CONFIDENTIAL

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NIPPON SHOKUBAI

Design and Performance of Novel SAP for Making Concrete Sustainable

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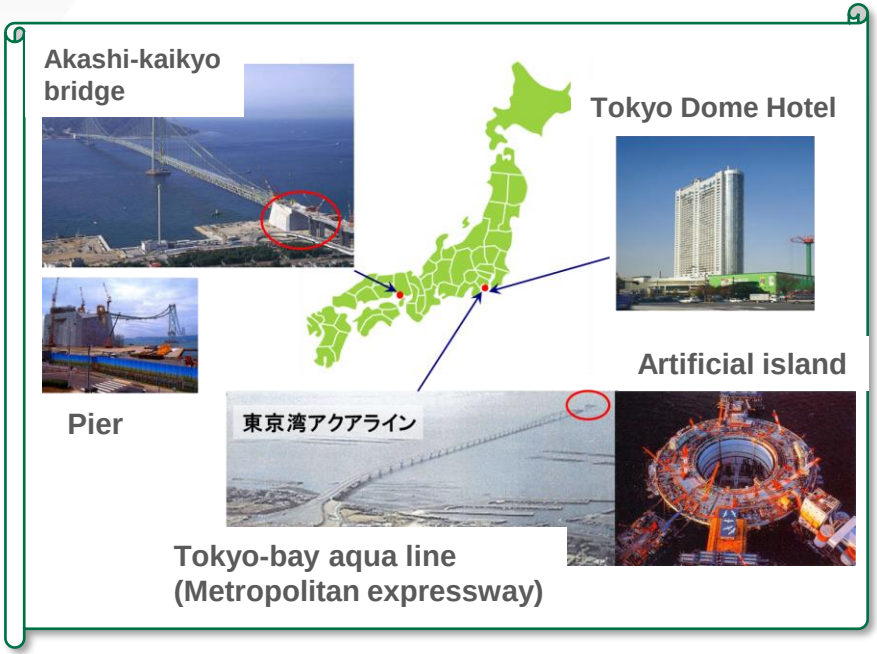
About Nippon Shokubai

PCE (AQUALOC™)

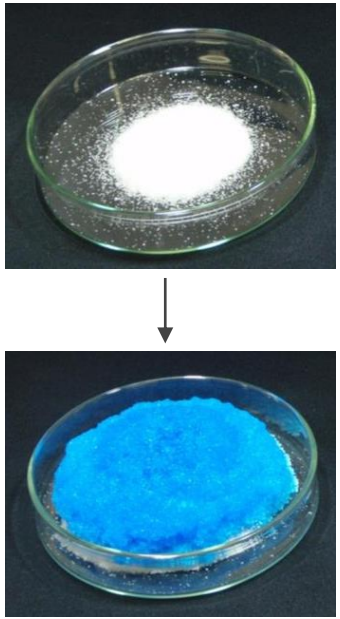
First to commercialized the Superplasticizer in 1987 in the world.



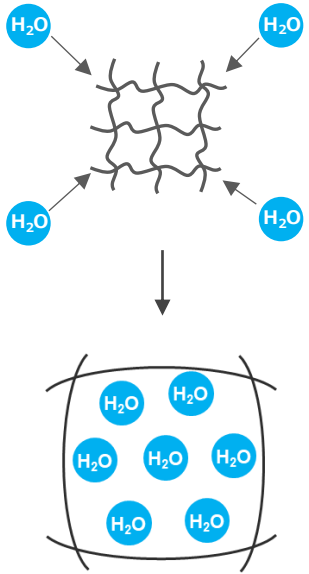
SAP (AQUALIC™ CA/CS)

- Applications

Diapers, Hygiene products, Water blocking agents etc.

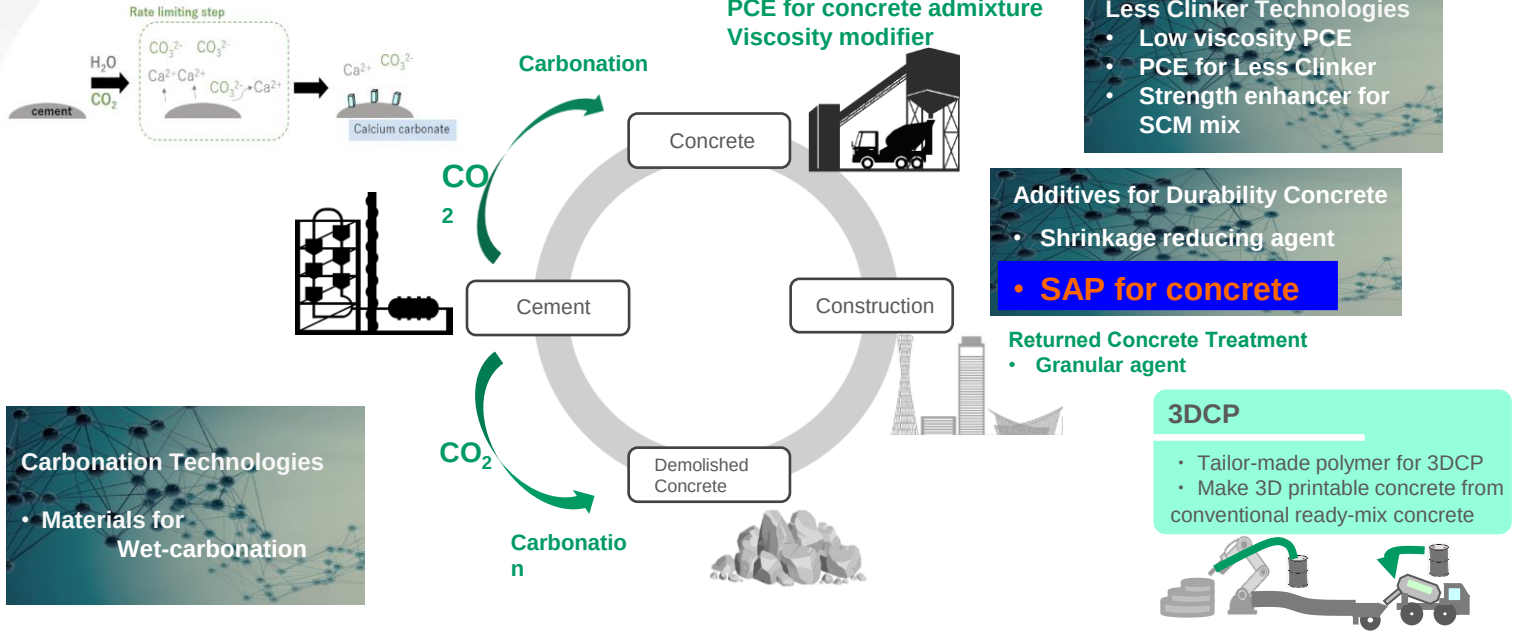


Crosslinked structure in SAP



NSCL approach to sustainability

✓ NSCL is developing various technologies from multiple angle



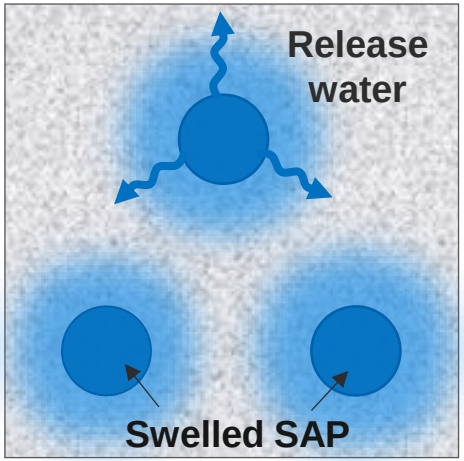
The reduction of CO2 emissions is an essential issue for the cement and concrete industries. According to the GCCA roadmap, less clinker factor and CCUS are necessary to achieve net. Nippon Shokubai is developing new technologies to contribute to CO2 reduction in the cement and concrete industries with various approaches.

