

# Eco-cement

Developed by TAIHEIYO CEMENT Corp. Tokyo Japan

- Manufacture and Performance -

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# Eco-cement contributes to environmental protection by providing a complete recycling system of wastes

- In Japan, municipal waste reached 50 million tons in 1997.
- Municipal and industrial waste problems are caused by limited availability of landfill sites.
- Rapid increase in waste is causing environment problems not only in the industrialized countries but also developing countries.
- The cement industry has contributed to society providing construction materials, and will also give the solution to waste problems.

# The development of Eco-cement

- 500 kg/ton-clinker of raw materials is replaced by incinerator ash.
- The cement has a wide application.
- The manufacturing process and the products are environmentally-friendly.
- The entire process is a complete recycling system.

# Chemical composition of incinerator ash (major composition)

- The ash contains  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  as useful elements for cement production.
- It contains high concentrations of  $\text{Cl}$  and  $\text{P}_2\text{O}_5$ .

	<b>LOI</b>	<b><math>\text{SiO}_2</math></b>	<b><math>\text{Al}_2\text{O}_3</math></b>	<b><math>\text{Fe}_2\text{O}_3</math></b>	<b><math>\text{CaO}</math></b>	<b><math>\text{MgO}</math></b>	<b><math>\text{Cl}</math></b>	<b><math>\text{P}_2\text{O}_5</math></b>
<b>Ash</b>	<b>11</b>	<b>22.9</b>	<b>19.7</b>	<b>5.6</b>	<b>30.4</b>	<b>4.8</b>	<b>8.5</b>	<b>1.8</b>
<b>Limestone</b>					<b>55</b>			
<b>Clay</b>		<b>60</b>	<b>20</b>	<b>5</b>				

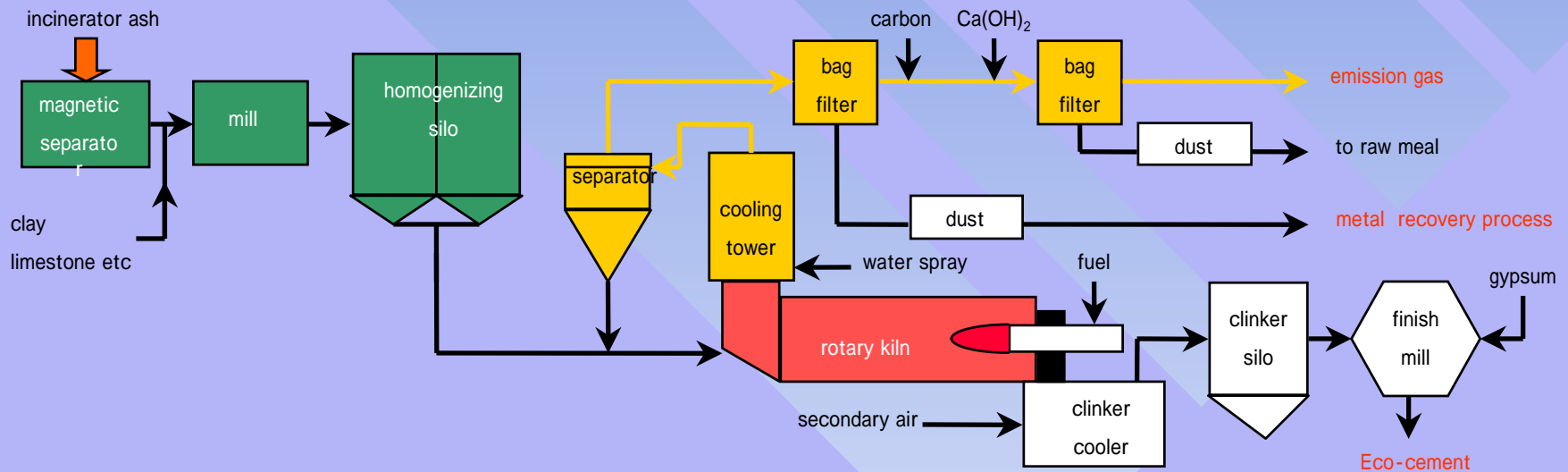
# Mineral design of Eco-cement

- Using incinerator ash as raw materials up to 50% leads to an increase of Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Cl.
- The two types are produced by controlling Cl-alkalis balance of raw meals.
- Cl vaporizes in the sintering process, combining with alkalis.

	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>11</sub> A <sub>7</sub> CaCl <sub>2</sub>	C <sub>4</sub> AF	CaSO <sub>4</sub>
Normal	49	12	14	0	13	6.3
RH	44	10	0	17	8	16
NPC	53	23	8	0	10	3.4
	C;CaO	S;SiO <sub>2</sub>	A;Al <sub>2</sub> O <sub>3</sub>	F; Fe <sub>2</sub> O <sub>3</sub>		

