelate effect
- -- steric hindrance

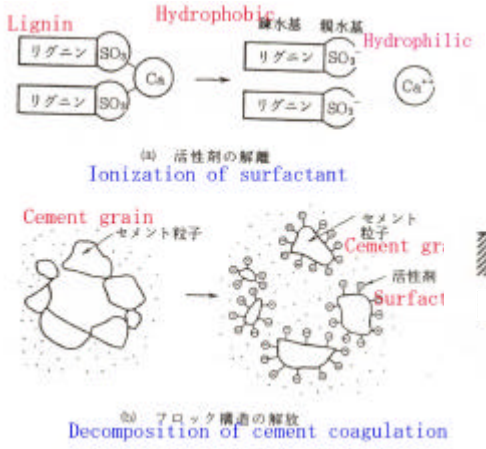


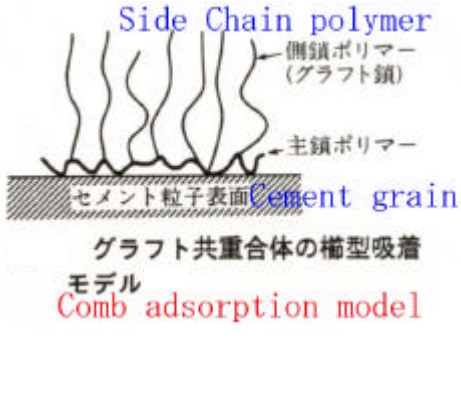



(a) Slump cone (a) スランプコーン (b) Shape of slump (b) スランプの状態








## 3) History of water reducer

### ① Long history

**Main water reducing admixtures used in concrete industry**

| Year | Raw materials | | Mechanism of effect |
|---|---|---|---|
| ~1920 | Lignosulfonate (LS) | By-product of pulp industry | Electrostatic repulsion |
| 1931 | Sodium Gluconate (SG) | Fermentation of glucose | Chelate of COO⁻ion |
| 1965 | Sulfonated naphtalene | Copolymerized by formaldehyde | Electrostatic repulsion |
| 1966 | Sulfonated melamine | Copolymerized by formaldehyde | Electrostatic repulsion |
| 1982 | Modified polycarboxylate | (Meth)acrylate copolymer | Steric hindrance |
| 1985 | Amino sulphonated | Aminosulphonate copolymer | Steric hindrance |
| 1990 | Comb type polycarboxylate | (Meth)acrylate copolymer | Steric hindrance |
| 1998 | Modified polycarboxylate | Polyamido modified aclylate | Steric hindrance |

Remark: Even LS & SG based admixtures are still under improvement, e.g. additives.
Market share of LS based admixture is over 50%.
(Meth)acrylate copolymer based admixture is still under development

**The 1st use of admixture in Japan might be in 1932.**

## ② 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 costis important for management because of water.



## 4) Water reducers

### (1) Lignosulfonate (LS) based Water Reducer

① Main use of LS (in 1997 / Solid content base)
105 k ton = Admixture (67k t) + Dye disperser (8k t) +……..

② Ca, Na, Mg base / High molecular electrolyte / Anion type
Molecular weight of LS : ～ 10,000 or more

③ 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.

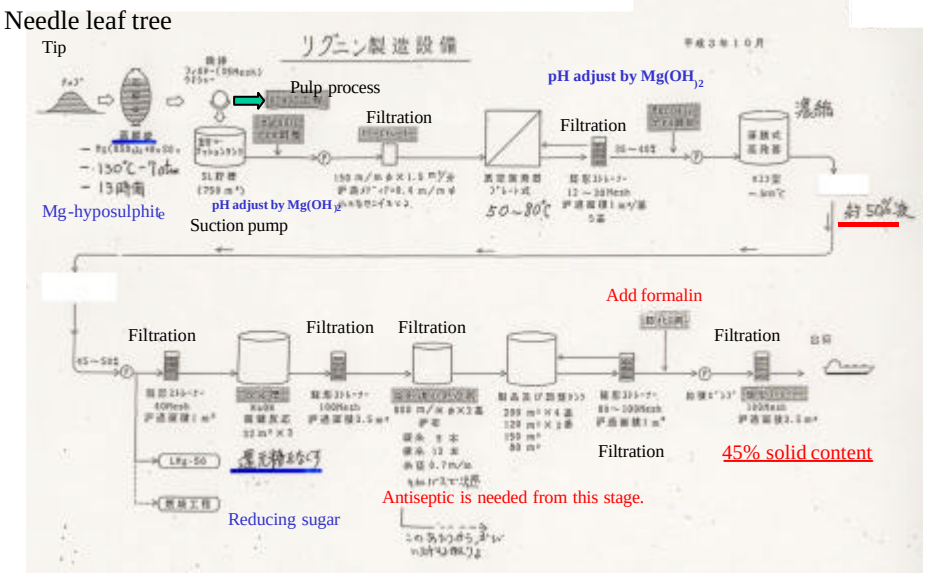
④ Cheapest raw material as admixture raw materials

⑤ Cement dispersion is done by electrostatic repulsion.

