Conceptual cement for environmental and durability requirements

Kazuo Yamada

R&D Center

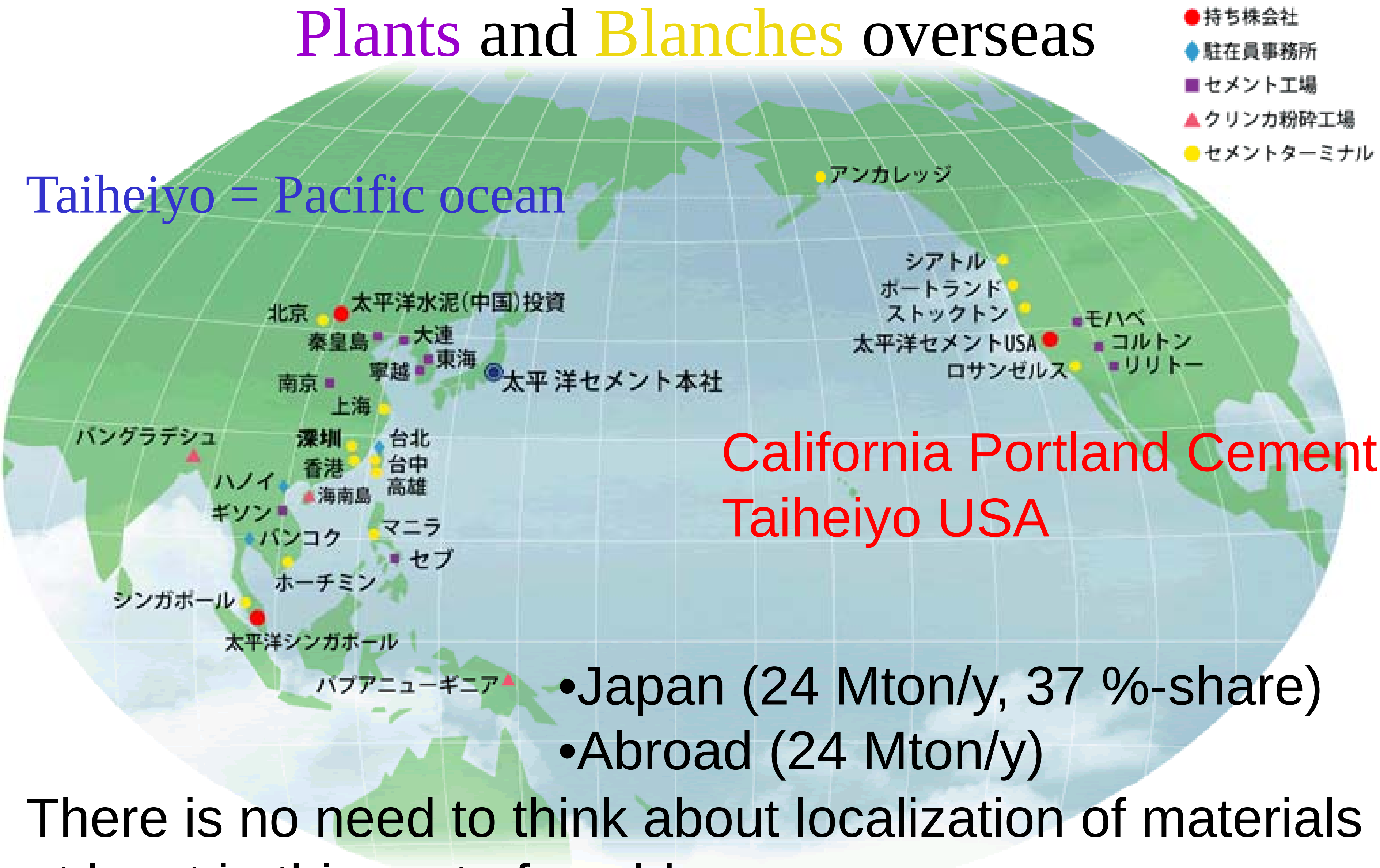
Taiheiyo Cement Corp.

Conceptual cement

- Conceptual cement
  - Today's proposal is just under personal consideration.
  - There is no quantification for environmental impacts.
  - Sales persons in our company disagree with this kind of new cement!
- High C_3A cement is really bad?
  - Why high C_3A cement is important,
  - The method how we can improve the negative parts will be explained.
- A proposal to produce a new type of cement
  - It has to satisfy the requirements from environments
  - It must have at least standard performance as conventional cement including durability. It is nonsense, if the performance of new environmental friendly cement is inferior.
  - This is a story of hybridization of our knowledge but not innovative.

Taiheiyo Cement

Plants and Blanches overseas



Taiheiyo = Pacific ocean

California Portland Cement
Taiheiyo USA

- Japan (24 Mton/y, 37 %-share)
- Abroad (24 Mton/y)

There is no need to think about localization of materials at least in this part of world.

Indispensable cement for buildings or road constructions.
Our business is to supply materials to active societies.

We are the Artery industry
and also the Vein industry

私たちは静脈産業です。

元気がみなぎる社会から大量に発生するゴミ。
それらを資源として再活用、環境を守るのも私たちの仕事です。

私たちは動脈産業です。

ビルや道路をつくるのに欠かせないセメント。
活気にあふれた社会へ資材を送りこむのも、私たちの仕事です。

Enormous amount of wastes produced from active societies.
Our business is to recycle them for the protection of environments.

Taiheiyo Cement Corp.

http://www.taiheiyo-cement.co.jp

If I could live life over again, I want to be a building.

Incinerator ash of municipal wastes treated as landfill
comes back life again as cement.

Waste material management

- Cement industry has already been an indispensable process to accept significant amounts of wastes in the human society at least in Japan.
- ***Without cement industry, it is impossible to keep our life!***

Example of Japan, 2004

Remained capacity of final landfill site for industrial wastes: 184 Mm^3

Its remained life: 7.2 y

Annual amount of industrial wastes: 25 Mm^3/y

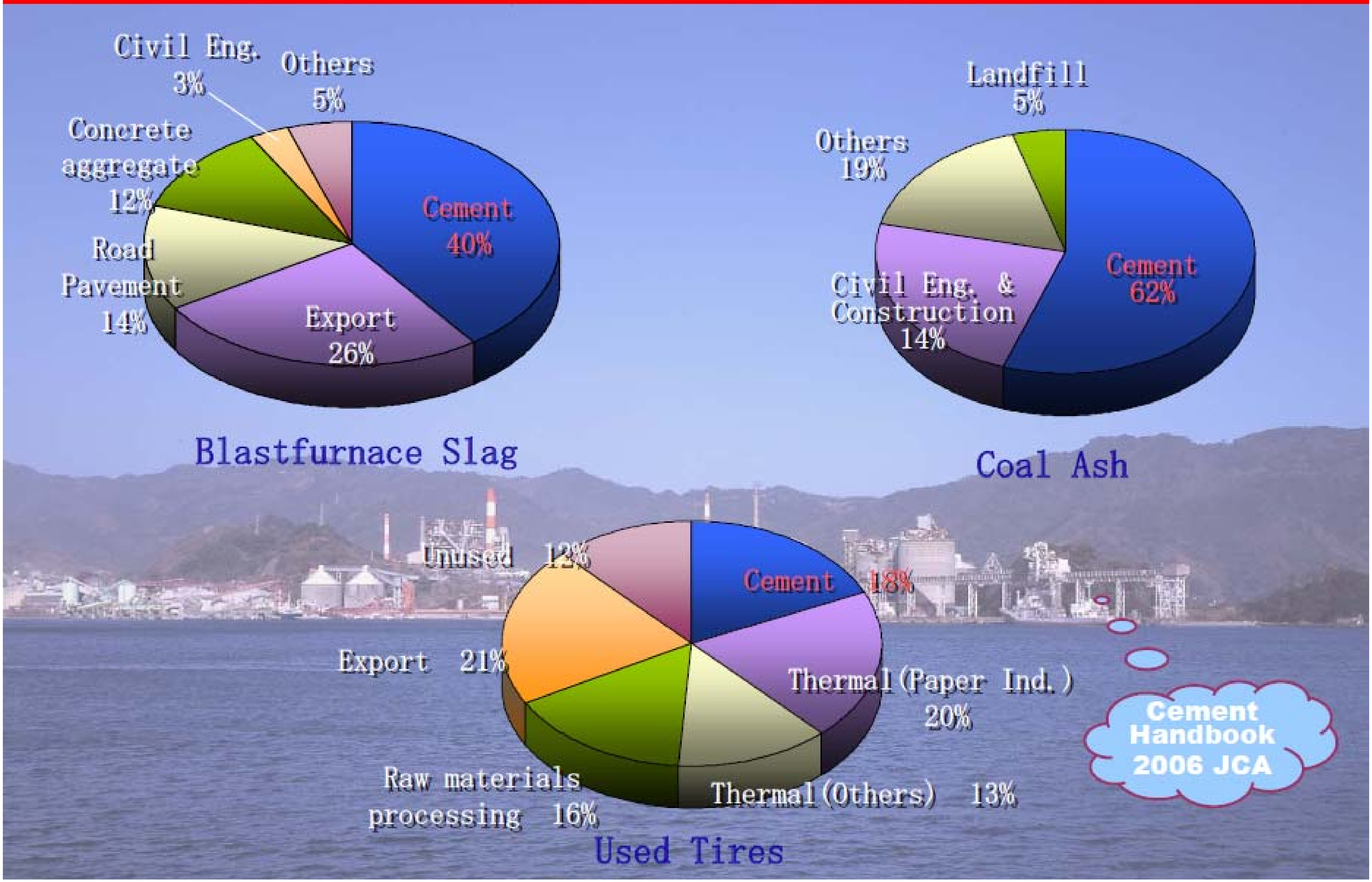
Annual amount of wastes received by cement plants 20 Mm^3/y

Cement industry save almost half size of landfill site.