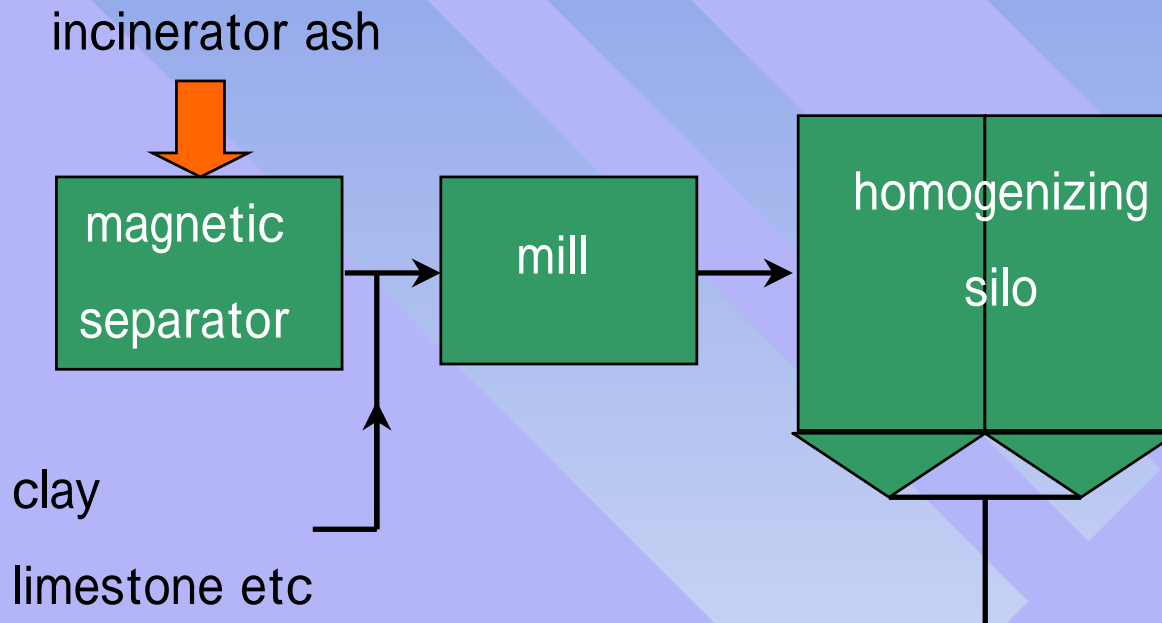
# Manufacturing process

- The process consists of the same unit processes used for NPC; Raw meal preparation, sintering, finish process.
- Metal recovery process is designed.



# Raw meal preparation

- Chemical composition of incinerator ash shows differences depending on their origin.
- The process is equipped the magnetic separator and the blending vessels.







# Controlling Cl-alkalis balance of raw meals

- Cl vaporizes in the sintering process, combining with alkalis and heavy metals in both types.
- Normal type;
  - (1)The amount of Cl in the raw meal is designed to be equivalent to the amounts of alkalis and the metal components.
- RH type;
  - (1)The excess Cl compared to the amounts of alkalis and the metal components, forms  $C_{11}A_7CaCl_2$ .
  - (2)It is important to maintain a constant amount of  $Al_2O_3$  developing high early strength.

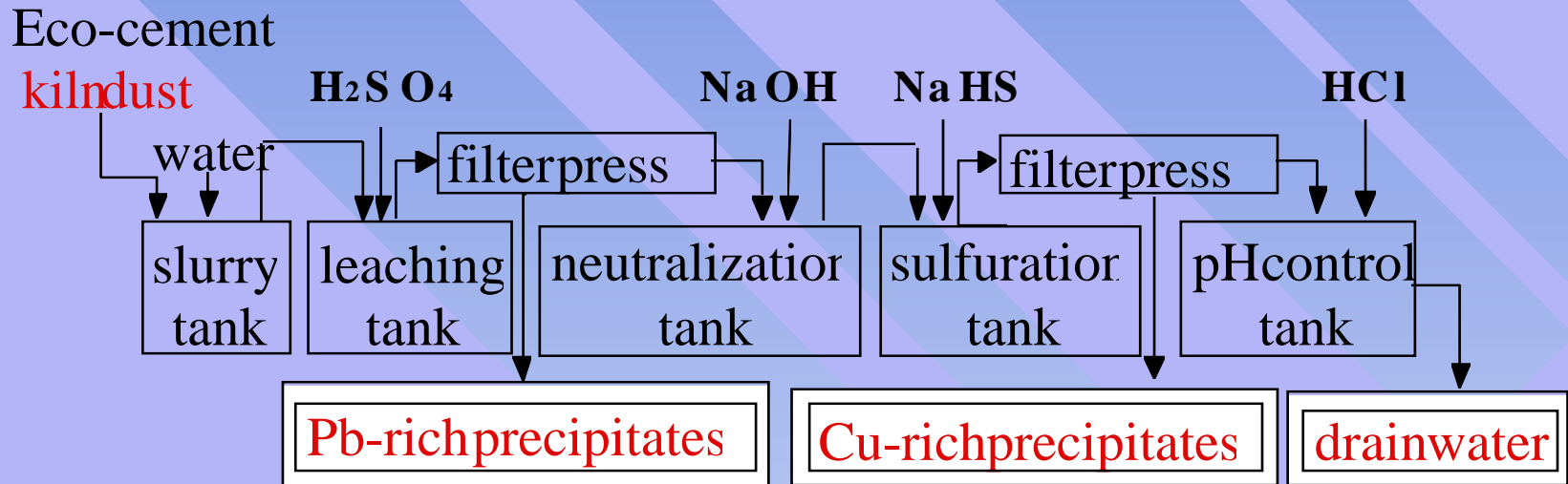
# Chemical composition of Eco-cement

- Normal type ; Cl is reduced to <0.1%.  
SO<sub>3</sub> is 3.7% to control the setting time of C3A-rich cement.
- RH type ; Cl is taken into C<sub>11</sub>A<sub>7</sub>CaCl<sub>2</sub>.  
The addition of Na<sub>2</sub>SO<sub>4</sub> and anhydrite at SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio 1.1 to control the setting time and ettringite formation.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl	%
Normal	17	8	4.4	61	1.8	3.7	0.2	0	0.04	
RH	15.3	10	2.5	57.3	1.7	9.2	0.5	0	0.9	
NPC	21.2	5.2	2.8	64.2	1.5	2	0.3	0.5	0.01	