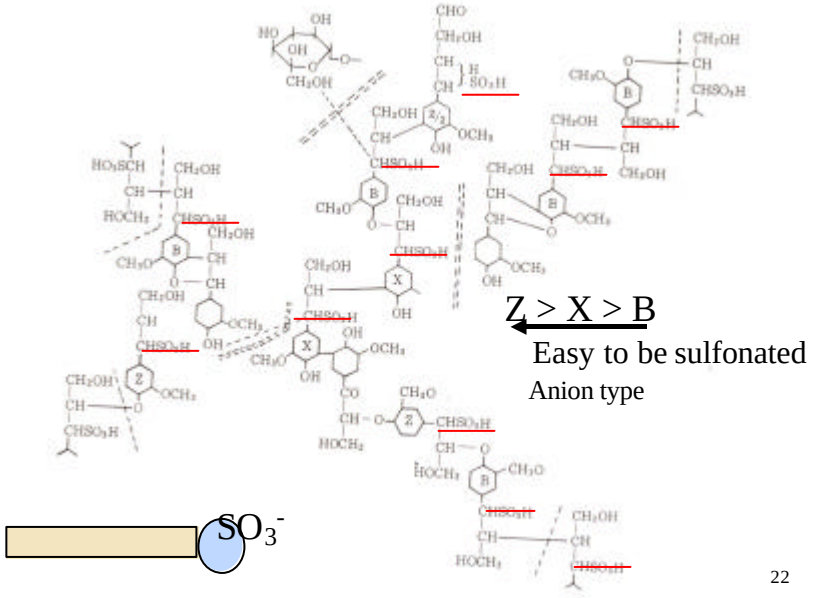
⑥ Basically sugar is contained in LS raw material, which is effective for retardation.



⑦ LS production at pulp factory (In case of Mg salt)




⑧ Structure of LS is complicated, because lignin is natural product.



## ⑨ 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) | 0～0.4 % (Seasonal adjustment) |
| Antiseptic* | 0～0.035 % (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) | 0～0.5 % (Seasonal adjustment) |
| Antiseptic* | 0～0.05% (Seasonal adjustment) |

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



## ⑩ Formaldehyde calculation

Base Cement 300 kg/m$^3$

LS base AE-WR Cement x 0.5 %

(Contain 0.3 % of 37 % formalin)

300 kg/m$^3$ x 0.5% x 0.3% x 37% =1.7 g/m$^3$ of formaldehyde is contained in 1m$^3$ of ready mixed concrete.

If concrete is applied to the floor, 10m$^2$ x 10cm$^H$ (1m$^3$) and if 1% of formaldehyde is emitted from concrete,

✍ 17mg of formaldehyde

If room height is 1.7m ✍ 1,000 μg/m$^3$

**Ventilation before use**

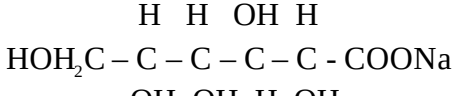
Guideline : 100 μg/m$^3$ 0.08ppm




## 2) Sodium Gluconate (SG) based Water Reducer

① SG is produced by fermentation of glucose.

② 




MW = 431

③ Reaction with cement particle

Water Reduction : Electrostatic force with cement grain like LS

Retardation : Strong chelate property above pH >12

Gluconate ion reacts with $Ca^{2+}$ initially released, and forms “protective layer” which causes retardation.


④ Advantage Hot season concreting

Superior surface finish



## ④ 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 |

Exposed concrete

**b Without formalin**

| | |
|---|---|
| Sodium gluconate | 31.0 % |
| Antiseptic material | 0.02 % |
| Coloring material | 0.2 % |
| Water | balance |

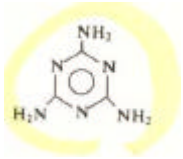
## 3) Melamine sulfonates & formaldehyde condensation polymer (MS) based High Range Water Reducer (HRWR)

① 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.