The utilization of SAPs in concrete mixture

✓ **SAPs can provide multiple benefits on concrete properties.**

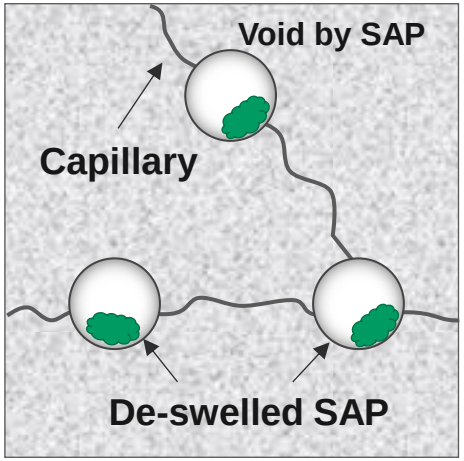
Concrete + SAP

Internal curing



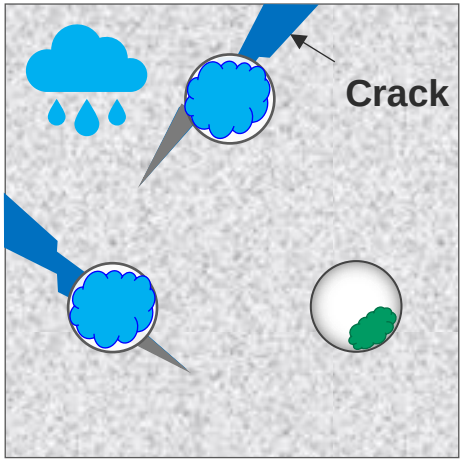
Strength enhancement
Shrinkage reduction

Air voids by SAP



Freeze-thaw resistance

Re-swelling



Self crack healing

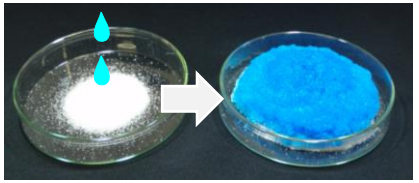
Mixing — After setting — Time

Mönnig, S., et al. (2006), K. Ichimiya, et al.(2012), Schröfl, C., et al.(2012),Hiroshi, K., (2013), Laustsen, S., et al., (2008), Snoeck, D., et al., (2014)

The main problem caused by using SAP

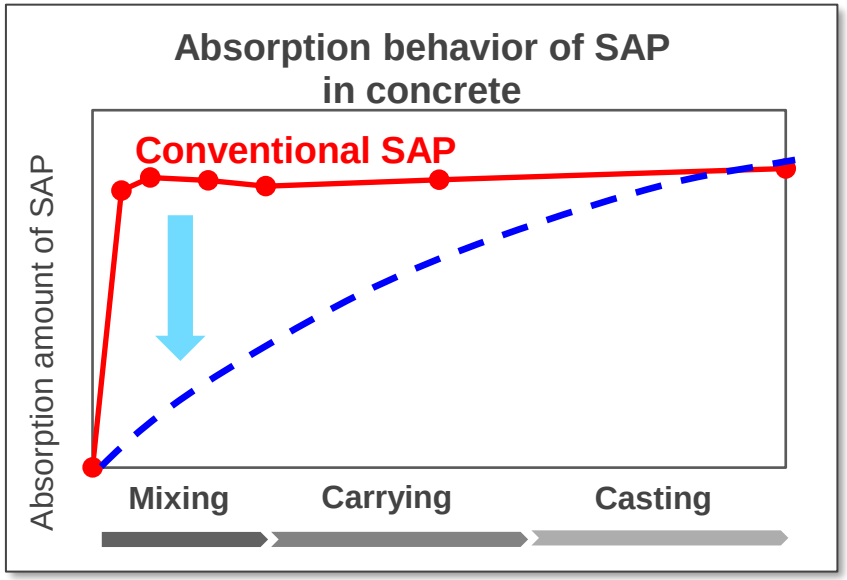
- Added only SAP powder

Poor flowability



- Added SAP and extra water

Good flowability
But decline in physical properties

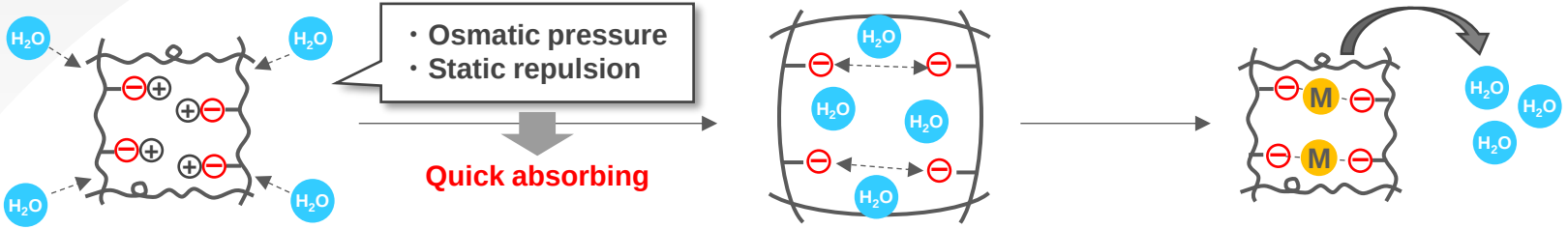


✓ Slower absorbing behavior is required for concrete.

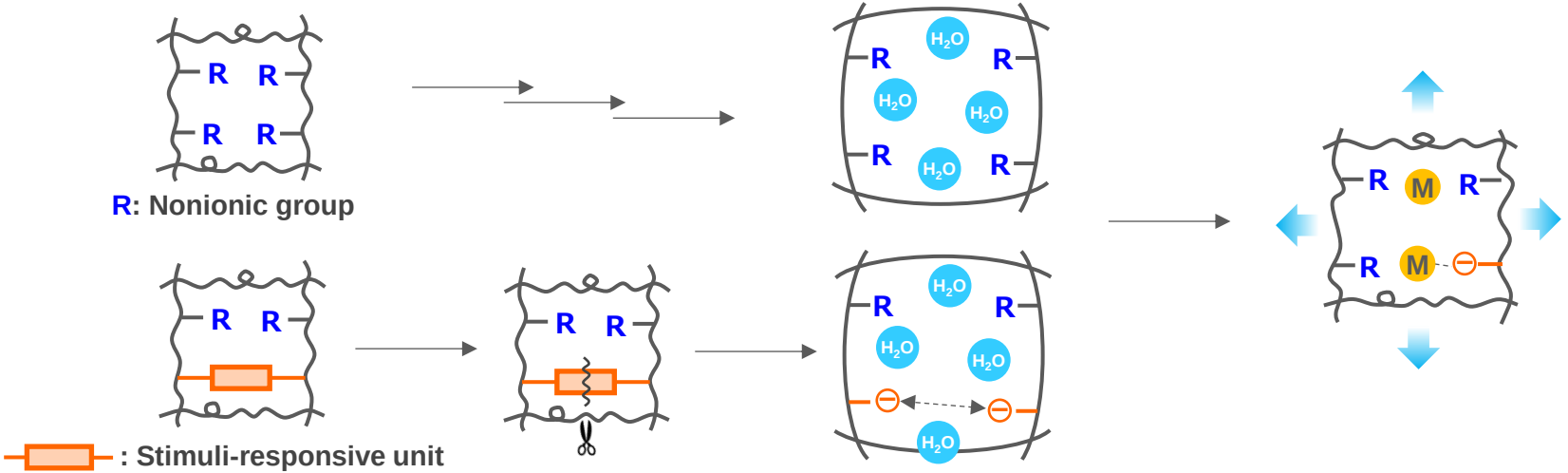
Design of crosslinked structure for slow absorption