Waste Materials Used in Cement Industry				kton/y				
		fiscal year						
Item		2001	2002	2003	2004	2005	2006	2007
Blast furnace slag (mainly blended)		11,915	10,474	10,173	9,231	9,214	9,711	9,304
Coal ash (mainly raw meal)		5,822	6,320	6,429	6,937	7,185	6,995	7,256
Gypsum by-product		2,568	2,556	2,530	2,572	2,707	2,787	2,636
Dirt, Sludge		2,235	2,286	2,413	2,659	2,526	2,965	3,175
Soil from construction		**0**	**269**	**629**	**1,692**	**2,097**	**2,589**	**2,643**
Non-ferrous slag		1,236	1,039	1,143	1,305	1,318	1,098	1,028
Unburned ash, soot, dust		943	874	953	1,110	1,189	982	1,173
Molding sand		492	507	565	607	601	650	610
Steel manufacture slag		935	803	577	465	467	633	549
Wood chips		20	149	271	305	340	372	319
Waste plastic		171	211	255	283	302	365	408
Coal tailing		574	522	390	297	280	203	155
Recycled oil		204	252	238	236	228	249	279
Waste oil		149	100	173	214	219	225	200
Used tire		284	253	230	221	194	163	148
Used clay		82	97	97	16	173	213	200
Bone-meal feed		2	92	122	90	85	74	7
Others		428	435	378	452	468	615	565
Total	27,359	28,061	27,238	27,566	28,782	29,593	30,890	30,720
Ratio: kg/t-cement	332	355	361	375	401	400	423	436
Cement production	82,407	79,045	75,451	73,504	71,771	73,931	73,931	70,600

Cement plant use

TAIHEIYO CEMENT



Role of cement industry

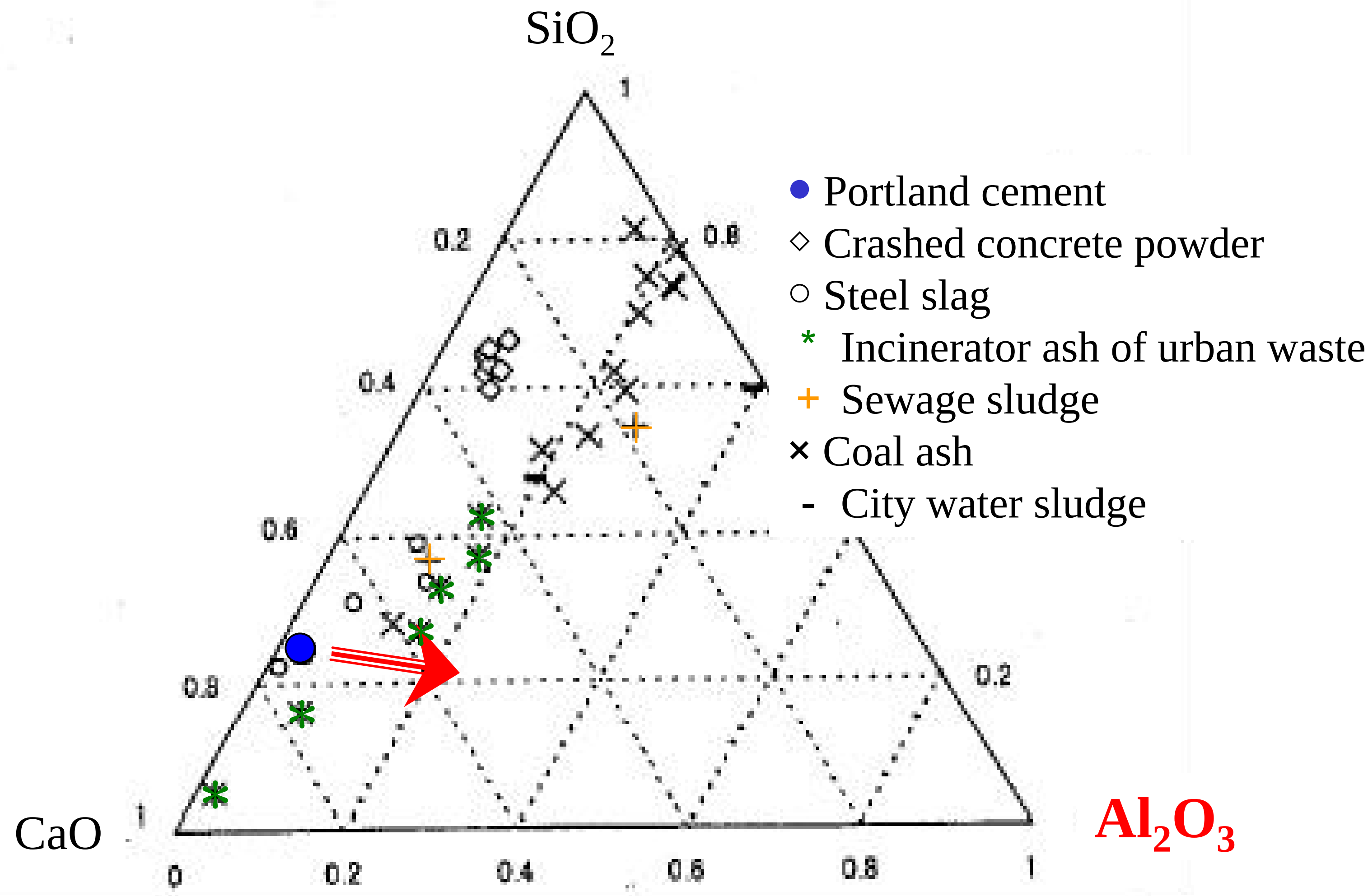
- We are the Artery industry
  - Binder in concrete
  - Corrosion inhibitor for steel reinforcement
- and also the Vein industry
  - Utilization of various and enormous solid wastes
  - Thermal recycle of combustible wastes
- under a control of environmental impacts
  - Less CO_2 and hazardous materials emissions
  - Purification of pollutants such as dioxins and recovery of heavy metals as resources

More wastes!

We have

- Economical reason.
- Environmental reason.

Using more wastes result in higher Al_2O_3 content



Typical example of high C_3A cement: Japanese ecocement

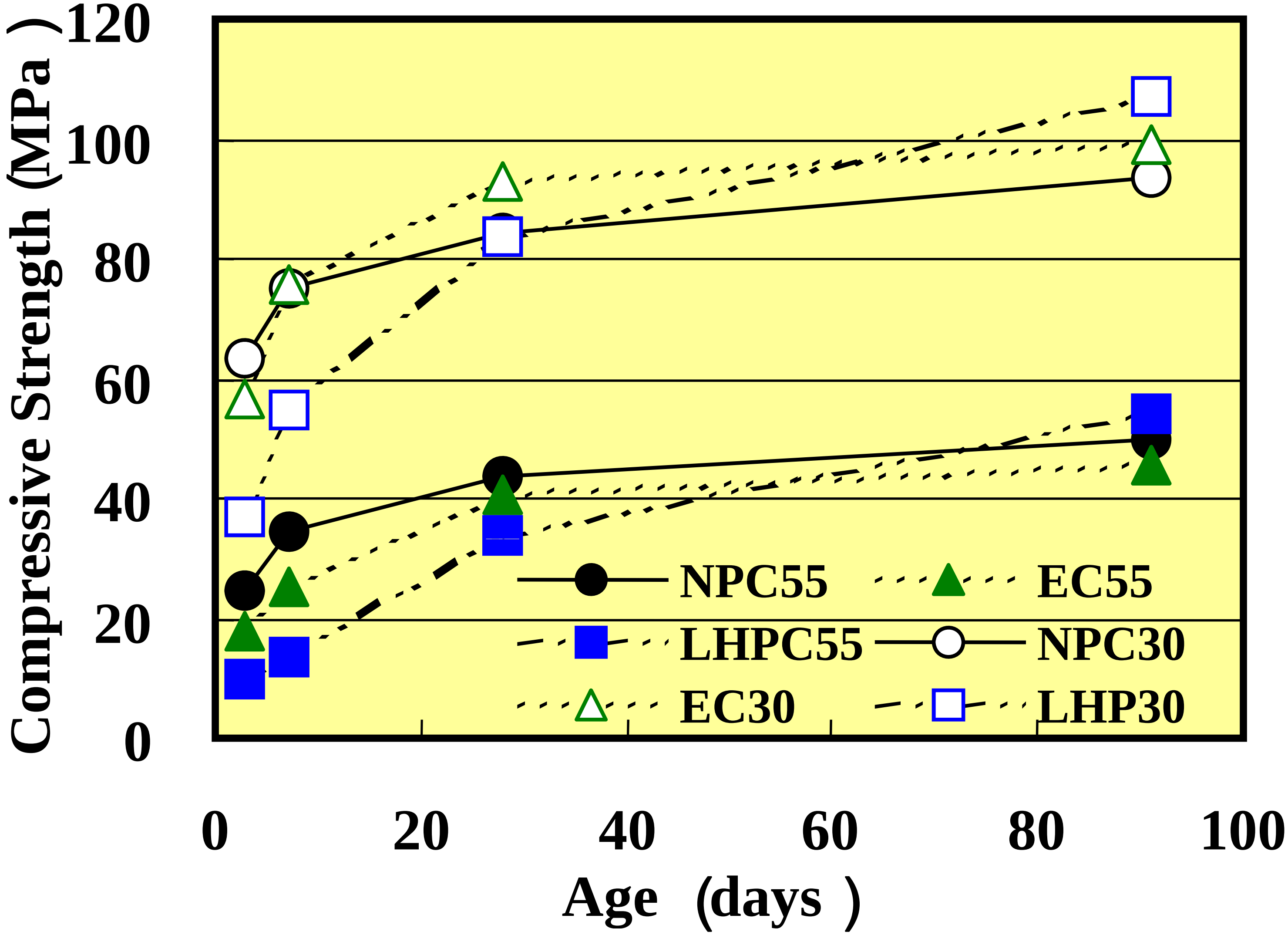
- Ecocement: Portland cement but more than half is wastes origin.
- It satisfies CEM I 42.4N by EN197-1:2000.
- Compared with JIS, Cl content is over. 0.05% in ecocement vs. 0.035% by standard.
- At present, two plants are in commercial operation in large Tokyo area to produce around 250 kton/y.