# Metal recovery process

- The qualities of precipitates are higher than that of natural ores.



	Ratios	Pb	Zn	Cu	Cd	Hg	As	Fe
	%	%	%	%	mg/kg	mg/kg	mg/kg	%
kiln dust	100	1.53	0.08	1.91	98	12.2	<1	0.01
pb-rich	4.7	32.1	0.02	0.52	3	2.7	2	0.26
Cu-rich	3.6	0.9	2.2	52.2	2730	2.3	<1	0.04

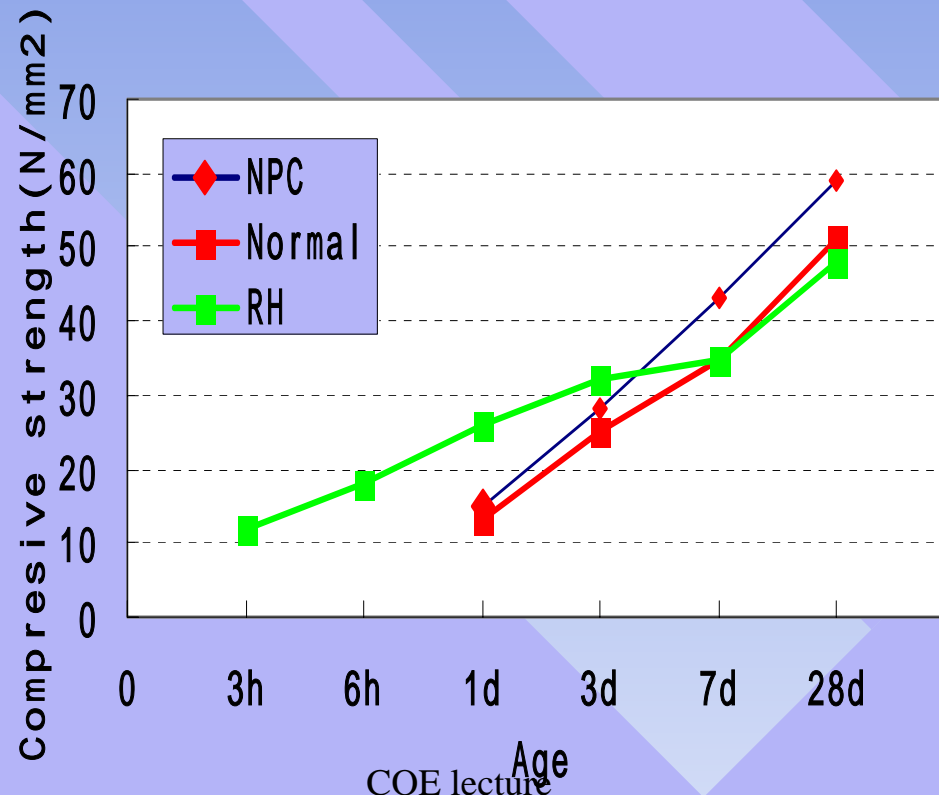
# Physical properties (Time of setting)

- Normal type has almost the same properties as NPC.
- RH type has very short setting time. The use of a retarder such as citric acid extends the setting time.

	Density g/cm <sup>3</sup>	Fineness Blaine cm <sup>2</sup> /g	Time of setting	
			Initial h-m	Final h m
Normal	3.17	4,250	2-30	4-00
RH	3.13	4,600	0-09	0-13
NPC	3.17	3,220	2-22	3-30

# Physical properties (Strength development)

- Normal type develops the same physical properties as NPC
- RH type develops high early-strengths at 3 hours and 1day



# Environmental Protection (Recovery of heavy metals)

- The waste water from the process contains NaCl and KCl of the concentration close to sea water.
- Heavy metals in the waste water meet the Japanese Clean Water Act regulation.

	<b>Pb</b> (mg/l)	<b>Zn</b> (mg/l)	<b>Cu</b> (mg/l)	<b>Cd</b> (mg/l)	<b>Hg</b> (ppb)	<b>As</b> (ppb)
<b>Waste water</b>	<b>0.01</b>	<b>0.48</b>	<b>0.38</b>	<b>0.01</b>	<b>&lt;0.5</b>	<b>&lt;0.01</b>
<b>Emission STD</b>	<b>&lt;0.1</b>	<b>&lt;5</b>	<b>&lt;3</b>	<b>&lt;0.1</b>	<b>&lt;0.5</b>	<b>&lt;0.1</b>

# Environmental Protection

## (Gas emissions from the plant)

- The gas emissions from the process meets every standard to protect the environment.
- The dioxins in the raw meal are decomposed in the kiln.
- SO<sub>x</sub> and HCl are combined with CaO and discharged from the process.