- Conventional SAP based on acid salt monomers

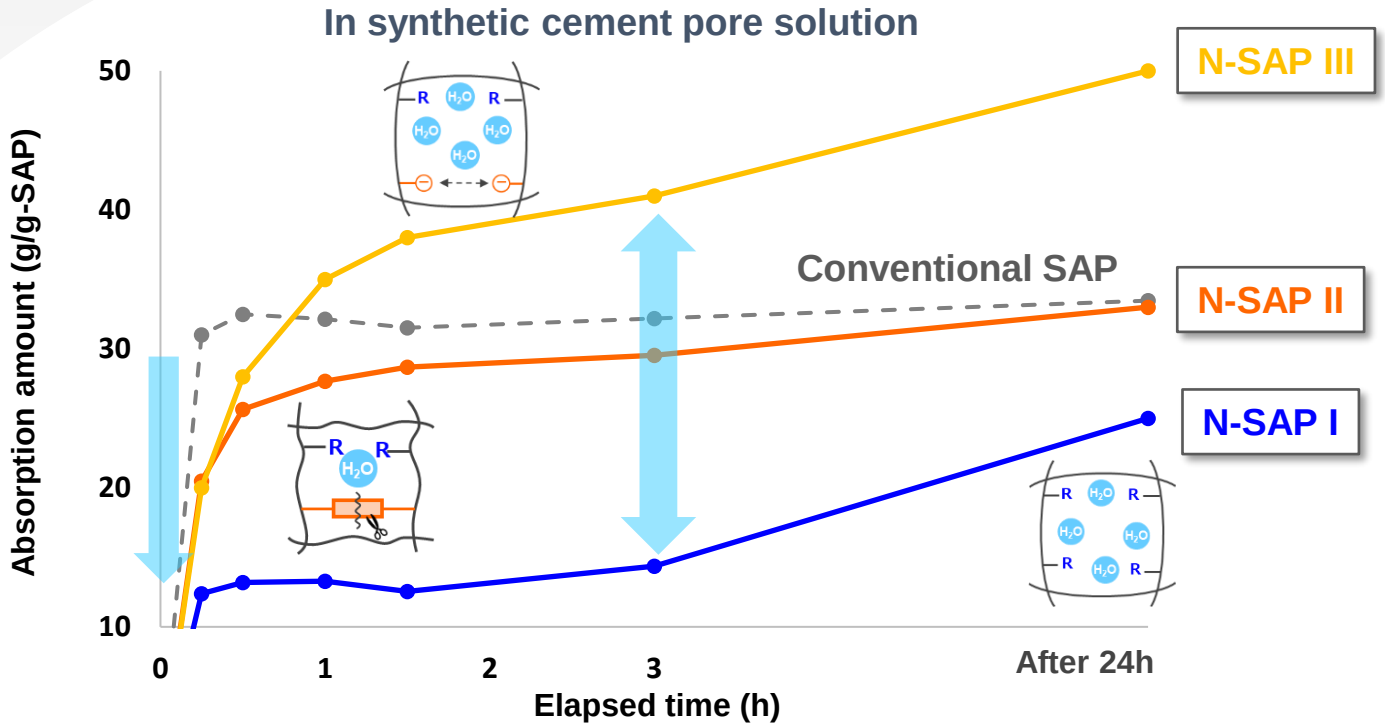
M : Multivalent cation (Ca^{2+} etc.)



- New design: Incorporation of nonionic groups and stimuli-responsive units



Absorption behavior of new SAP

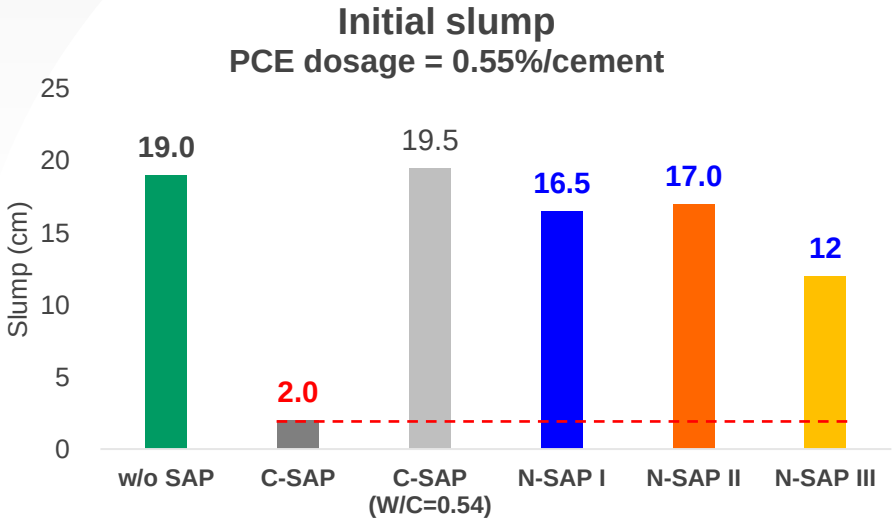


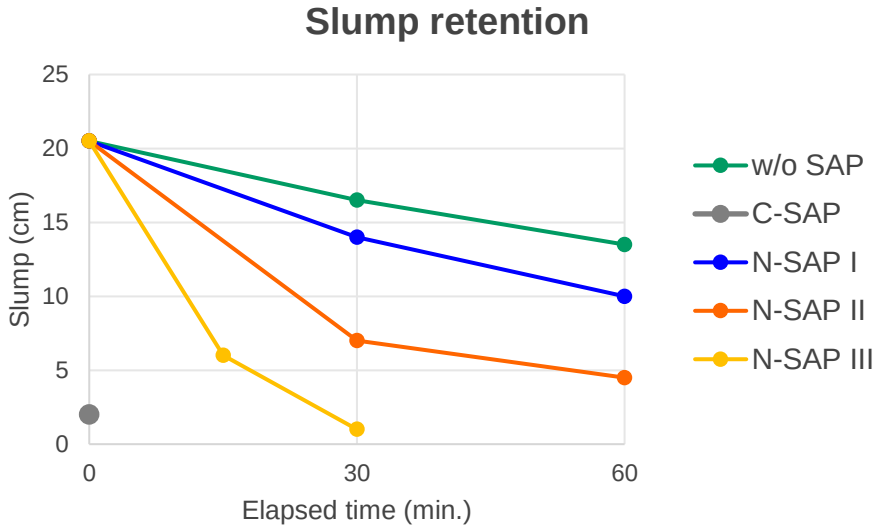
✓ This design allows to realize wide range slow absorption behavior by adjusting the amounts of nonionic groups and stimuli-responsive units.

Impact on flowability of fresh concrete

- **Concrete mix design**

W/C	Water (kg/m3)	Cement (kg/m3)	Fine aggregate (kg/m3)	Coarse aggregate (kg/m3)	**Dosage of SAP (kg/m3)**	Air
0.45	172	382	825	930	**1.15**	4.5%

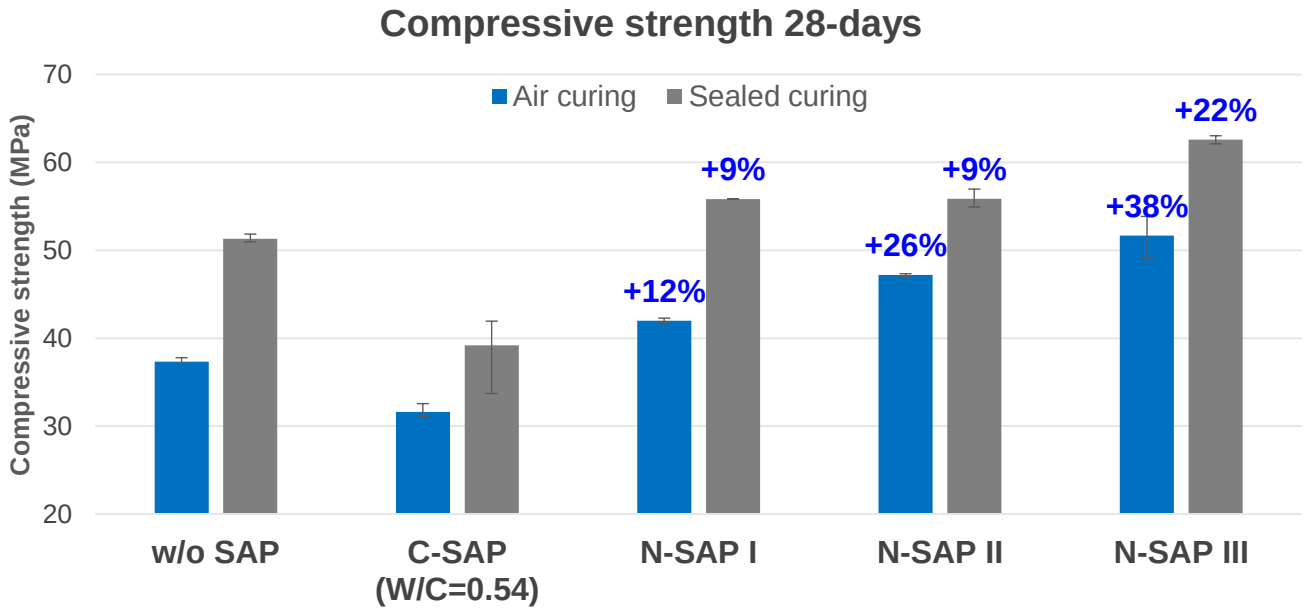




✓ **N-SAPs have less impact on initial slump of fresh concrete.**
✓ **N-SAPs affect slump retention due to slow absorbing in concrete.**