Comparison of chemical and mineral compositions of ecocement compared to normal and low heat portland cements

Type	Chemical Composition (%)							
	ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O_{eq}	Cl
EC	0.3	17.0	8.0	4.4	61.0	3.7	0.26	0.053
NPC	0.6	21.2	5.2	2.8	64.2	2.0	0.65	0.005
LC	0.6	26.3	2.8	3.1	62.4	2.3	0.45	0.004

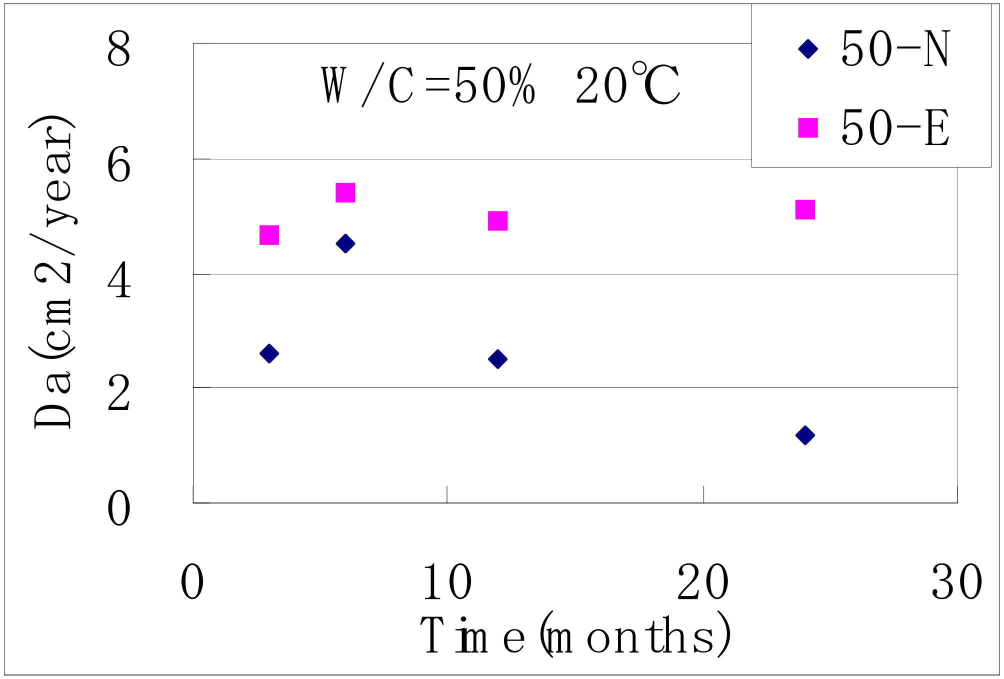
Type	Mineral Composition (%)			
	C_3S	C_2S	C_3A	C_4AF
EC	47	15	13	13
NPC	59	15	8	9
LC	31	53	3	8

Compressive Strength Development



Strength development is acceptable.

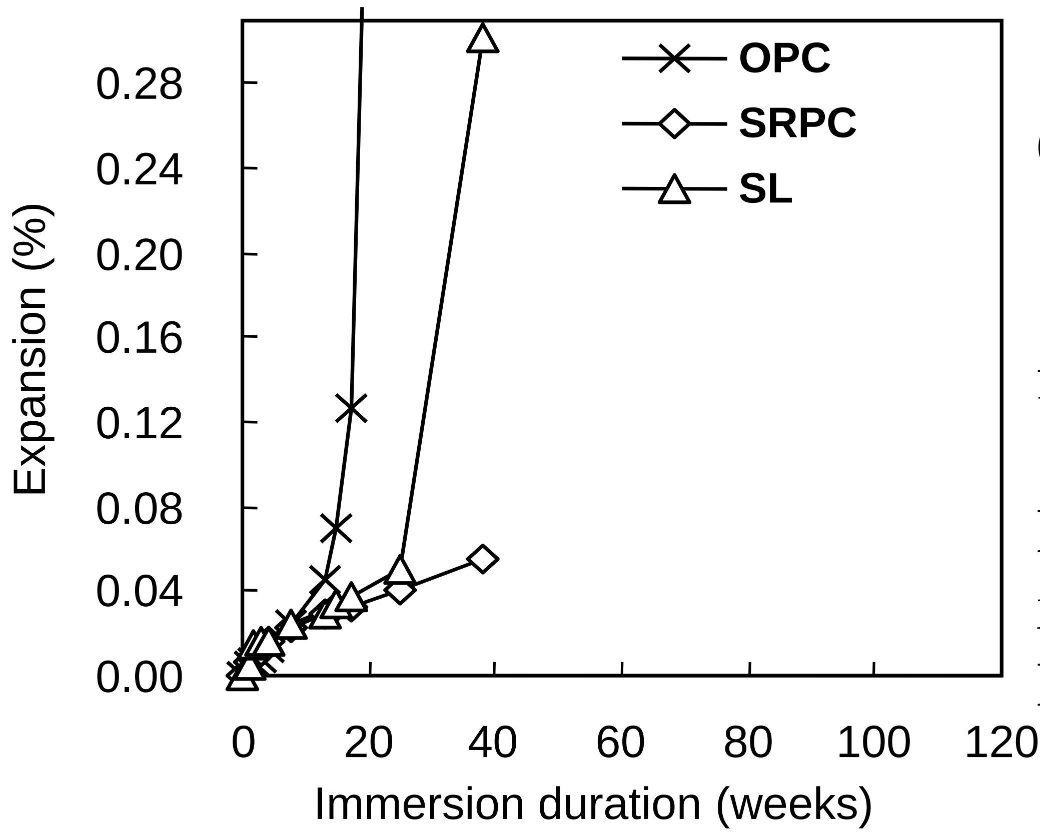
Chloride ingress by immersion test in 3% NaCl solution



Apparent diffusion coefficient of Cl is higher in ecocement than NPC. Problem is the no time reduction of Da for ecocement, possibly due to the perfect hydration at early ages.

Sulfate attack

ASTM C1012, 5%Na_2SO_4



OPC: Japanese
SRPC: Canadian
SL: Japanese 40% blast furnace slag (Al_2O_3=15%)

High reactive alumina content is basically bad.
Ecocement will be worse!

Under a collaboration with Prof. D. Hooton

Conflicting requirements

- For durability
  - Lower C_3A & C_3S
- For waste materials utilization
  - More Al_2O_3

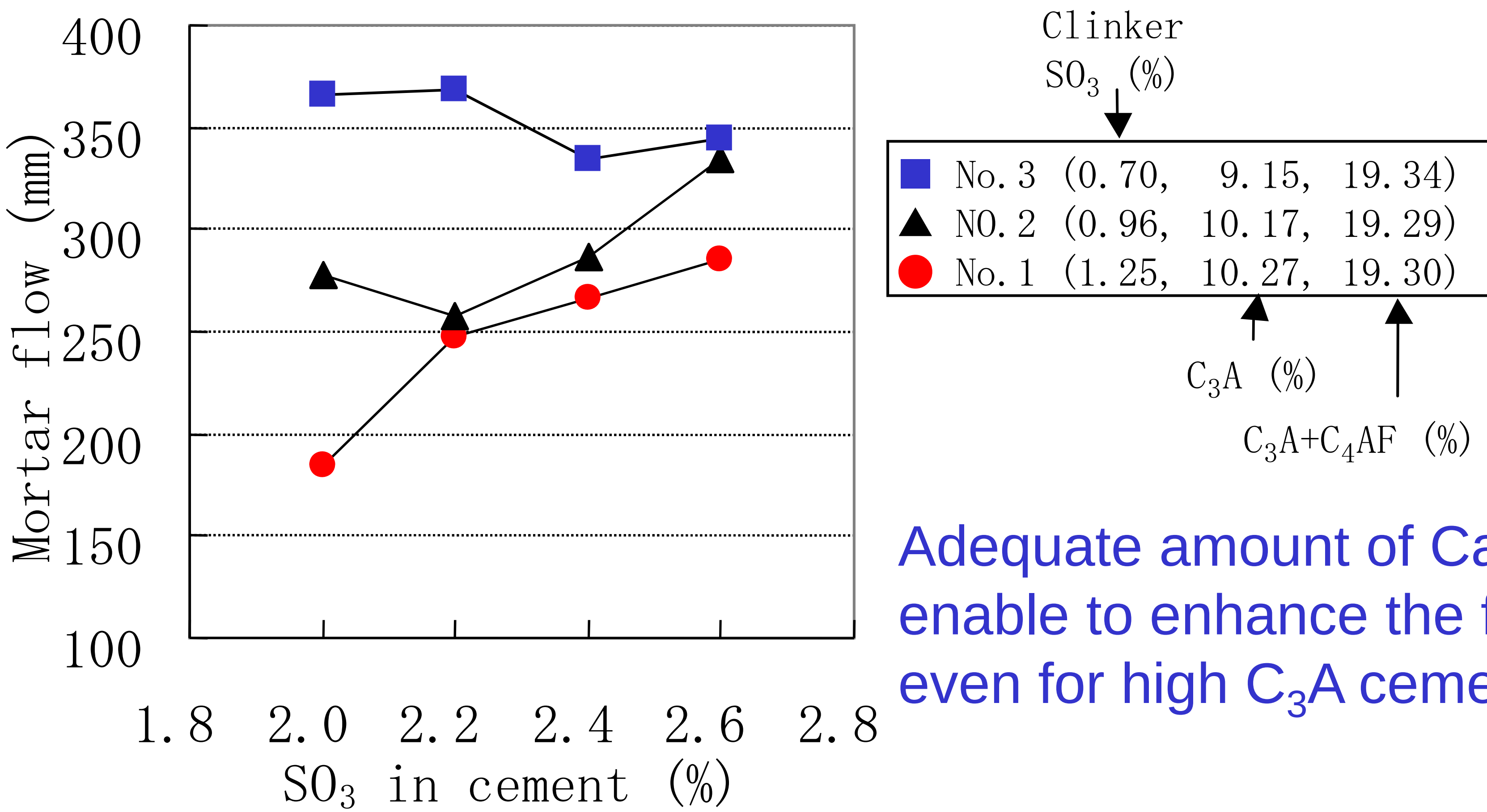
Durability

- Workability to eliminate defects during placement: Lower C_3A? Ultra-high strength more than 100-200 MPa is only possible with low heat cement with low C_3A.
- Hydration heat: Lower C_3A? For mass concrete, belite-rich and low C_3A cement is preferable.
- Early age strength development of cover concrete: Belite-rich cement or blended cement is questionable because of the lower early age strength.
- Crack by autogeneous and drying shrinkage?
- Chloride ingress?
- Sulfate attack: High Al slag is deteriorative?
- Carbonation?
- ASR: In Japan, it is better to assume every aggregate is reactive.
- F/T
- Leaching

Checking and proposing improvement!