	<b>NO<sub>x</sub></b> (ppm)	<b>SO<sub>x</sub></b> (Nm <sup>3</sup> /h)	<b>HCl</b> (mg/m <sup>3</sup> N)	<b>Dioxins</b> (ng-TEQ/m <sup>3</sup> N)	<b>Dust</b> (g/m <sup>3</sup> N)
<b>gas</b>	<b>45</b>	<b>0.23(&lt;20ppm)</b>	<b>32(&lt;20ppm)</b>	<b>0.05</b>	<b>0.001</b>
<b>STD</b>	<b>&lt;250</b>	<b>&lt;4.76</b>	<b>&lt;700</b>	<b>&lt;0.1</b>	<b>&lt;0.08</b>

# Environmental Protection

(Leaching of heavy metals from mortar)

- Leaching of heavy metals from hardened Eco-cement mortar meets the Japanese Environment Protection Agency regulations.

	<b>Cd</b> (mg/l)	<b>Pb</b> (mg/l)	<b>As</b> (mg/l)	<b>CN</b> (mg/l)	<b>Cu</b> (mg/l)	<b>Hg</b> (mg/l)	<b>Cr6+</b> (mg/l)	<b>Se</b> (mg/l)
<b>1d</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>
<b>28d</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>	<b>ND</b>
<b>Emission ST</b>	<b>&lt;0.01</b>	<b>&lt;0.05</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;1</b>	<b>&lt;0.0005</b>	<b>&lt;0.05</b>	<b>&lt;0.01</b>



# The Properties of Concrete with Normal Type Eco-cement

# (1) Mix Proportion of Concrete

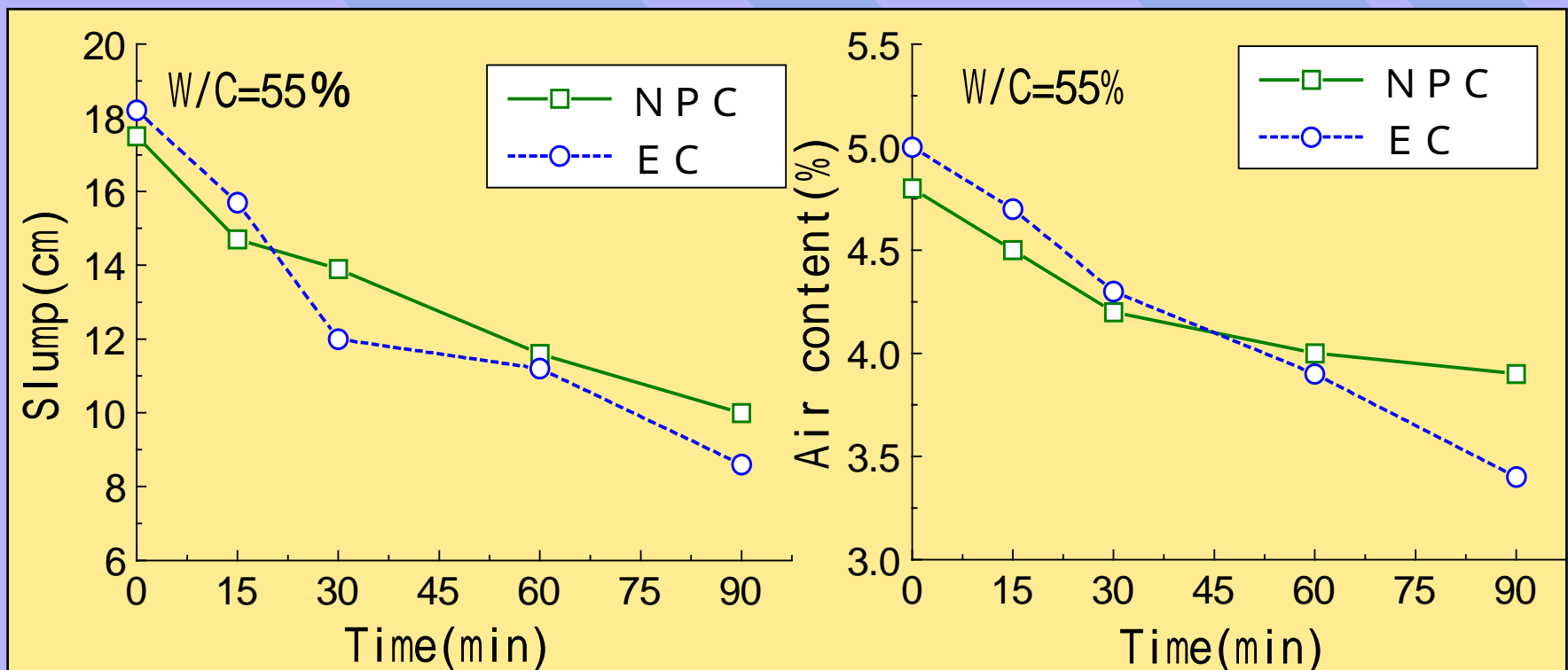
- The unit water content of EC concrete is larger than that of NPC concrete because of its fineness.
- The dosage of air entraining agent is also larger than that of NPC concrete.