Impact on compressive strength

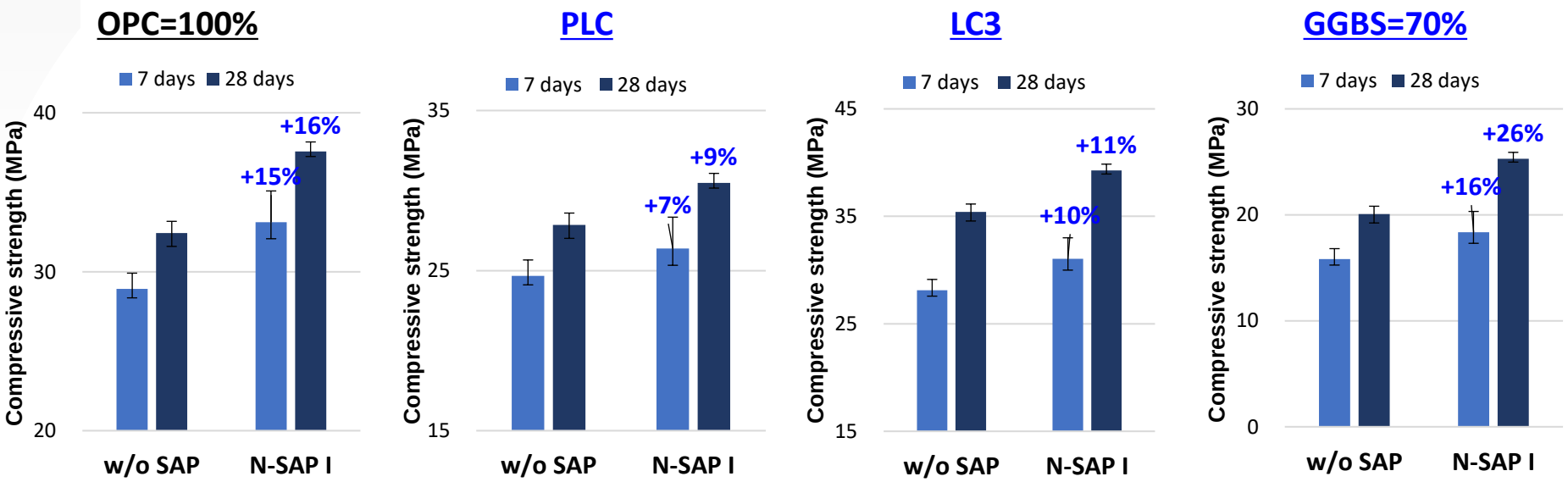
- Concrete test results (W/C=0.45)



✓ N-SAPs can enhance strength of concrete by internal curing effect.

Impact on alternative cement mix

- **Concrete mix designs (W/B=0.45)**
  - Simulated PLC: Limestone ratio = 15%
  - Simulated LC3: Cement/Calcined clay/Limestone/Gypsum = 50/30/15/5%
  - GGBS 70%: Cement/GGBS = 30/70%
  - Dosage of SAP = 1.15kg/m3
  - Curing condition: Air curing

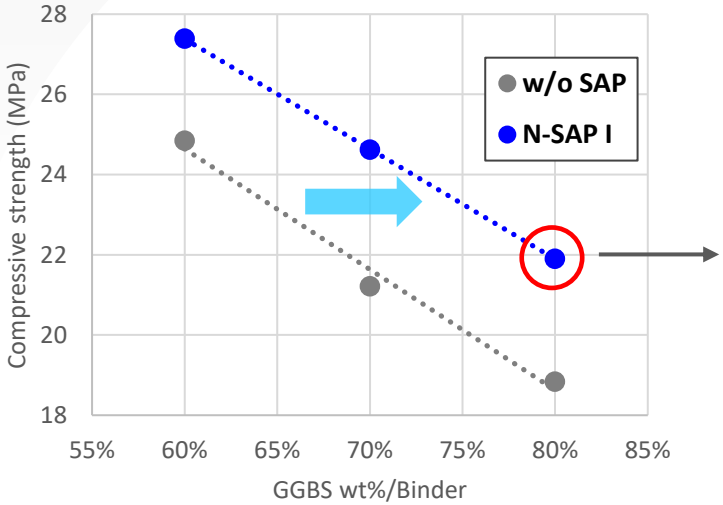


✓ **Internal curing effect of N-SAP was also confirmed in alternative cement mixes.**

Impact on alternative cement mix

● GGBS ratio vs Compressive strength

- W/B =0.45, Dosage of SAP = 1.15kg/m3
- Curing condition: Air curing



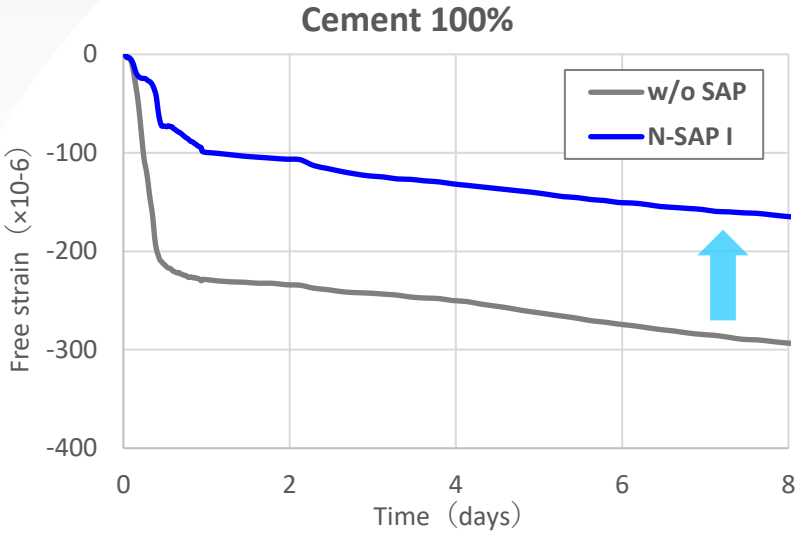
● Production scale test at a precast concrete plant

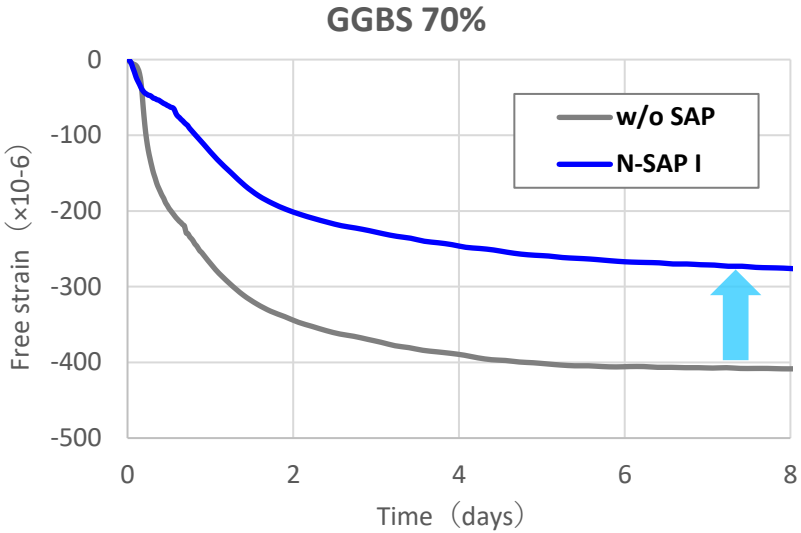
- Binder mix: Cement/GGBS = 20/80%
- Fabricated a Slab and a U-shaped gutter.