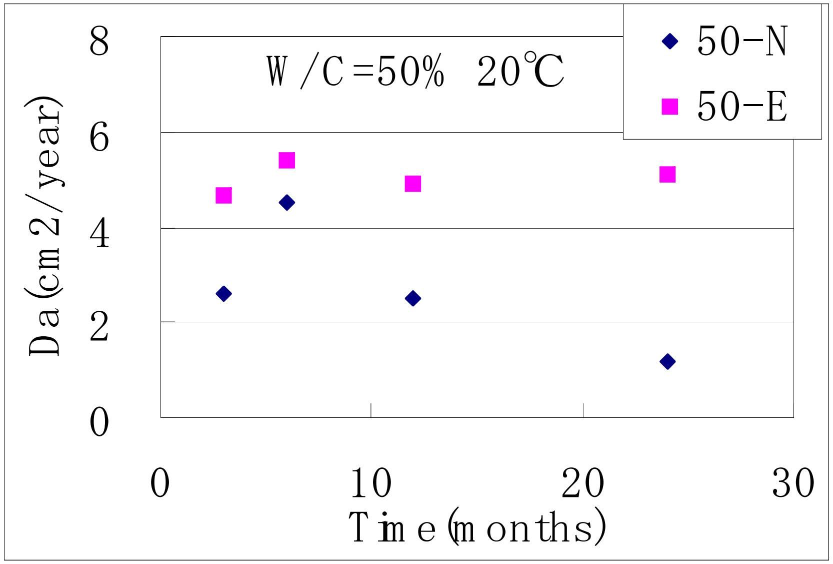
Effects of Ca sulfate on fluidity for different C_3A content

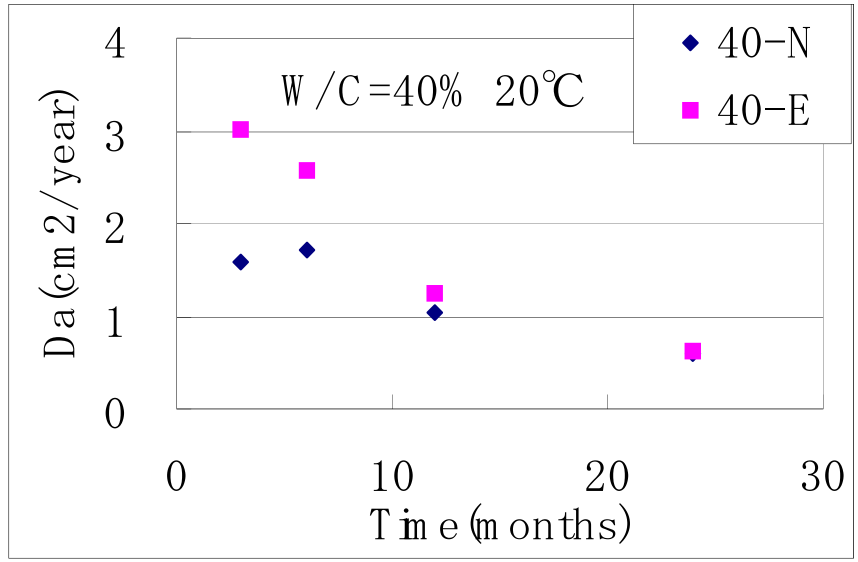
Mortar flow with polycarboxylate

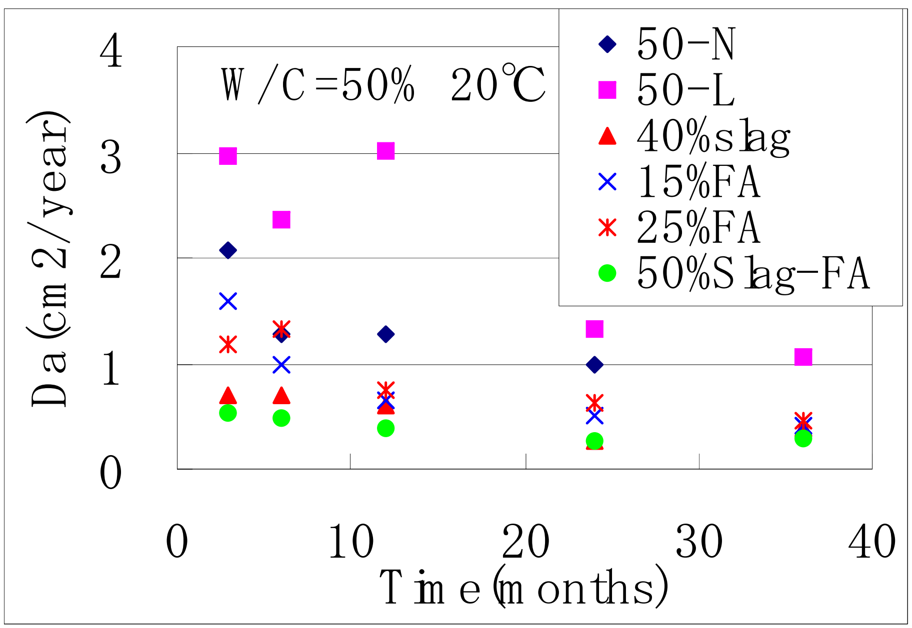


Adequate amount of Ca sulfate enable to enhance the fluidity even for high C_3A cement.

Chloride ingress

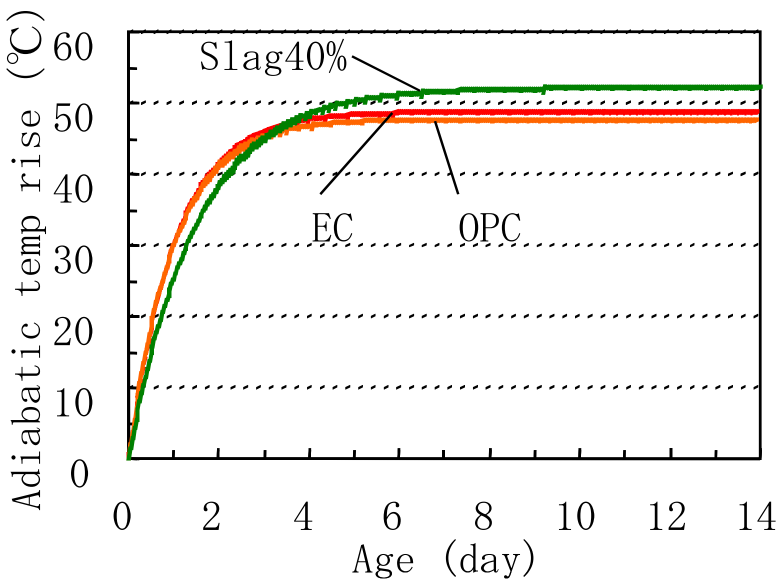




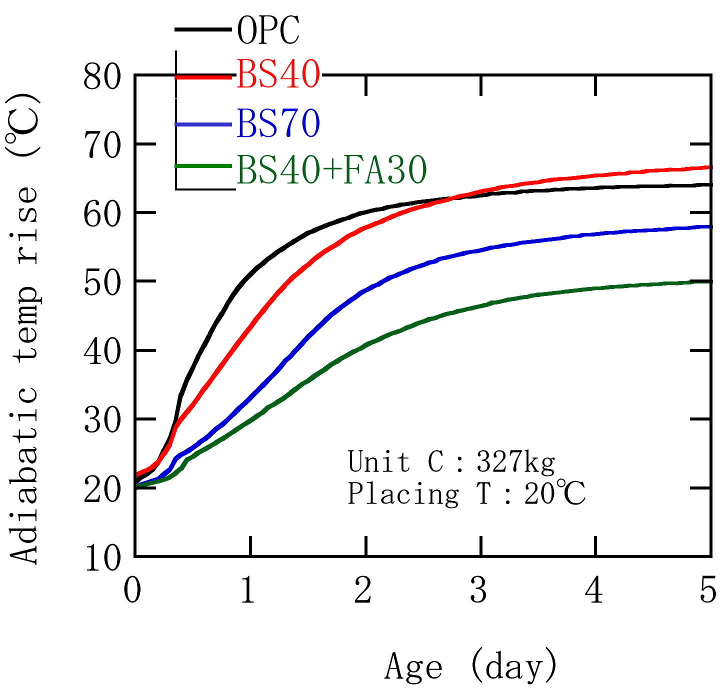


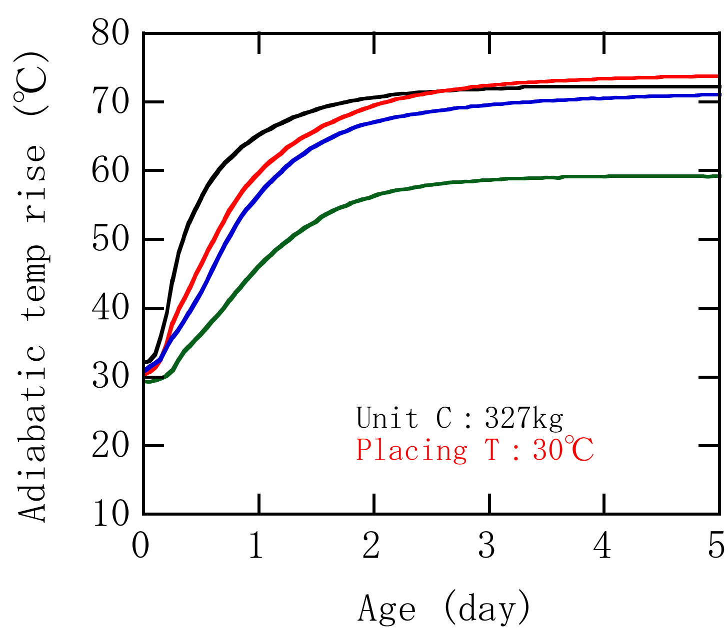
- Ecocement is inferior to NPC in relatively high W/C.
- Lowering W/C is one way to enhance the durability.
- SCM addition is a very effective way to reduce Da.