② Production of MS

a For melamine-formaldehyde copolymer, mole ratio of
Melamine : Formaldehyde = 1 : 3
(from operation 1 : 3.3)



b Sulfonation can be done by $SO_3$ base, e.g. pyrosulfite, sulfamic acid, sulfanilic acid.



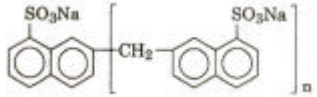
④ Recent tendency is moving to PC based admixture, because :--
-- Higher water reduction / Better workability
-- No eye & skin irritation

⑤ Formaldehyde (FA) calculation
Cement 400 kg/m³
MS base HRWR Cement x 1.0 % (Remain 1% of free FA)

400 kg/m³ x 1% x 1% =40g/m³ 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 develope
by Dr.Hattori in 1965.





## ⑥ Formaldehyde problem happened in Switzerland

a In 1990 formaldehyde problem was pointed out by Swiss government with data, if concrete, mixed with melamine or naphthalene based admixture, is wasted at the source of water-supply.

b Swiss Admixture Association (FSHBZ) checked and re-tested the contents of complaint.

c FSHBZ submitted the opposition report with the proposal.

d Proposal says all criteria, covered from production to waste, are checked by 3rd party.
FSHBZ label is allowed if all check points are approved by auditor.


e This is self-control norm.
⇨ There is limitation. Ex. Formalin content < 0.5%



## 4) Polycarboxylic acid (PA) polymer based admixture.

### ① Background of development

a In 1986 JASS 5 requires water content to be less than 185kg/m³. "New RC Project" headed by MLIT started for high strength concrete, 60N/mm². (MLIT = Ministry of Land Infrastructure & Transport)

b 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.

c To meet the requirements, many chemicals are tested, e.g. polycarboxylate ether, maleic acid co-polymer.

d In 1984 Nippon Shokubai invented the polymer for admixture.
⇔ Epoch-making in chemical admixture technology

## ② Base technology of Nihon Shokubai

A Monomer of Polyalkylene glycol ester and (meth)acrylic acid

B (Meth)acrylate monomer (90～5 wt%) 10~95 wt%

C Monomer able to copolymerize with A & B (0～50 wt%)

**A**

$$CH_2 = \underset{\underset{\|}{O}}{C}(R_1)-C-O-(R_2O)_n-R_3$$

**C**

**B**

$$CH_2 = C(R_1)-C(=O)OX$$

$R_1$ : H or Methyl $CH_3$

$R_2$ : Alkylene $C_nH_{2n}^{2+}$

$R_3$ : H or alkyl $C_nH_{2n+1}$

Here Acrylic acid $CH_2=C(H)-COOH$

Methacrylic acid $CH_2=C(CH_3)-COOH$

Glycol $C_nH_{2n}(OH)_2$

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

ACBABB AACA



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.



## ③ Example of formulation (wt.%)

| Product name | 80N | 80S |
|---|---|---|
| Polymer-600 | 37.1 | 22.3 |
| Polymer-700 | ----- | 29.7 |
| Ethylenediamine | 1.2 | 1.2 |
| TEA | 0.8 | 0.8 |
| Coloring | 0.3 | 0.3 |
| Water | 59.4 | 44.6 |
| AE agent | 0.2 | 0.2 |
| AF agent | 1.0 | 0.9 |

Polymer combination

To get longer workability time



## ④ High flowing & high strength concrete

**Concrete Mix Proportion :**

W / B : 25 % , S / A : 45.3 %

B : 85 % Moderate Heat Cement (Mitsubishi)
15 % undensified Silicafume (ELCEM U 904)

140 kg Water / m³ , 560 kg Binder / m³
crashed and pit sand , crashed aggregate

3 m³ were produced in placed in a lorry

**Concrete Mixing :** Double Mixing Methode
Total Mixing Time : 70 sec

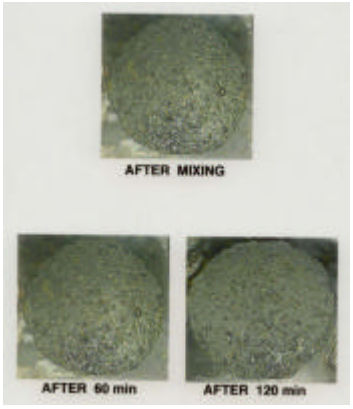
**Test Result :** 3.2 % SM 1200 N , air content < 1 %