✓ **The amount of clinker can be reduced more than 10% by utilizing N-SAP I.**
✓ **We've successfully done a production scale test at a concrete plant.**

Impact on shrinkage

- **Autogenous shrinkage test (concrete, W/B=0.30)**
  - Cement 100%: Portland cement = 100%
  - GGBS 70%: Portland cement/GGBS = 30/70%

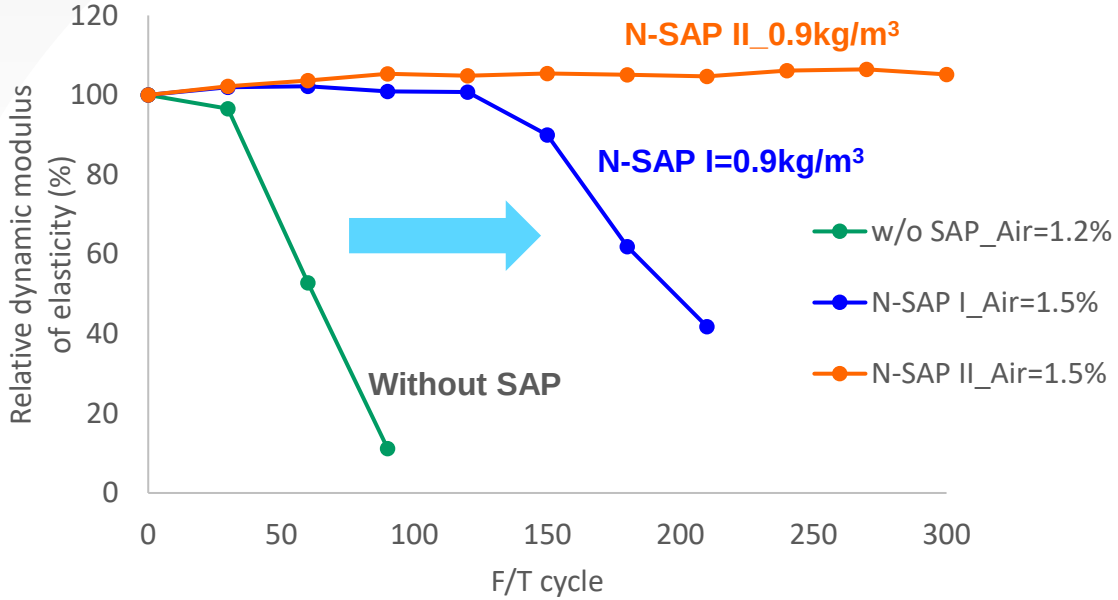




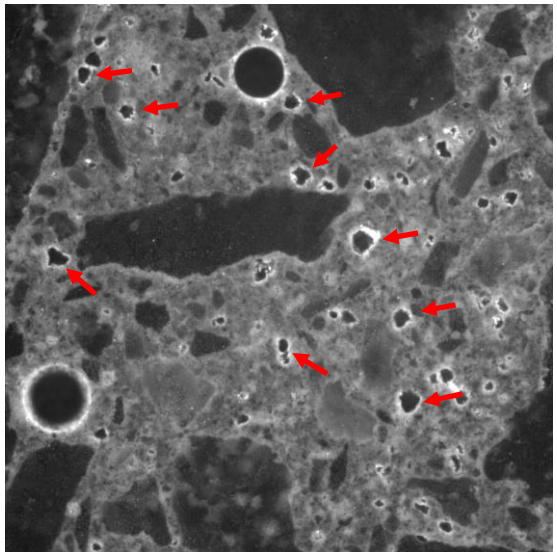
✓ **The shrinkage-reducing effect of N-SAP was also confirmed in the GGBS mix.**

Impact on freeze-thaw resistance

- **Freeze-thaw resistance test**
  - W/C=0.42 (Cement = 100%), Dosage of SAP = 0.9 kg/m3
  - Freeze-thaw test method: JIS A 1148 based on ASTM C 666



- **Microscopic observation on cutting surface of a specimen**

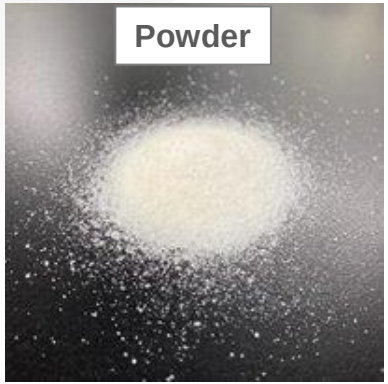


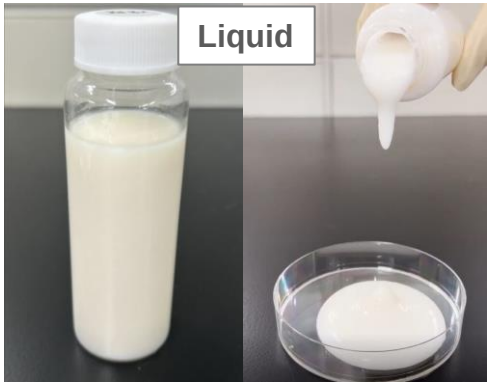
Air voids formed by SAP

✓ **N-SAPs have the ability to improve freeze-thaw resistance.**

Potential as admixture for 3D concrete printing

● Our new SAPs





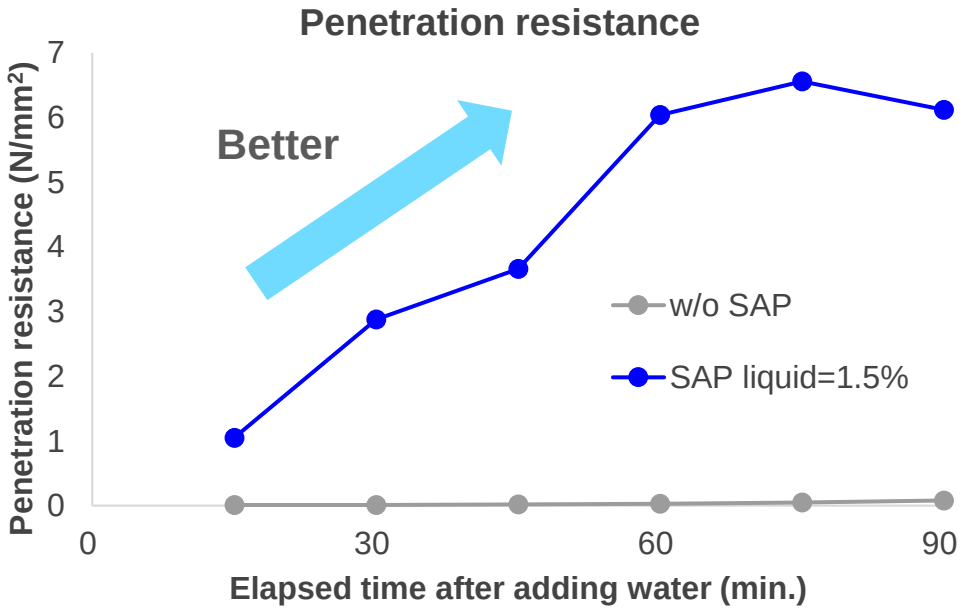
● 3D concrete printing (3DCP)

Features and Benefits
- Slow absorbing behavior
- Internal curing effect

Required performance
- Buildability (rheological control)
- Early strength
- Shrinkage mitigation

The test result for buildability

- **Mortar mix for low carbon concrete**
  - W/B=30%, cement = 315g, Calcined clay = 132g, Limestone = 277g, water = 218g, Sand = 1350g
  - Dosage of PCE = 0.7%/cement, SAP: Liquid type (conc. = approx. 20%)
  - Penetration resistance test was used for evaluation of yield stress.



✓ **N-SAPs seem to be effective for buildability.**

Summary

- Our new design of SAP can realize a wide range of slow absorption behavior in concrete.
- New SAPs based on our design have less impact on the flowability of fresh concrete.
- Internal curing effect, improvement of freeze-thaw resistance and potential for 3DCP have been confirmed.
- New SAPs will be expected as new concrete additive materials that can improve the durability of concrete and reduce environmental impact.

Thank you,
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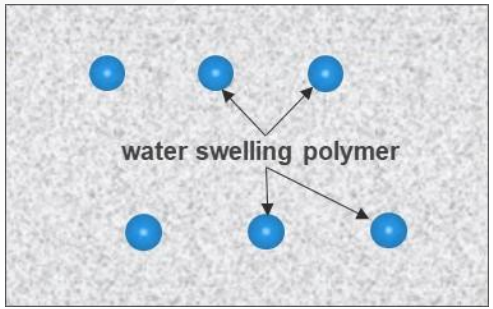
https://www.shokubai.co.jp/en/

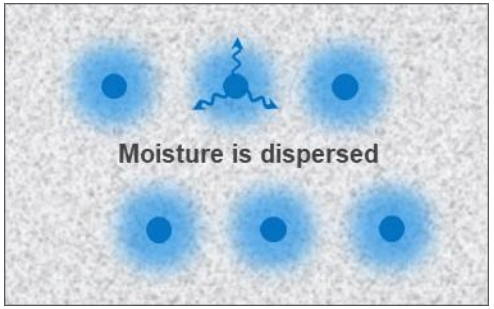
Super Absorbent Polymer for concrete

Our New SAP can accelerate hydration of cement by internal curing.