Hydration heat



- Temperature rise of ecocement is slightly higher than OPC.
- Slag is not a good way to reduce temperature rise in hot climate.
- Other pozzolans such as fly ash are indispensable.

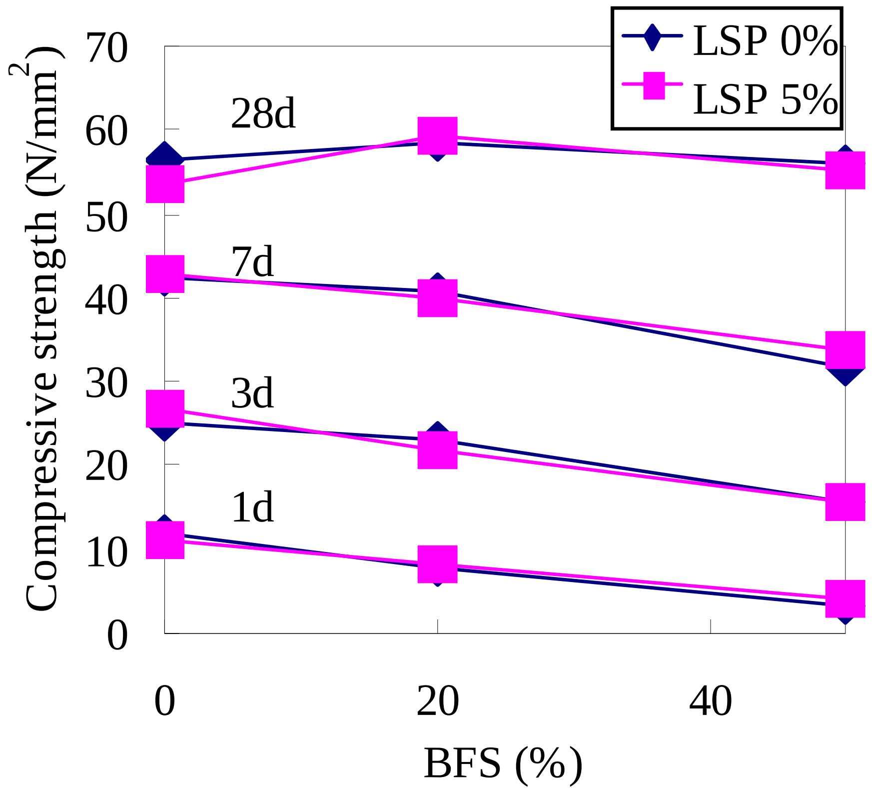




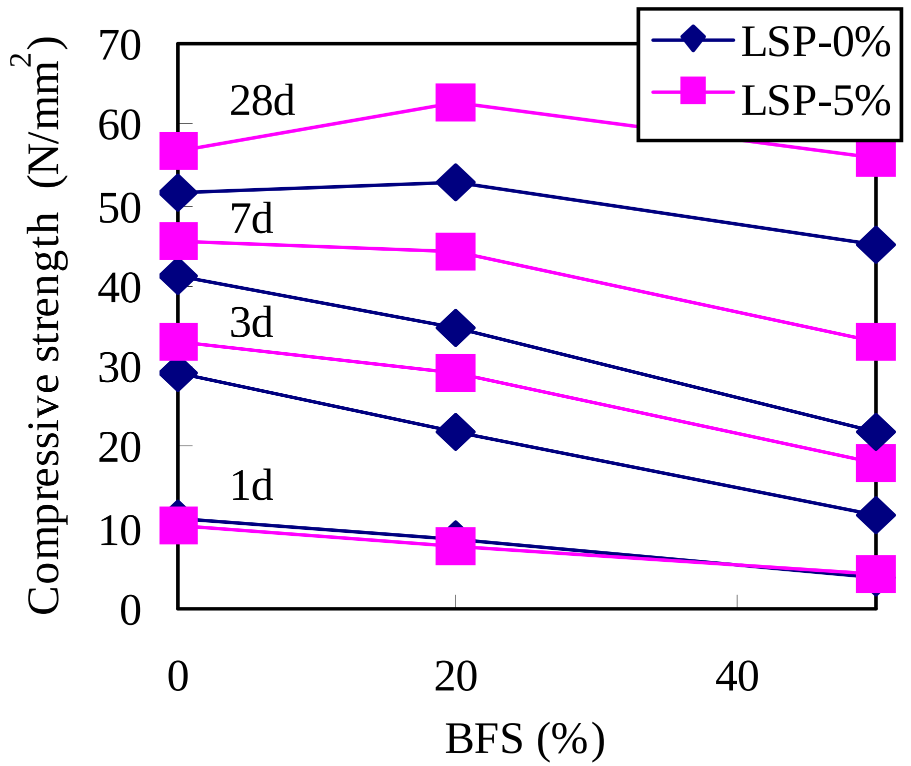
SCM seems indispensable

- FA?
  - Yes, it is effective to reduce hydration heat, ASR, sulfate & Cl attacks. But controlling the carbon content and reactivity is the problem.
  - Electricity company says "We are producing electricity but not fly ash. We can not pay much attention for the quality of wastes."
  - Who want to work so hard for such electricity company?
- Blast furnace slag?
  - A specialist of Nippon steel says "If the blast furnace is designed by Japanese companies, it means the quality of slag is perfectly designed and controlled as SCM. Quality of slag is equal to that of steel"
  - Every slag from various blast furnace has equivalent chemical compositions and shows compatible strength developments and effectiveness for durability. But hydration heat and cracking resistance are the problems.
- Are there other candidates?