cement	W/C (%)	s/a (%)	unit content		A.E.A (C × %)
			W	A.E.W.RA	
NPC	45.0	46.0	176	0.98	0.0025
	55.0	48.0	176	0.80	0.0025
	65.0	50.0	176	0.68	0.0025
EC	45.0	44.0	178	0.99	0.0050
	55.0	46.0	178	0.81	0.0050
	65.0	48.0	178	0.68	0.0050

A.E.W.R.A : air-entraining water reducing agent  
A.E.A : air-entraining agent

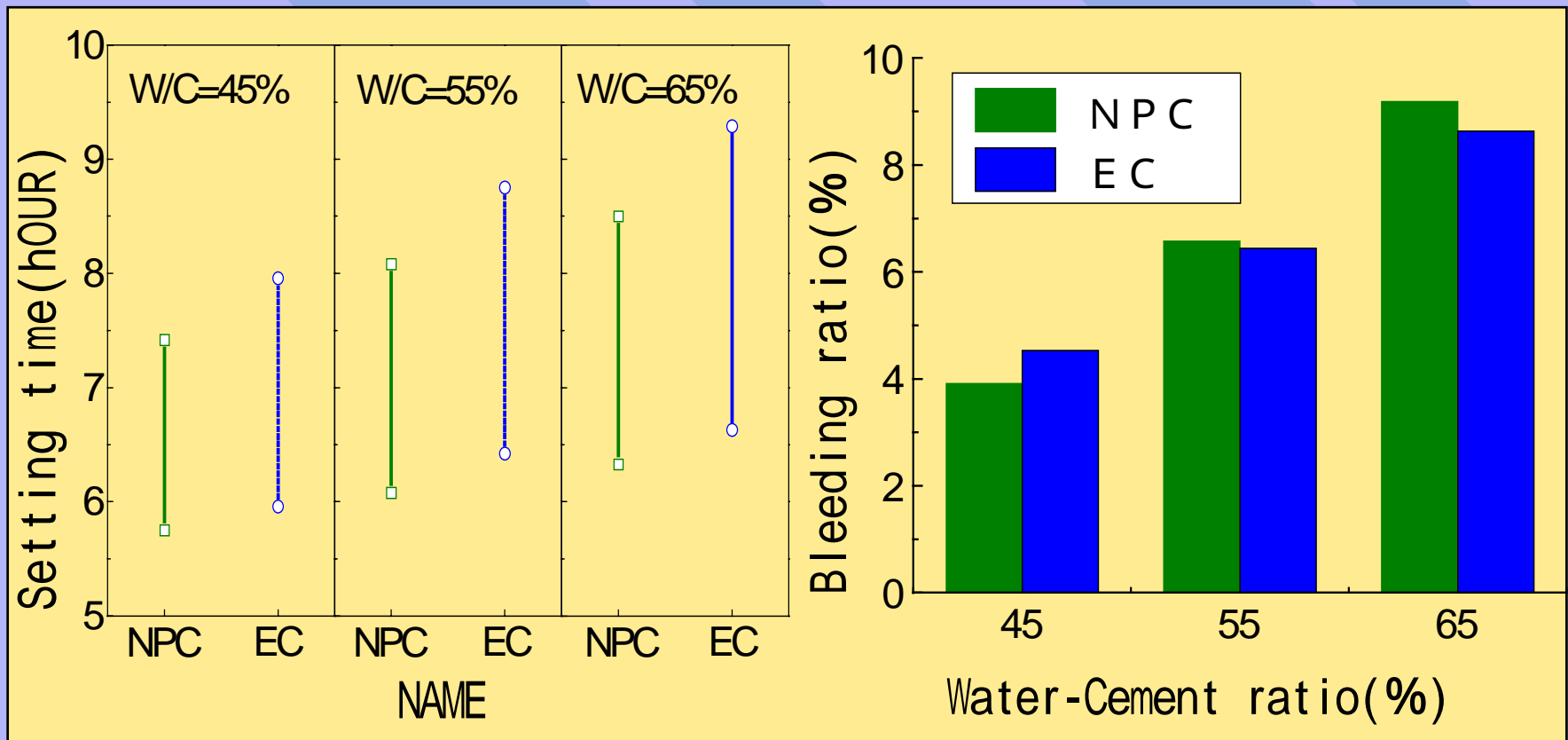
## (2) Consistency of Concrete

- The slump loss of EC concrete is almost the same as that of NPC concrete.
- The air-content of EC concrete is almost the same as that of NPC concrete.