In fresh concrete



After setting

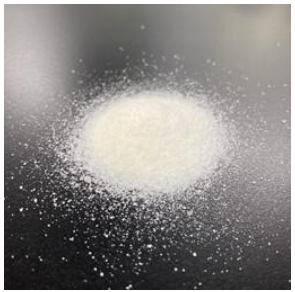


Material Information

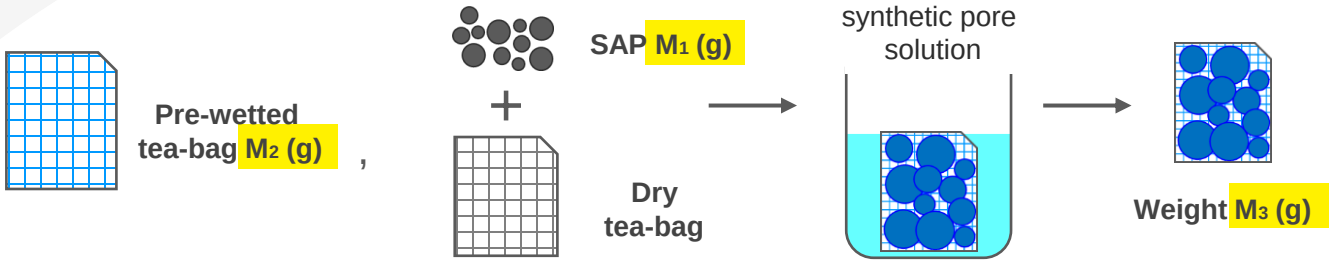
Form	Dry powder
Appearance	Slightly pale yellow
Chemicals	Cross-linked modified acrylic polymer
Particle size	Ave. 200-400μm
Density	Bulk density: 0.6-0.7g/cm^3 True density: about 1.8g/cm^3

Polymers gradually desorb water while the internal humidity drops, which lead to greater hydration of cement.

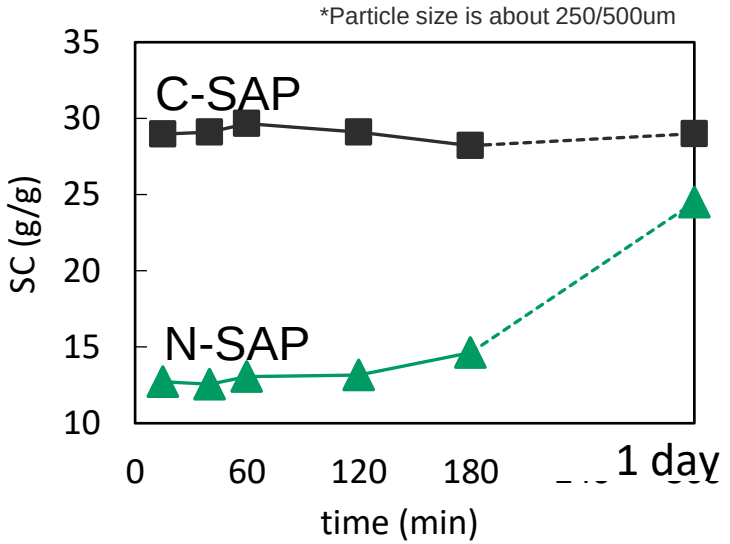
As a result, **the strength and autogenous shrinkage of concrete are improved.**