Surprising effect of limestone

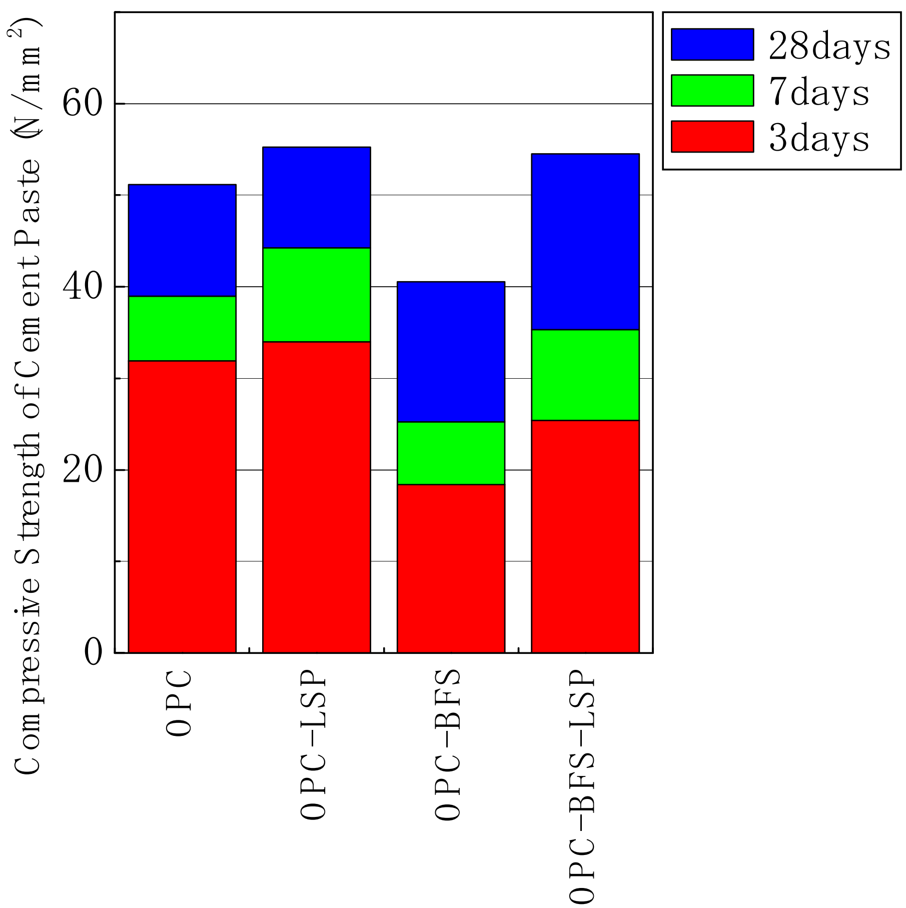


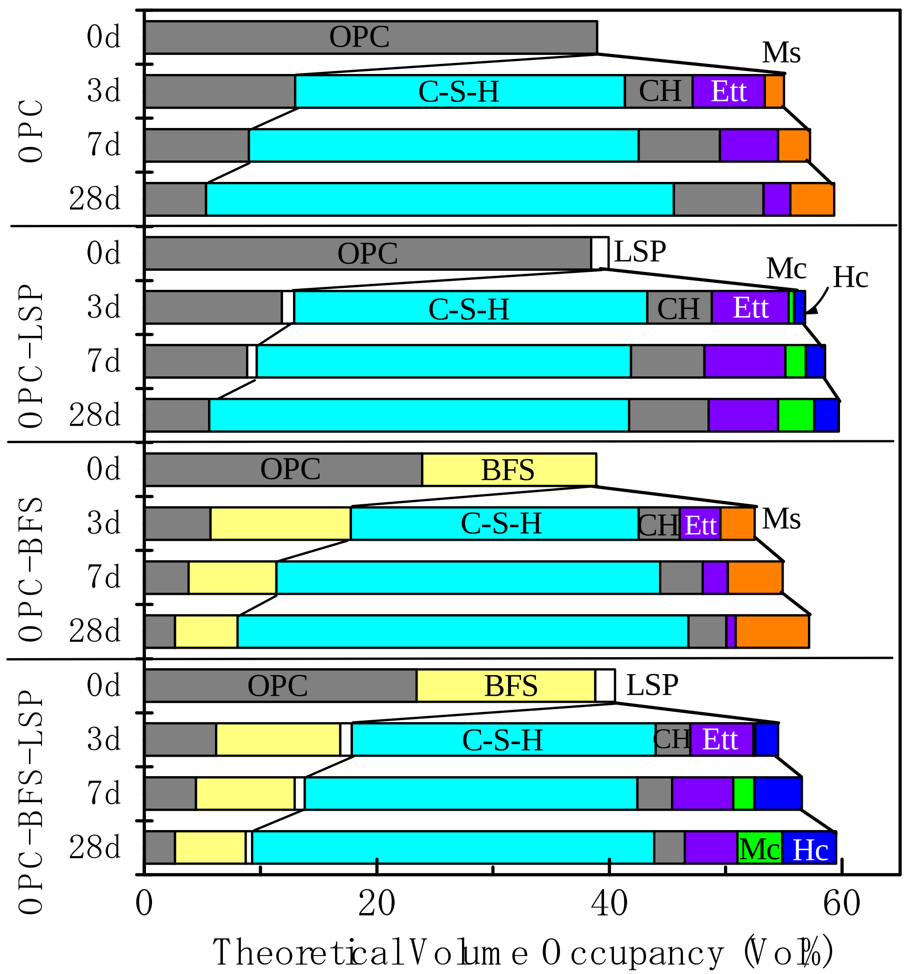
Base cement: OPC



Base cement: Ecocement

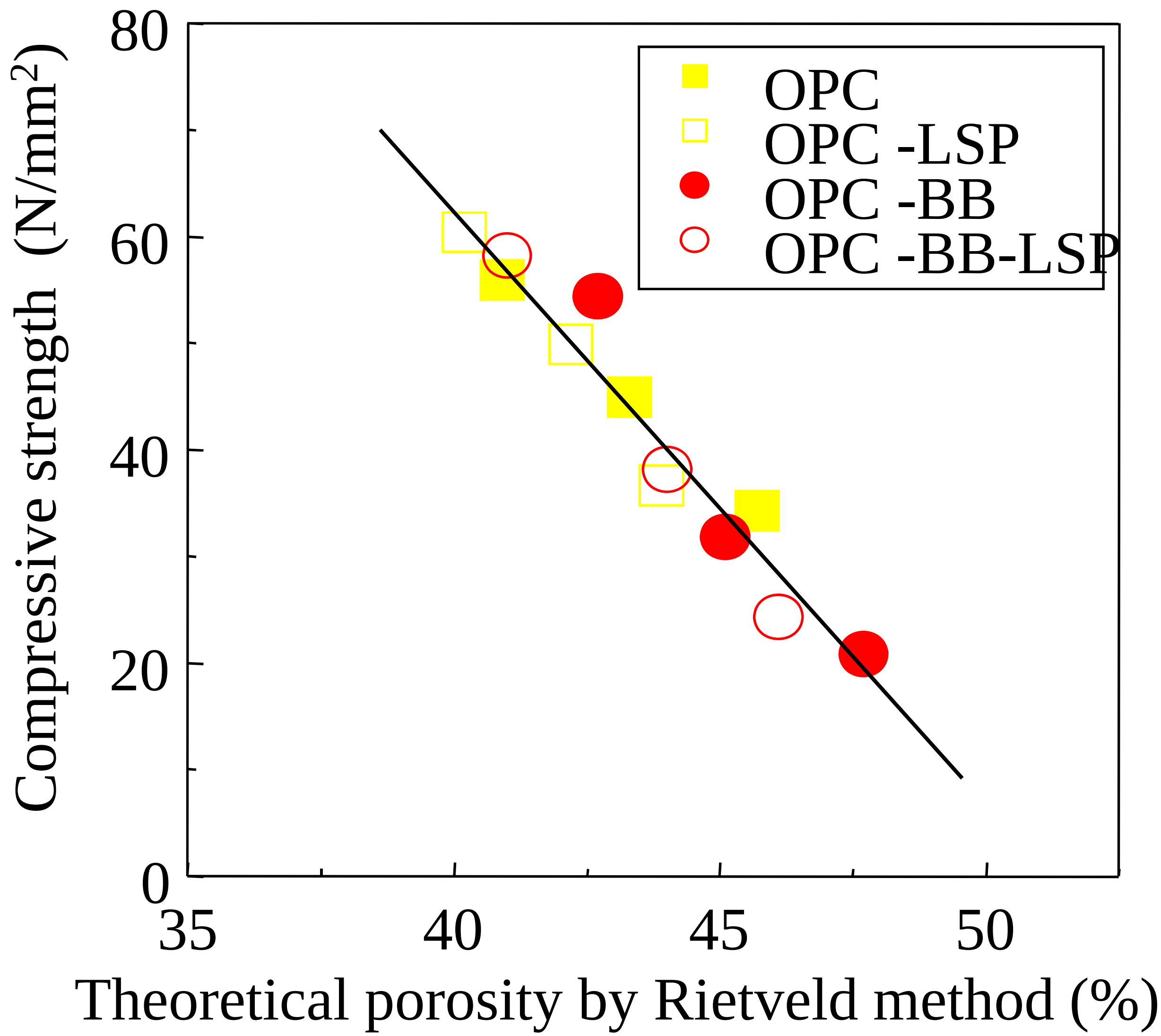
Analysis of the effect of LS addition



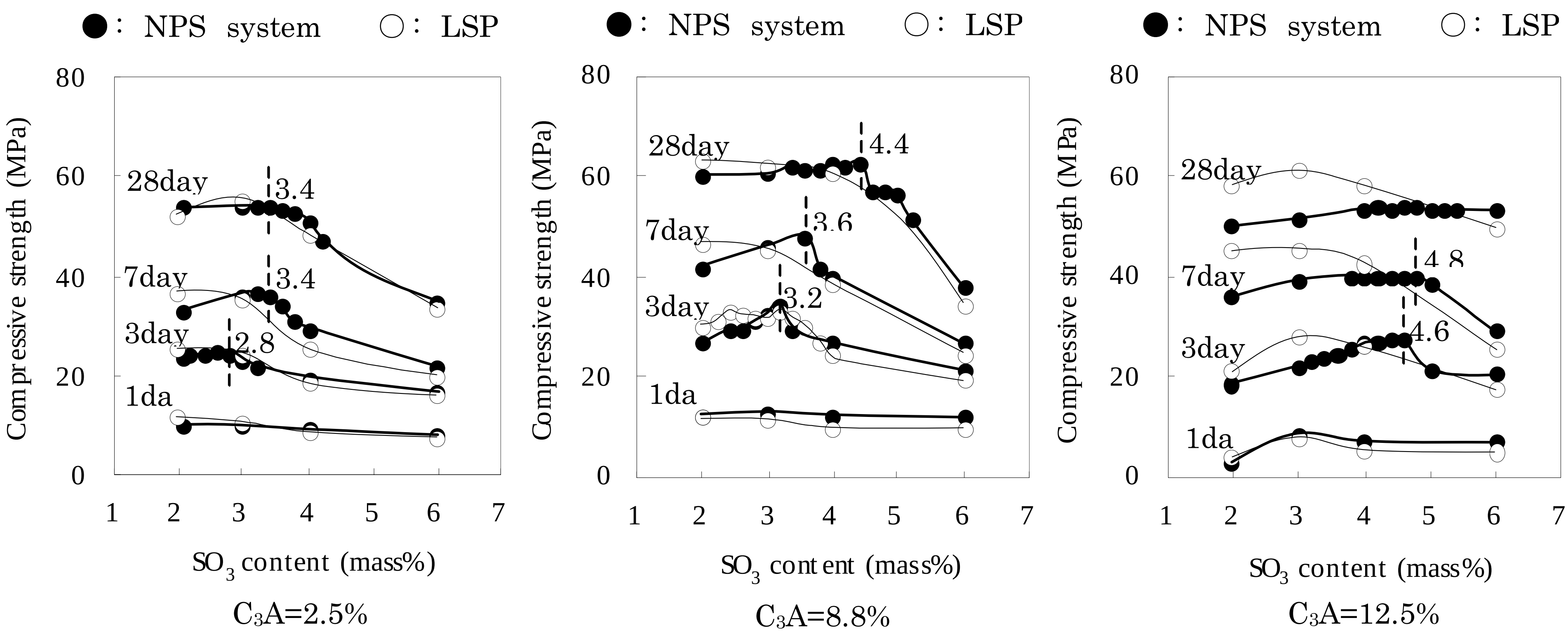


XRD/Rietveld analysis with selective dissolution method

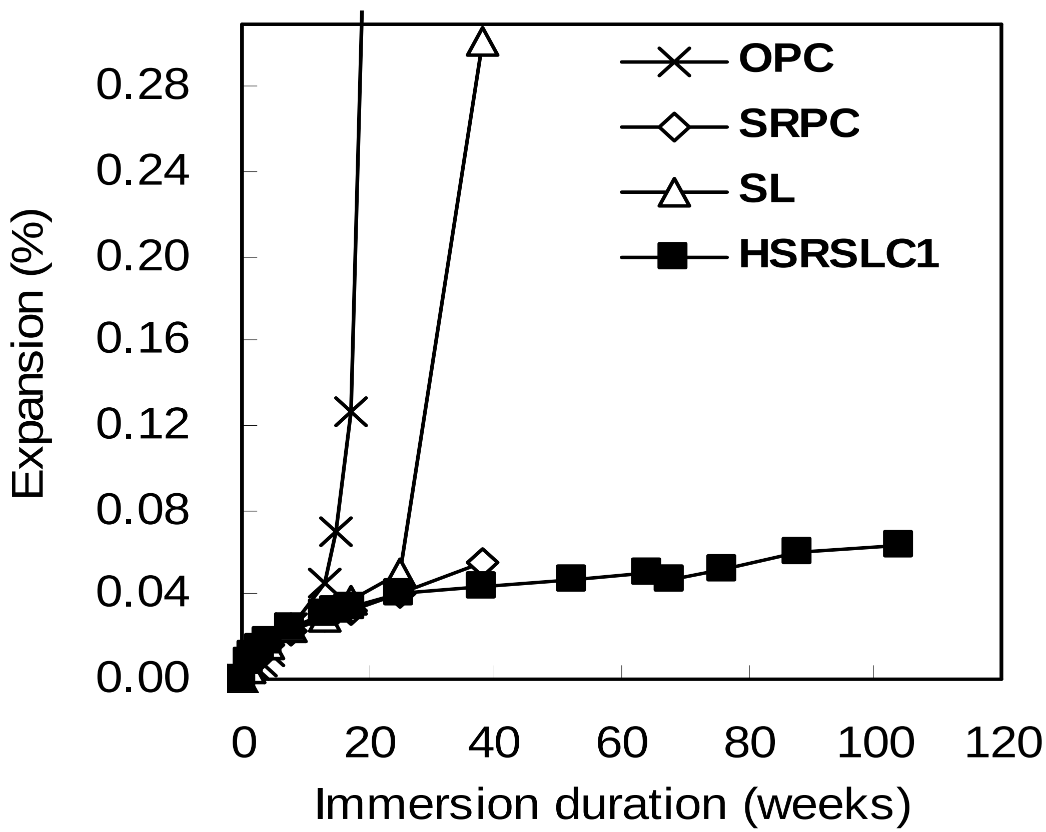
Mechanism is simple!