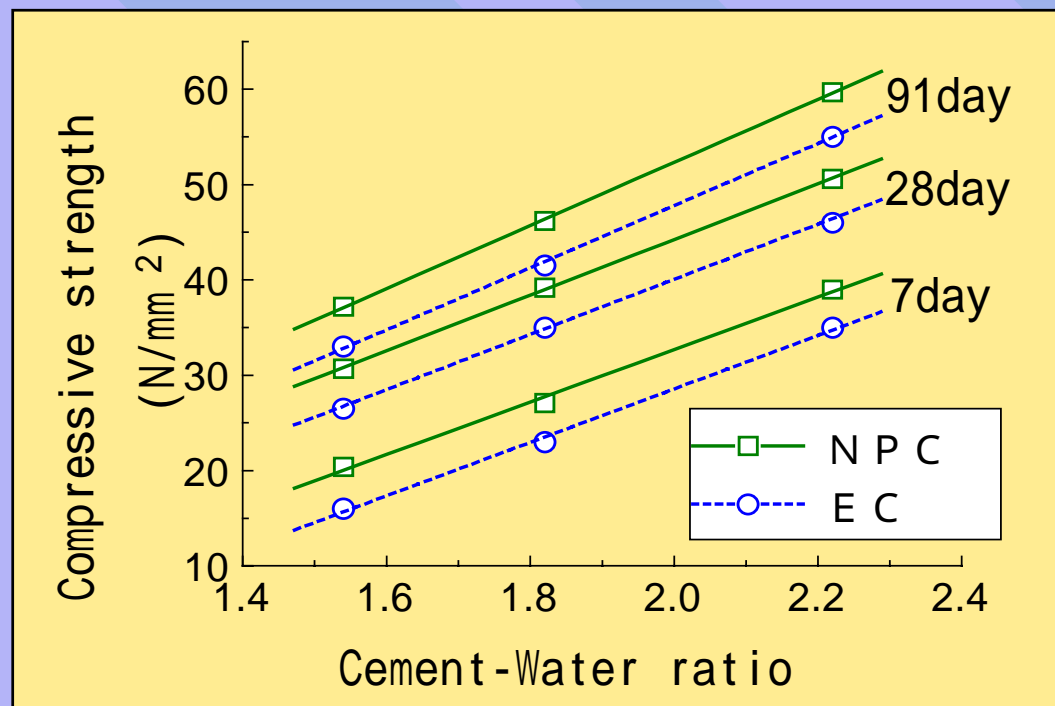
### (3) Setting time of Concrete

- The setting time of EC concrete is longer than that of NPC concrete.
- The bleeding of EC concrete is similar to that of NPC concrete.



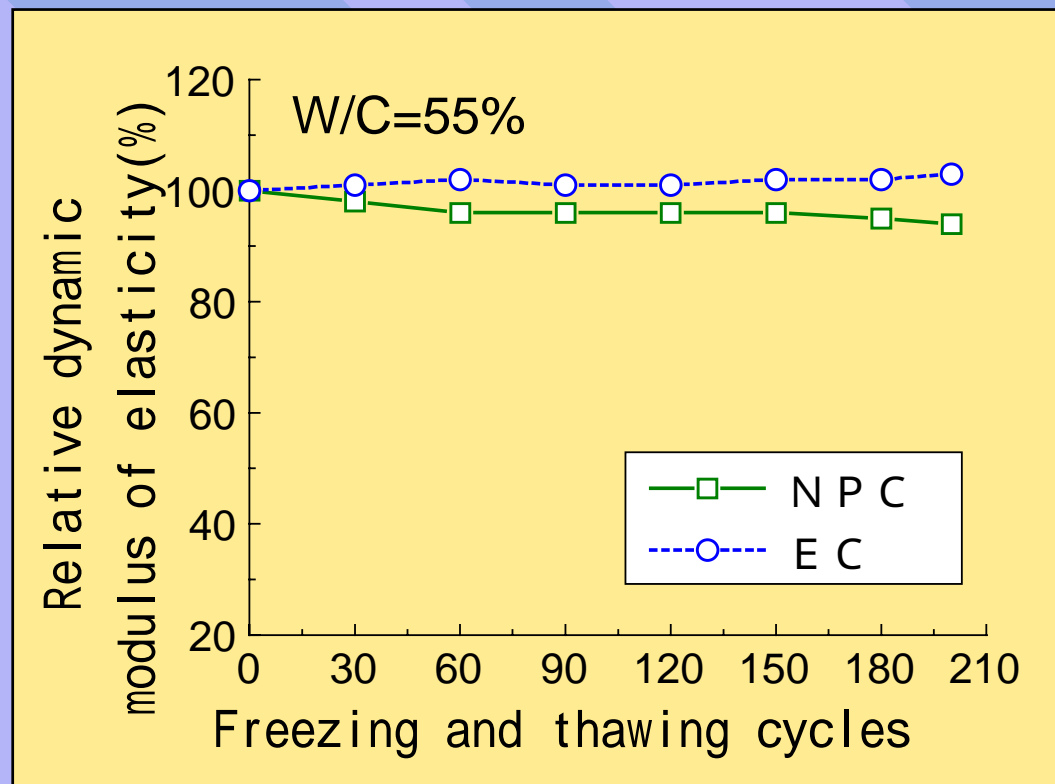
## (4) Compressive Strength

- The compressive strength of EC concrete is lower than that of NPC concrete at the same ages.
- The same strength can be obtained by decreasing water-cement ratio by 3-5% compared with NPC concrete.