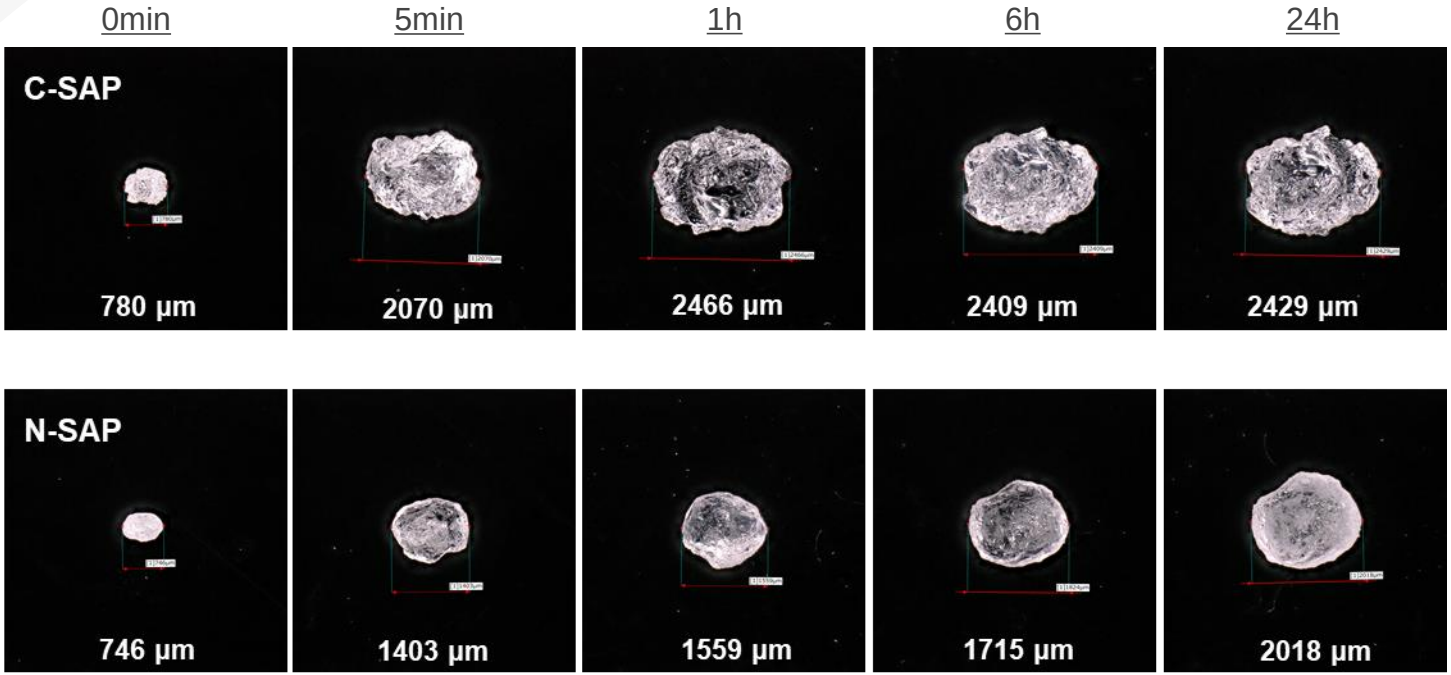
Absorption capacity evaluation



$$AC\ (g/g) = \frac{M_3 - M_1 - M_2\ (g)}{M_1\ (g)}$$

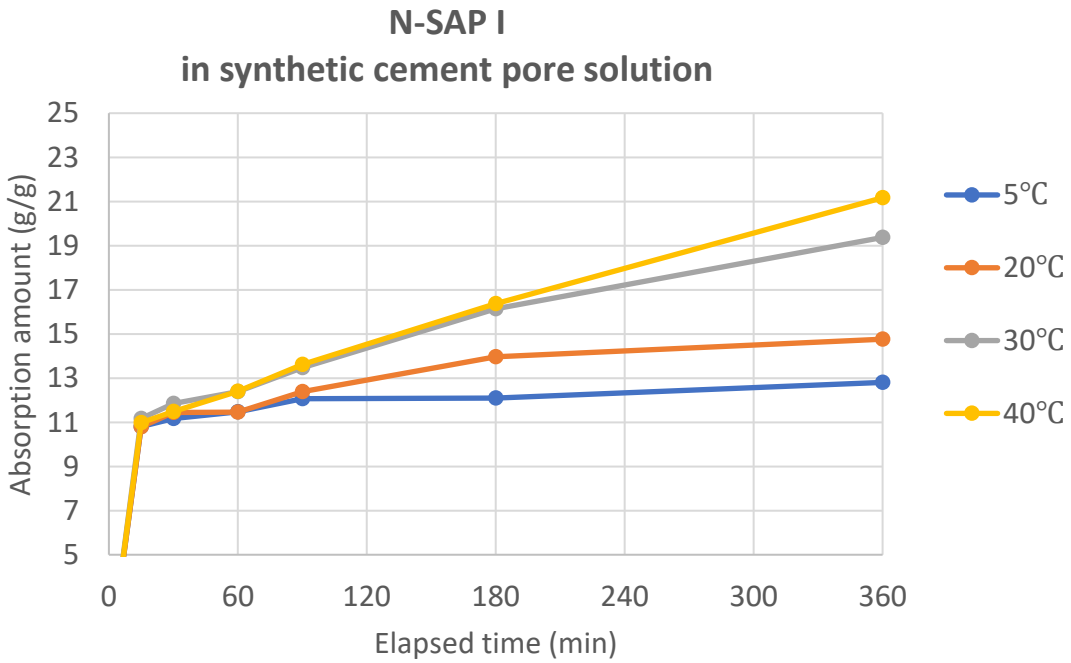


Microscope observation



Compared to C-SAP, N-SAP was swelling gradually in cement filtrate solution.

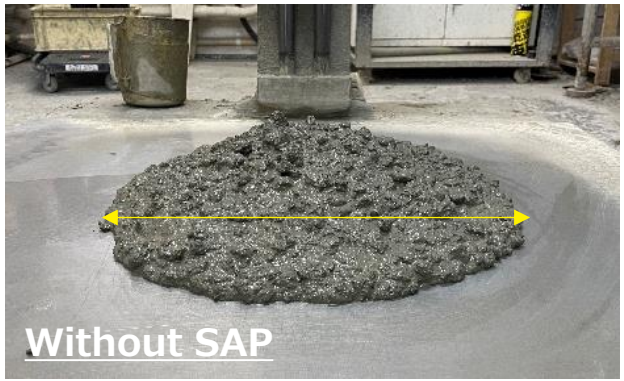
Temperature dependence of absorption rate



Workability of fresh concrete

【Materials】OPC(Taiheiyo), Land sand, Crashed sand, PCE(NSCL)
【Mix design】W/C=45%⇒C:380kg、Aggregate: Fine 800kg、Corse 930kg、W:172kg、s/a=47.0、air 45L
【Mixing Procedure】C+A+Additive → 10s mixing (60rpm) → PCE+W → 90s mixing (60rpm)

PCE wt%/C	Defoamer wt%/C	AEA wt%/C	Additive	dosage kg/m^3	Slump cm	air %
0.145	0.004	0.0042	-	-	22	4.7
0.145	0.004	0.0026	Conventional SAP	1.14	17	4.0
0.145	0.004	0.0032	New SAP	1.14	21	4.4

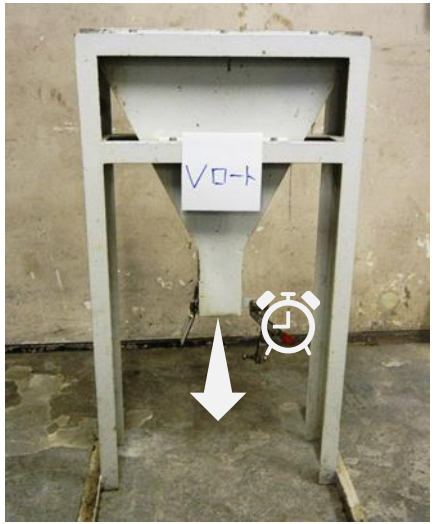


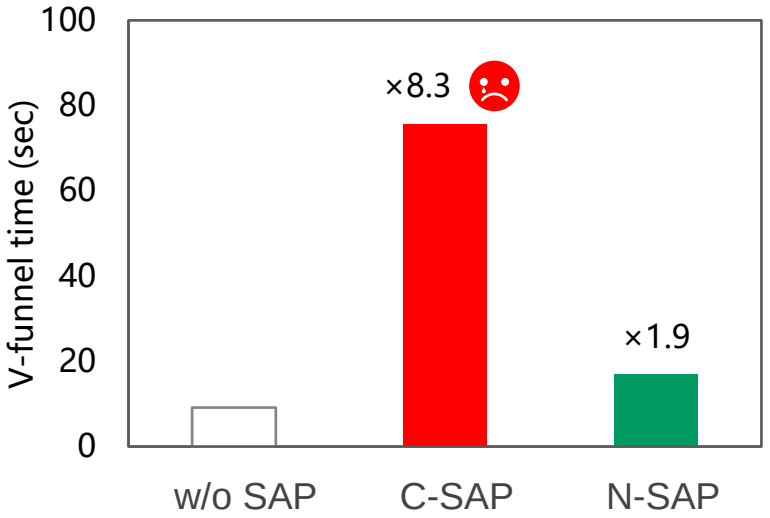
Our new SAP has no significant influence on fluidity.

V-funnel flow time measurement

- **Concrete mix designs (W/C=0.45)**
  - Dosage of SAP = 1.15kg/m^3

Japanese standard : JSCE-F 512

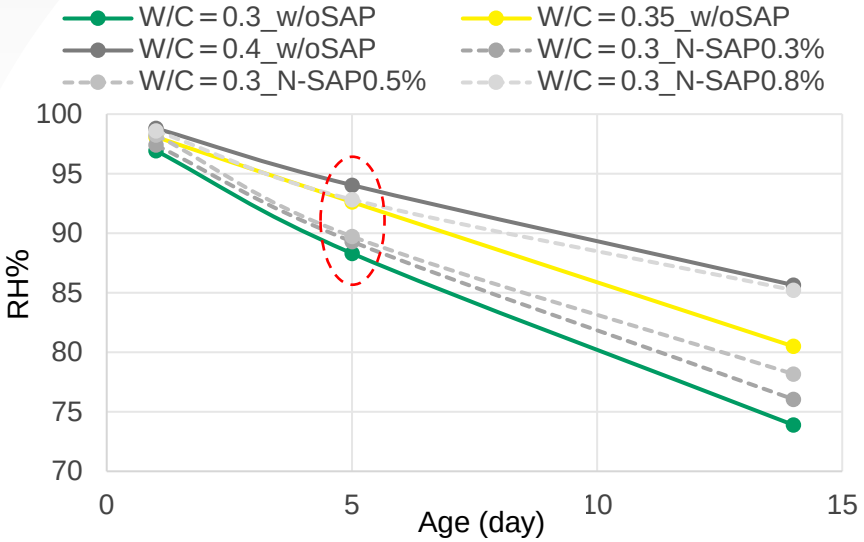


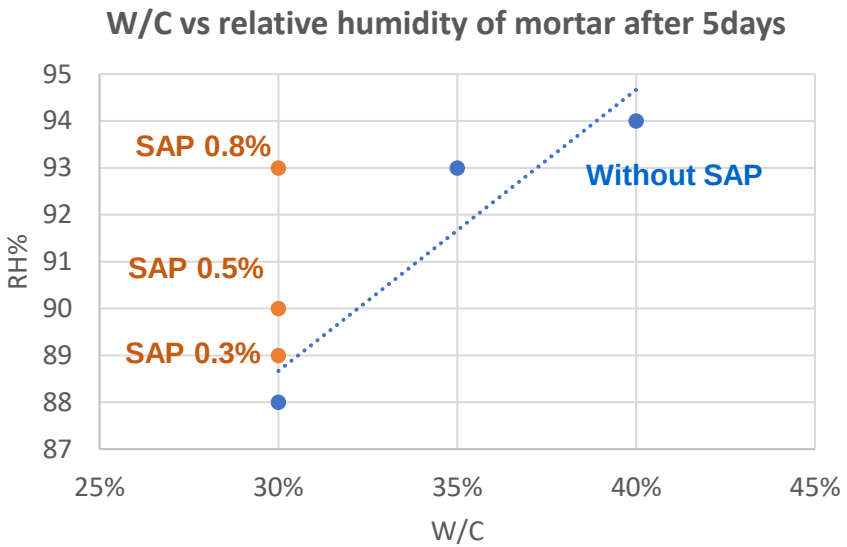


Relative humidity of mortar

Evaluation of relative humidity of mortar

- W/C=0.3, 0.35, 0.45
- After sealed curing, mortar specimens were crushed.
- Measuring instrument: AQUALAB 4TE water activity meter
- Temperature: 20℃