Effect of limestone addition on the optimum sulfate content



Impressive effect of LS for sulfate resistance

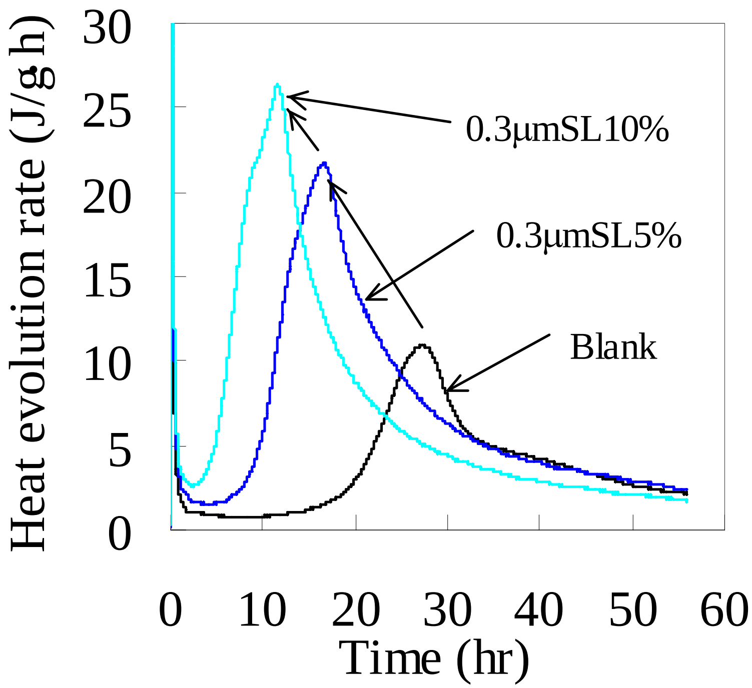


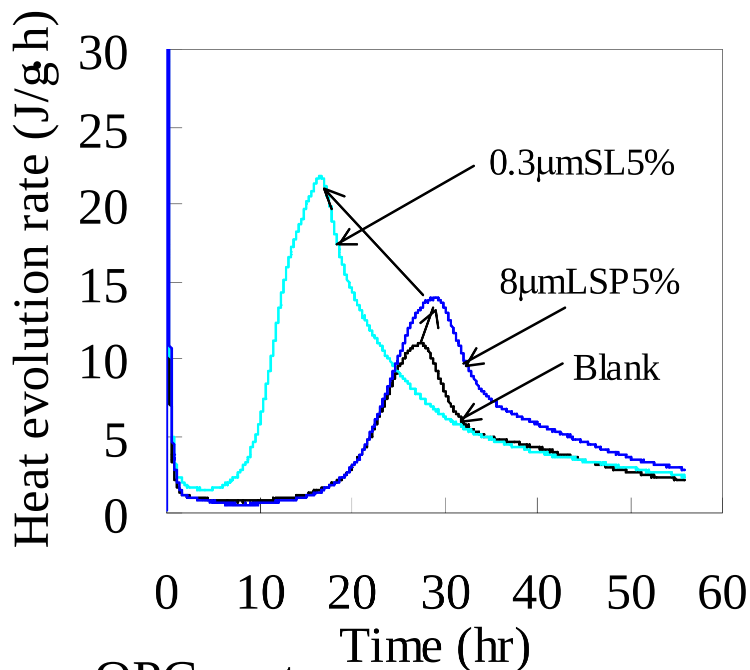
OPC: Japanese
SRPC: Canadian
SL: Japanese 40% blast furnace slag (Al_2O_3=15%)
HSRSLC1: Modified SL by several % addition.

High reactive alumina content is basically bad.
By the addition of small amount of calcite, it is possible to improve sulfate resistance drastically.

Under a collaboration with Prof. D. Hooton
My colleague is presenting this in Ho Chi Minh City this week at ACF conference.

Early strength enhancement by fine limestone

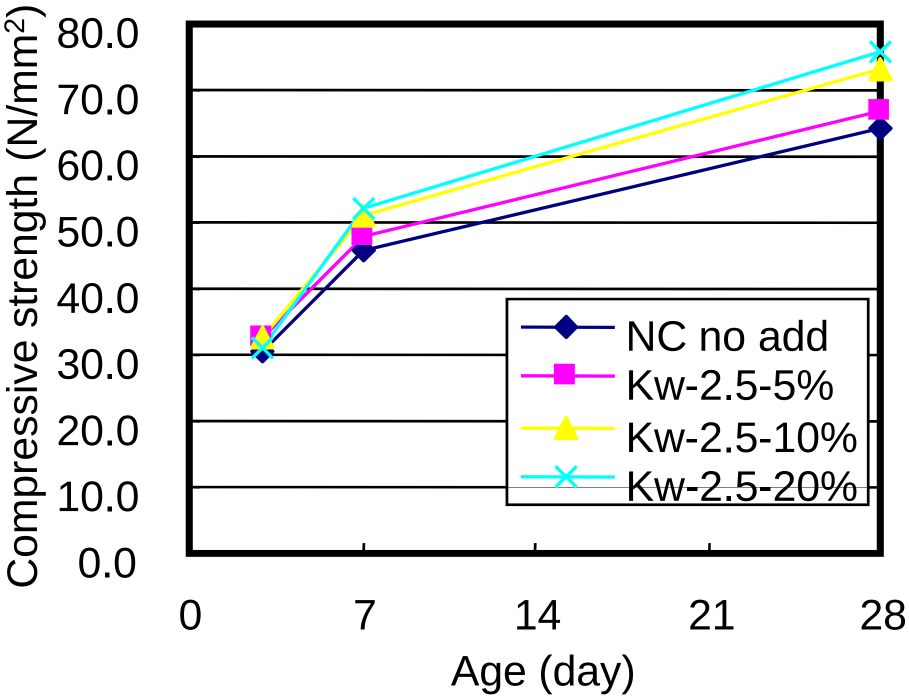


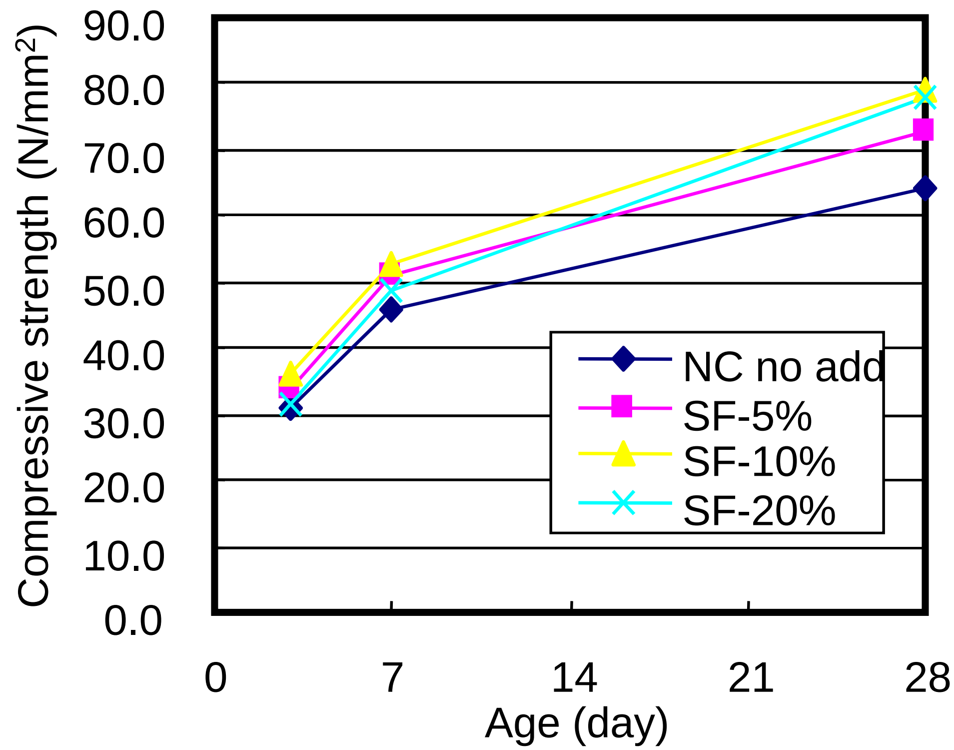


OPC paste
W/C=0.30
Polycarboxylate superplasticizer

Fine calcite activate the early hydration of C_3S.