| Time min | Slump Flow cm | Flow Speed 50 cm | C. T. °C | V 1 | V 2 cm / sec | V 3 |
|---|---|---|---|---|---|---|
| 0 | 66 x 66 | 4 | 30 | 16.9 | 17.0 | 14.6 |
| 30 | 66 x 65.5 | 4.5 | 29 | 12.7 | 10.1 | 9.5 |
| 60 | 65 x 64.5 | 5 | 28 | 12.5 | 9.8 | 8.7 |
| 90 | 65 x 65 | 4 | 28 | 13.0 | 14.0 | ---- |
| 120 | 65 x 65 | 4 | 27.5 | 16.2 | 12.1 | 11.2 |

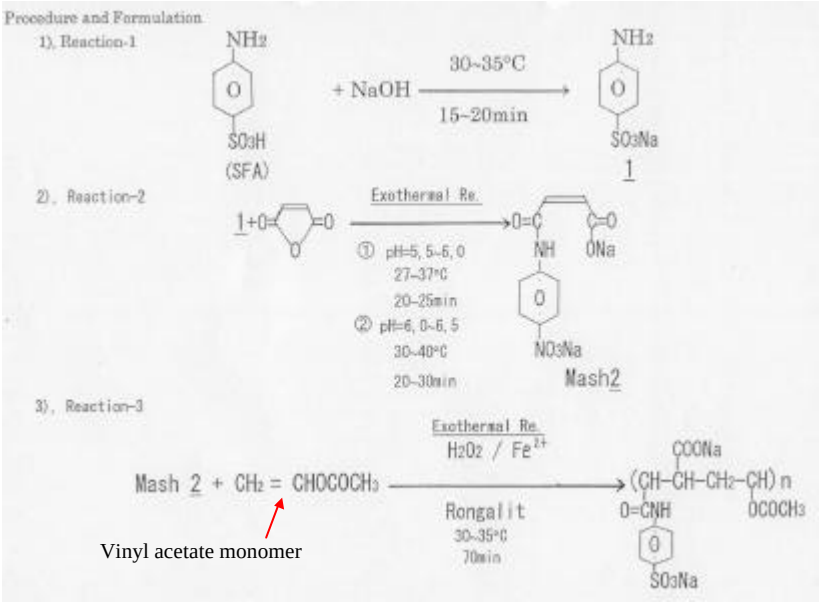
V 1, 2, 3 : L - Flow Meter

**Compressive Strength :**

| | after concrete mixing | after 90 min | cores |
|---|---|---|---|
| 1 week | 54 N / mm² | 54 | --- |
| 4 weeks | 88 | 92 | 75 |



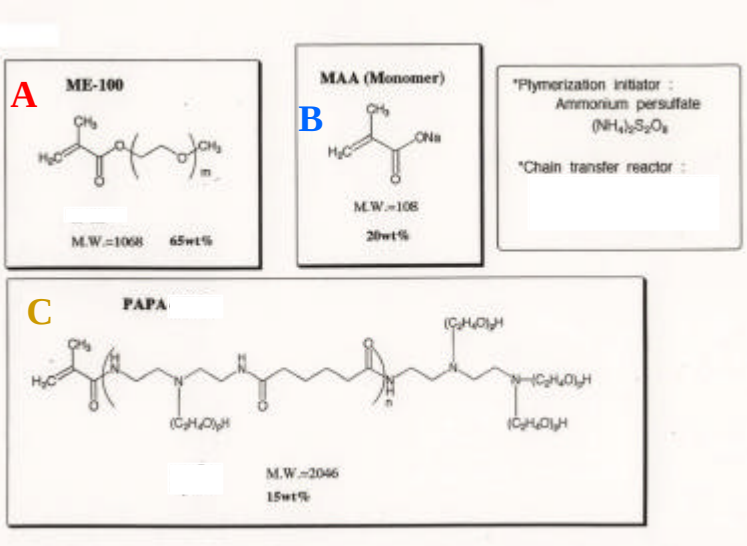
## ⑤ Example of polymer synthesis ：Radical chain reaction