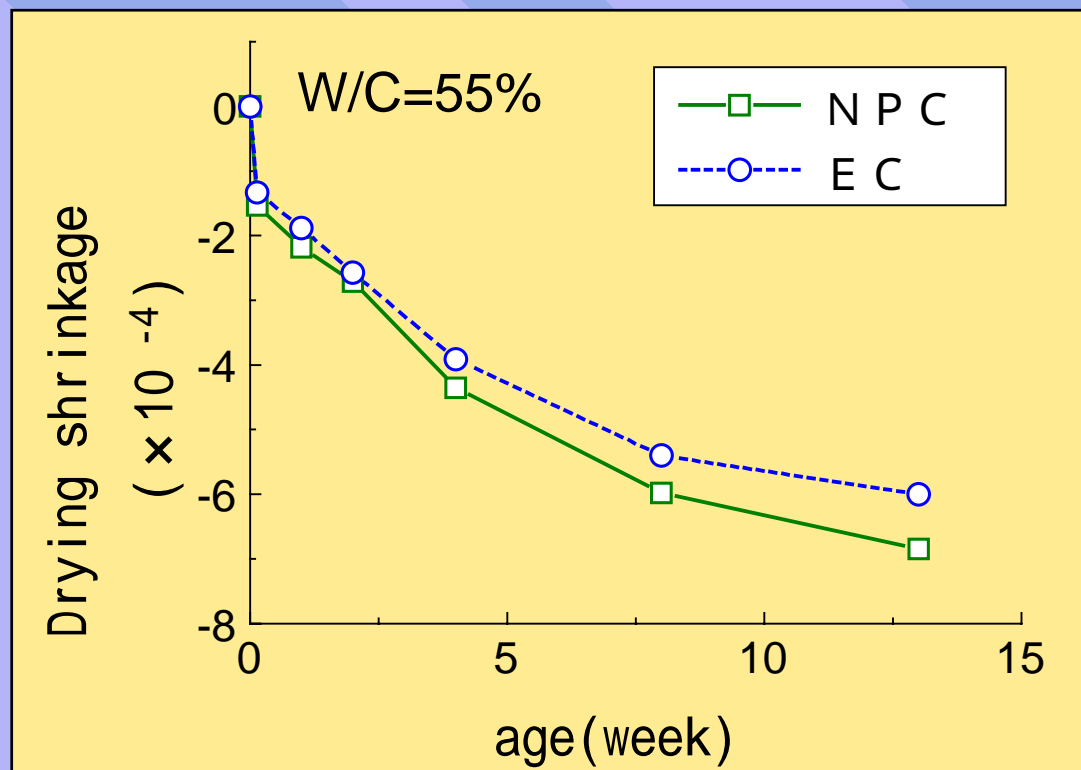
## (5) Resistance for Freezing and Thawing

- The resistance for freezing and thawing of EC concrete, which contains sufficient air content, is equal to that of NPC concrete.



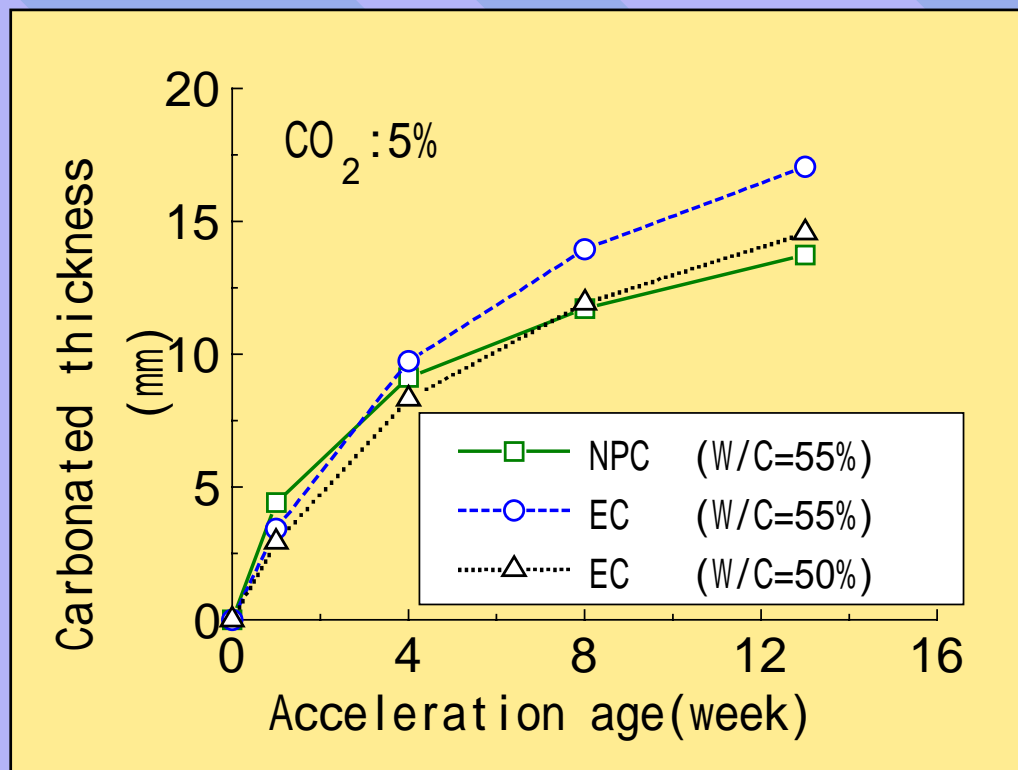
## (6) Drying Shrinkage

- The drying-shrinkage of EC concrete tends to be smaller than that of NPC concrete.