For ASR: Siliceous shale

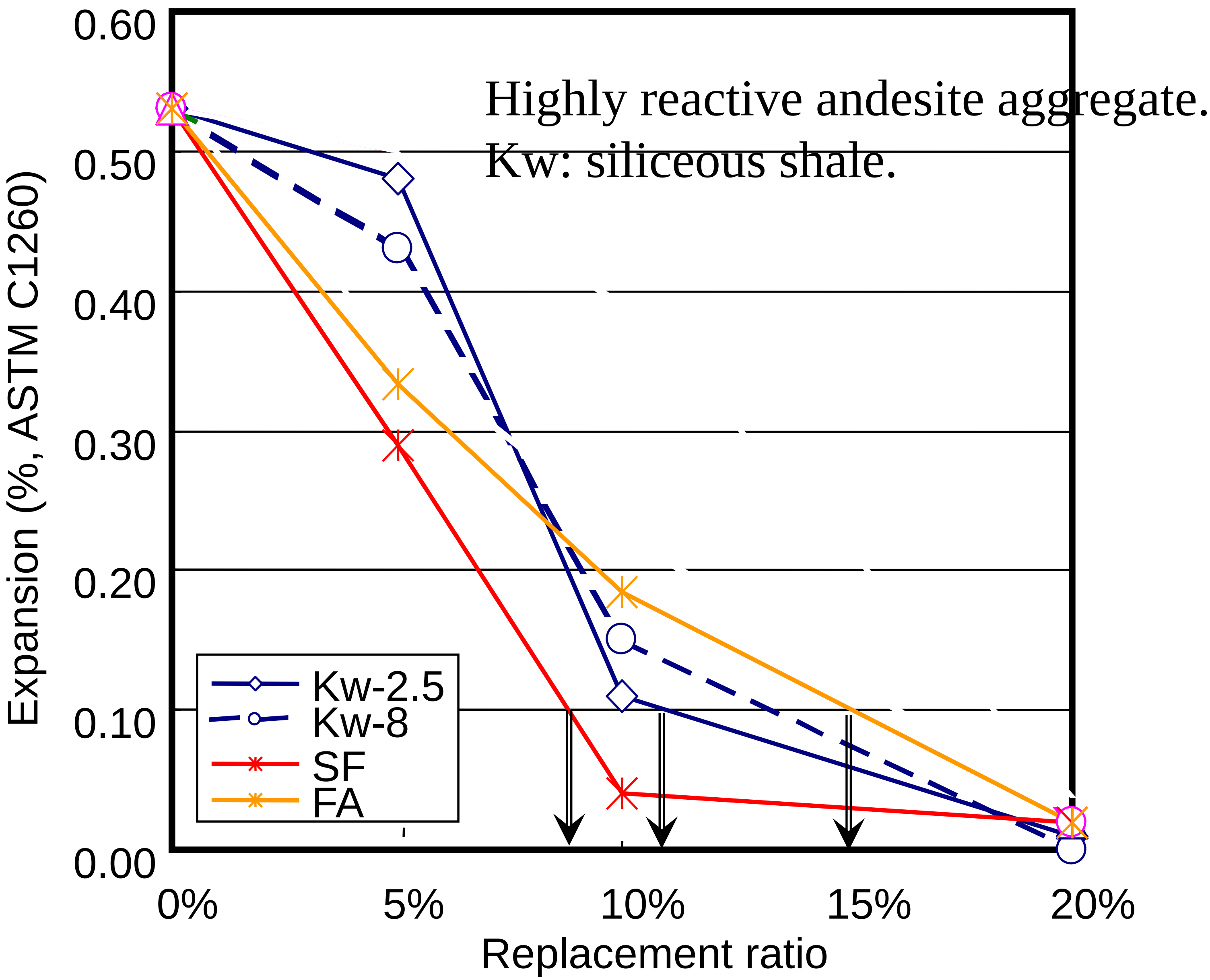




Main component: Opal-CT
Huge amount of resource. Some are used as silica source for cement production.
Superplasticizer is required because of the large absorption caused by SSA 120m^2/g.

Close to silica fume!

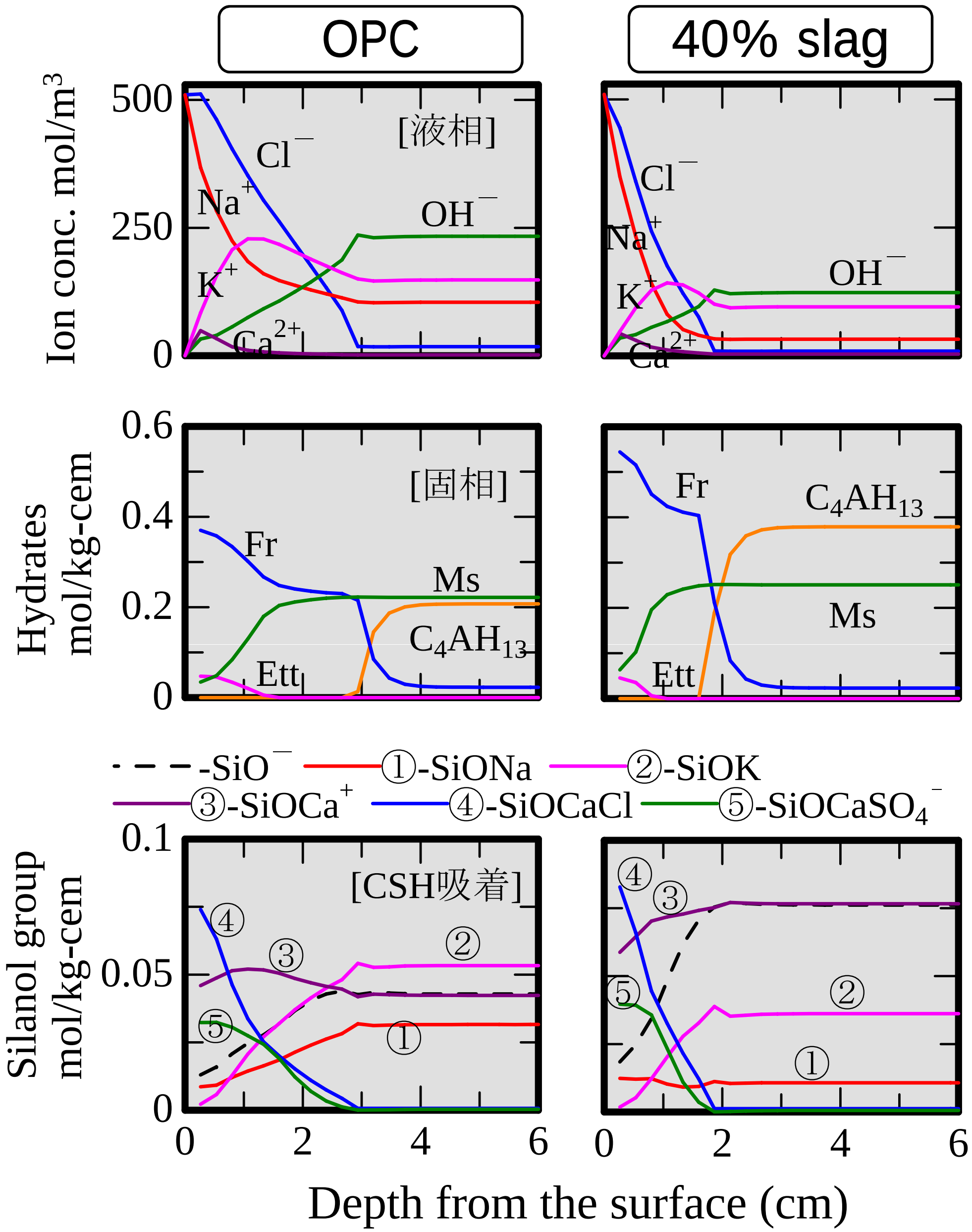
Effect on ASR expansion



Proposal of new cement under the balance of requirements from environmental and performance in concrete

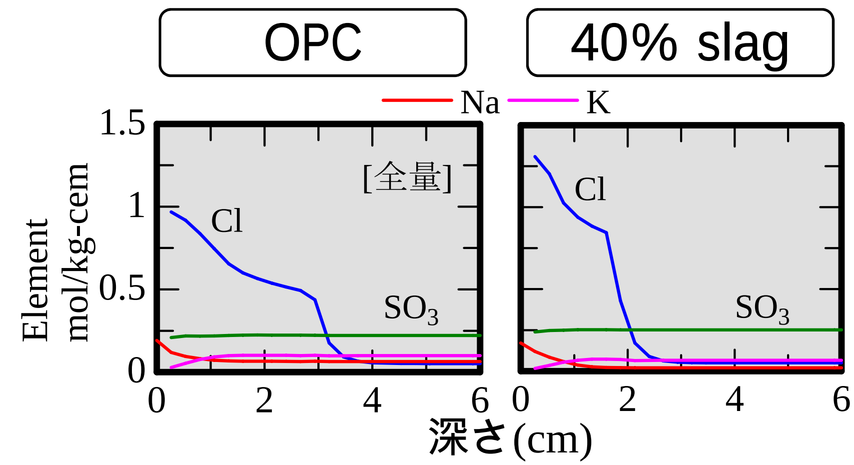
- High C_3A cement base,
- With the addition of
  - Blast furnace slag,
  - Fine limestone,
  - and Siliceous shale.
- Calcite has a great function only for high alumina conditions.
- In order to optimize the formula….

Thermodynamic calculation will be a good way.



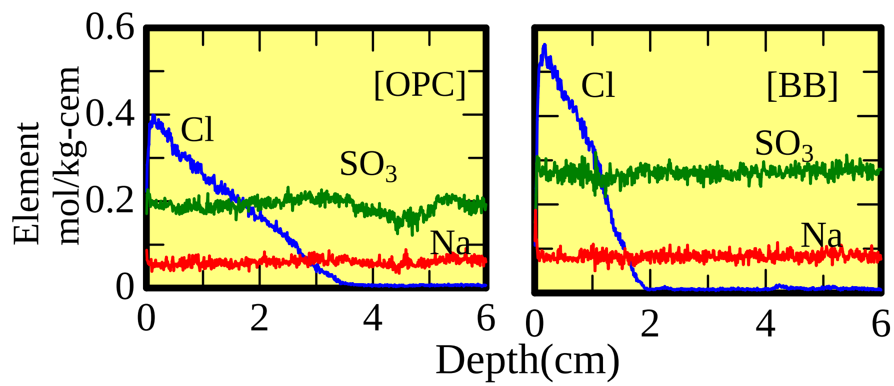
Immersion into NaCl

Total amount



EPMA Measurement

（ Same mix and immersion cond. ）



Conclusions

- We have to use Al_2O_3 rich waste in some way.
- High C_3A cement is a candidate.
- Combining slag, limestone, and siliceous materials seems a reasonable solution for durable concrete material.
- Thermodynamic calculation will be an effective tool to estimate the performance.
- Al behaviors in C-S-H is the next topic of study.