## ⑥ Example of polymer synthesis --- Modified Nihon Shokubai

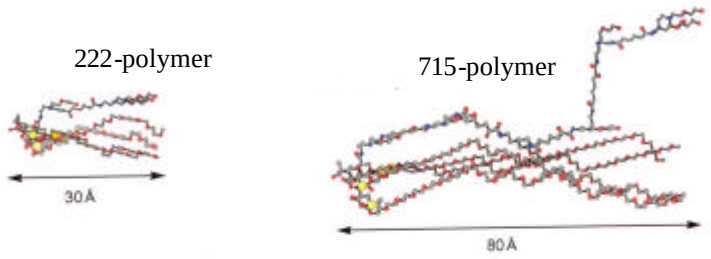
3 intermediates co-polymerize, in the case of 715Mpolymer



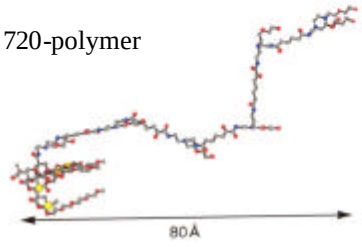



222-polymer

715-polymer



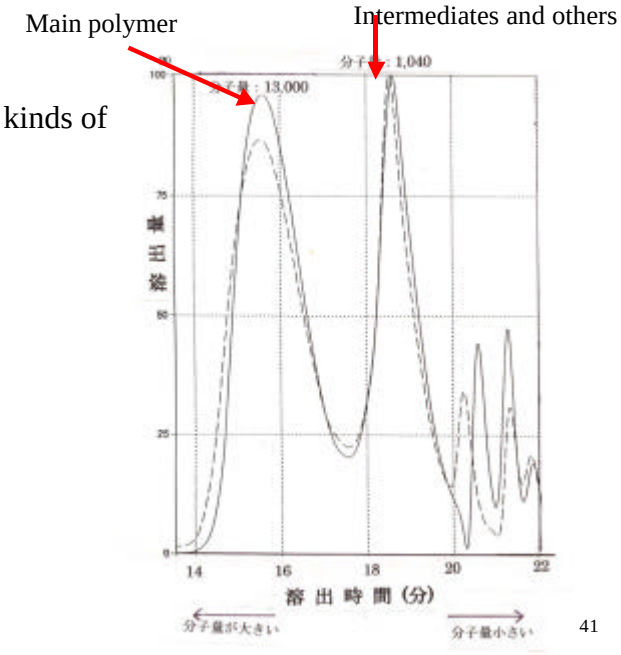

720-polymer




-COONa




Composed of many kinds of Polymers !!



## 5) Mid range AE-Water Reducers

① AE-WR ➡ Mid range AE-WR ➡ AE-HRWR

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

② 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 & Oosaka area.

--- Especially 20-30 N/mm² concrete

--- Water content is checked at job site.

③ Then requirements are just between AE-WR & AE-HRWR regarding water reduction, slump keeping & price.



## 6) High range water reducer (HRWR)

① HRWR has been mainly used for **PCa** & **PC**, not for RMC factory.

② 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.

③ Main raw materials of HRWR are :--

-- **Melamine** sulfonate & formaldehyde condensation polymer (MS)

-- **Naphthalene** sulfonate & formaldehyde condensation polymer (NS)

④ Polycarboxylate (PA) polymer based admixture has gradually been used, because of better water reduction.

-- Utilize the technology of PC based admixture



④ Idea of formulation

a Based on AE-HRWR

i 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 |

ii 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



## ⑤ 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

PCa mold preparation

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

① After setting of cement, strength development starts.
② 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
③ Chemicals used for hardening accelerator effects on setting a little, followings are famous raw materials:
Ca-nitrite, Ca-thiocyanate, Ca-formate, TEA
④ $CaCl_2$ was used for this purpose, but stopped.
⑤ Example of formulation (wt.%)

| | |
|---|---|
| Lactic acid | 5.0 |
| Ca- nitrite | 13.5 |
| Methyldiethanolamine | 6.5 |
| Water | Balance? |



## 8) Anti-freezing admixture

① 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.
② Technical bases of anti-freezing admixture are :--
Accelerating the initial hydration of cement
Lowering freezing point
③ 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 |



⑥ Example of formulation (wt.%)

| | |
|---|---|
| Ca- thiocyanate | 18.0 |
| Na- thiosulfate | 15.0 |
| Tri-ethanol amine (80% soln) | 2.0 |
| Ca –LS (40% soln) | 32.5 |
| Water | Balance |

⑦ Caution to be taken
Ⅰ Don't use together thiocyanate type and nitrite type
Ⅱ Nitrite is the cancer suspicious chemical in EU.
Ⅲ In summer nitrite & nitrate dissolved in capillary water may cause NOx gas emission problem.