## (7) Carbonation

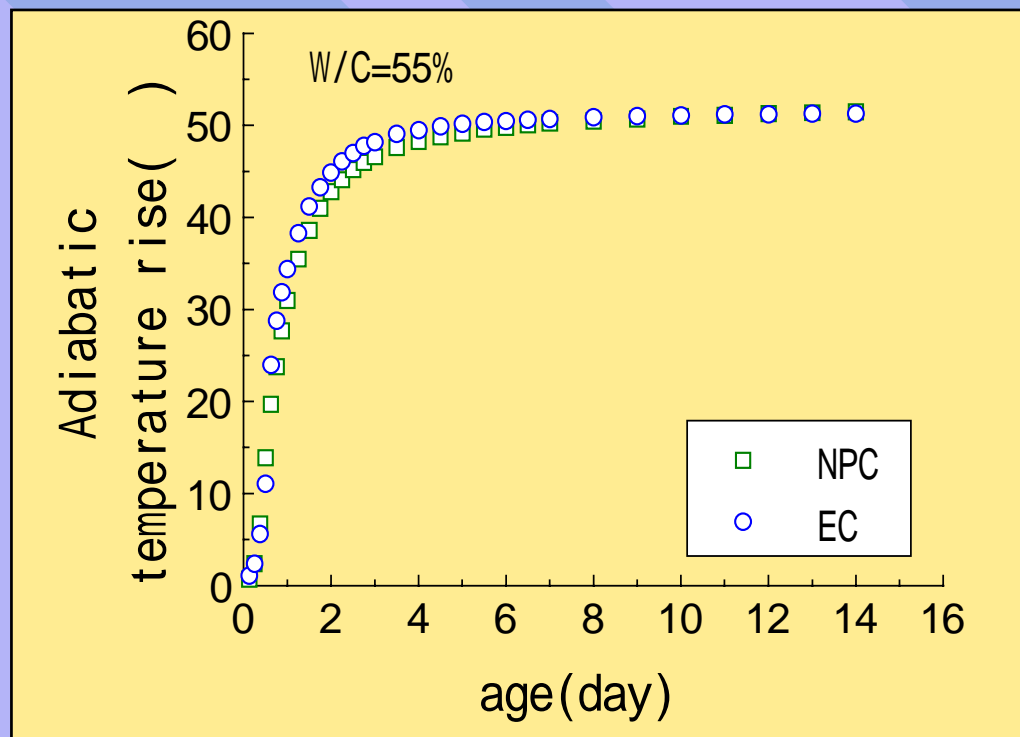
- The carbonation of EC concrete is slightly larger than that of NPC concrete.
- The same resistance for carbonation develops by decreasing W/C by 3-5% compared to NPC concrete.





## (8) Adiabatic temperature rise

- The final temperature rise is almost similar to that of NPC concrete.
- The rate of temperature rise in EC concrete is higher than that in NPC concrete at the early stage.



## (9) Chloride Ion Content and Corrosion of Bar

### (a) Chloride ion content in fresh EC concrete

No.	Use	Slump	W	EC	Ad.	Chloride ion (kg/m <sup>3</sup> )
1	pavement	8	170	283	WRAE	0.04
2	building	18	184	369	WRAE	0.07
3	building	18	175	317	HWRAE	0.04
					Spec.	0.30>

- Chlorine in eco-cement is stabilized mainly in cement minerals.
- A part of chlorine in eco-cement can be dissolved in fresh concrete as chloride ion.

## (b) Corrosion of bar

- No corrosion was observed by accelerated corrosion test
- Exposure specimens in joint-research with Ministry of Construction and Ministry of Transport are under investigation
- In hardened concrete, chloride ion is stabilized in Freidel's salt and calcium silicate.

# Eco-cement Plant Construction with Eco-cement Concrete

- Location : Ichihara, Chiba pref.
- Production ability : 110,000ton/year approx.
- Now under operation



panorama

- Ichihara eco-cement plant, under construction -

# Mix Proportions of EC Concrete Compared with NPC Concrete

Design strength	Type of cement	Slump	W/C	s/a	W	C	S	G	AE
24	EC	15	55.5	43.0	174	314	756	1046	3.14
	NPC	15	57.5	44.0	167	291	789	1049	1.16
27	EC	18	51.0	44.0	175	351	730	1037	3.51
	NPC	18	53.5	45.0	171	342	748	1036	1.37
30	EC	18	55.3	47.1	175	317	826	968	2.85*
33	EC	18	52.3	46.7	175	335	813	968	2.68*

\*High Water Reducing Air Entrained Agent



Placing



Slump Test



Finishing



Finished surface

# Recent topics

## ■ Eco-cement plants

- » Ichihara plant started to work at April 2001, which is able to produces 110,000t/year.
- » Tokyo plant which produces 190,000t/year is at designing stage, will work at 2006.

## ■ TR was published by the Ministry of International Trade and Industry at May,2000.

## ■ The study on utilization and durability of concrete has been performed.

- collaborated between the Ministry of Construction, local governments and universities.
  - » Some field tests were carried out. i.e. pavement of Inokashira Park, bank of Shirakogawa supported by Tokyo government.
  - » concrete products such as inter rocking blocks, wall blocks etc.



# Conclusion

- Eco-cement process is a complete recycling system.
- Eco-cement is a quality cement changed incinerator ash into an industrial resource.
- Currently, Ichihara Eco-cement plant is under operation.
- Tokyo plant is under construction.