## 9) Quick setting admixture

① 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/mm$^2$

② 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.
③ As non-alkali type, Ca-aluminate, Ca-sulfoaluminate and aluminum sulfate are gradually used.

④ 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.




⑤ Example of steel segment

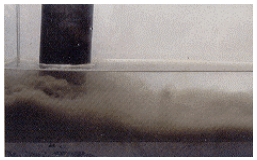
| | | |
|---|---|---|
| Cement | 1000 kg | W/C = 46.7 % |
| Acryl emulsion (44% solid) | 160 kg | Polymer/C = 7 % |
| Water | 380 kg | |
| Crashed glass sand | 500 kg | |
| Admixture (45% $Al_2(SO_4)_3$) | 60 kg | |

Spray = 1 $m^3/h$ ⇒ No dust / Easy to trowel / Good adhesion



## 10) Anti-washout admixture for underwater concrete

① 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?

⇩

Increase viscosity

Turbidity by suspended particles  Self leveling

How to minimize environmental impact of cement washout?

② Viscous admixture

Main component ; Water soluble polymer, such as Cellulose base & Acrylic acid base

Other components ; Anti foam agent, (AE)Water reducer, etc.



## ④ From norms on anti-washout admixture

Guideline of underwater concrete is described in JSCE's norm.

Japan Society of Civil Engineers

Mix proportion of under-water concrete

| Gmax | Flow | W/C | S/a | Water | Cement | Sand | Gravel | Viscous | HRWR |
|---|---|---|---|---|---|---|---|---|---|
| mm | cm | % | % | Kg/$m^3$ | | | | | C x % |
| 25 | 50 ± 3 | 55 | 40 | 220 | 400 | 635 | 960 | 2.5 | 1.5 |

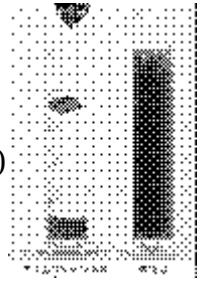
Viscous material is cellulose derivatives.

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 ( $\sigma_{water}/\sigma_{air}$ =90%)





## 11) Corrosion inhibitor admixture

① Formulated to protect embedded reinforcing steel from corrosion, and to provide an effective means for **extending the service life** of concrete structures.

② Basically surface of steel in high alkali is protected from corrosion because of being covered by hydrophobic thin layer, 20～60Å, of $\gamma$ –$Fe_2O_3$.

By carbonation &/or chloride ion migration in concrete, steel corrosion starts, and then cracks are formed. (Volume of $Fe_2O_3$ is 1.5 times larger than that of steel.)

Once crack forms, corrosion speed is enhanced.

④ **Two types of corrosion inhibitor**

a Anode action type : $NO_2^-$ ion / JIS A 6205

Depresses oxidation of steel & forms $Fe_2O_3$ 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 Å thickness

Hydroxide at steel surface are replaced by AMA

AMA can displace $Cl^-$ ions from steel surface

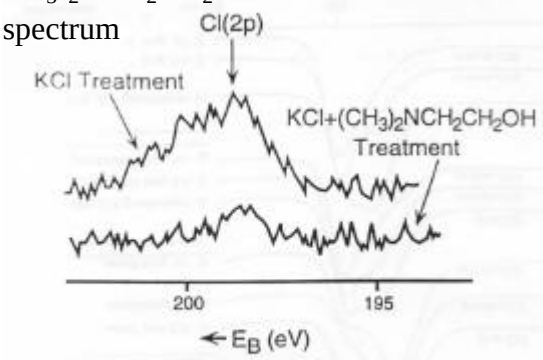


⑤ After immersing Pt foil in dimethylethanolamine ,
surface material was checked by SIMS.

Mass 58 ⟶ $(CH_3)_2NCH_2^+$ ion

Mass 72 ⟶ $(CH_3)_2NCH_2CH_2^+$ ion

⑥ Chlorine part of XPS spectrum

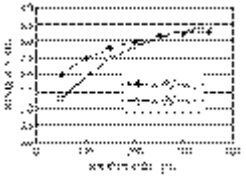



Note the almost complete elimination of chlorine at the surface by the aminoalcohol treatment

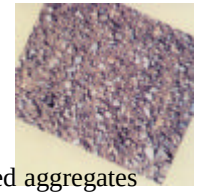


## 12) Surface retarding agent

① 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.



Washing out



Exposed aggregates

② **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
Otaru North Break Water

Exposed concrete in
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 ?**