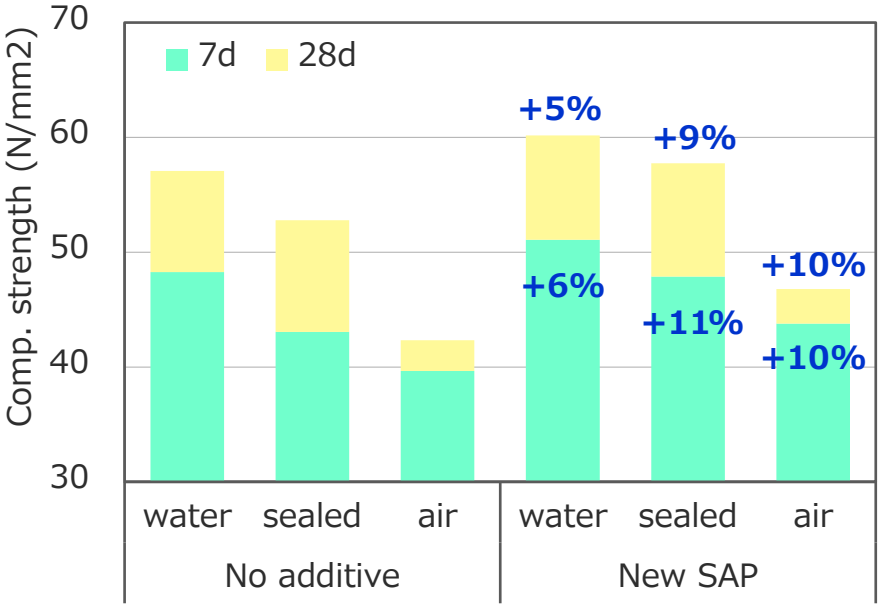




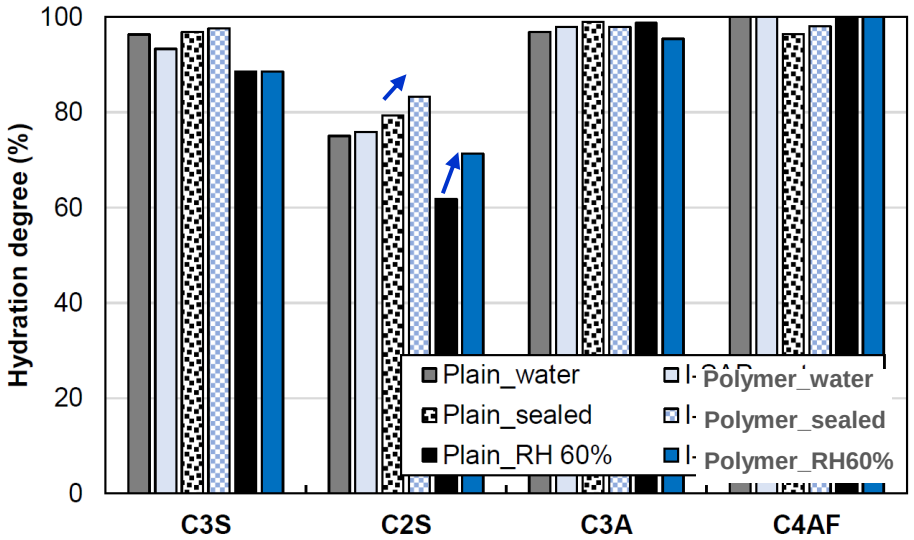
- **The higher the W/C, the smaller the decrease in relative humidity over time.**
- **The higher the amount of SAP added, the smaller decrease in relative humidity over time.**

Compressive strength

PCE (wt%/C)		SAP kg/m^3		Slump (cm)	air (vol%)	7d comp. strength (N/mm^2)			28d comp. strength (N/mm^2)		
						water	sealed	air	water	sealed	air
NS product	0.23	-	-	22.5	5.2	48.3	43.1	39.7	57.1	52.8	42.3
	0.29	New SAP	1.14	22.0	4.8	51.1	47.9	43.8	60.2	57.7	46.8



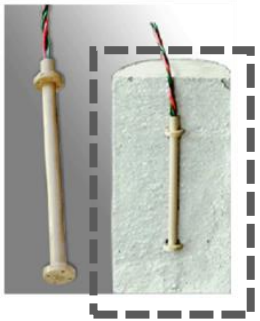
Hydration degree of individual clinker after 28days



Materials **2022**, *15*, 2727.

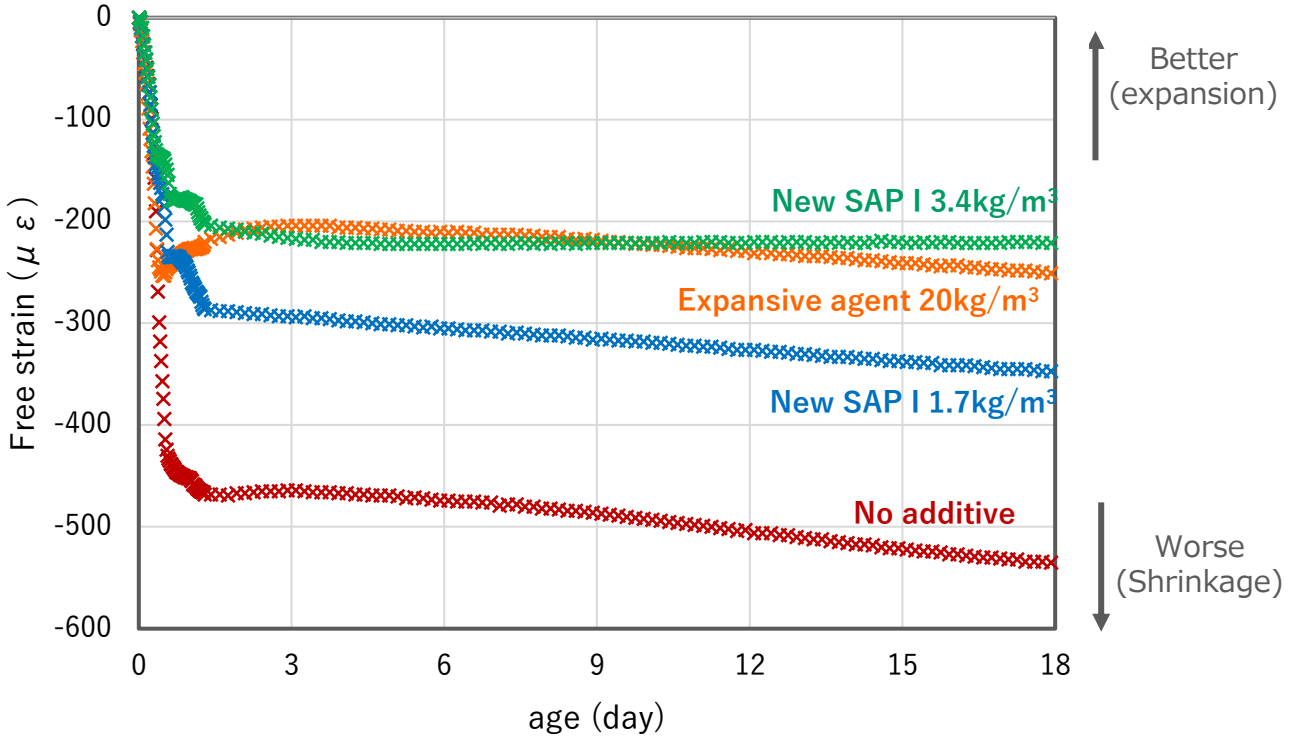
Autogenous shrinkage

【Materials】OPC(Taiheiyo), Land sand, Crashed sand, PCE(NSCL), Expansive agent (Taiheiyo materials)
【Mix design】W/C=30%⇒C:573kg、Aggregate: Fine 765kg、Coarse 866kg、W:172kg、s/a=47.0、air 45L
【Mixing Procedure】C+A+Additive → 60s mixing (60rpm) → PCE+W → 90s mixing (60rpm)
【details】Expansive agent 20kg/m3 was replaced with OPC cement. Additive was added to cement.



Φ100×200mm
Cylinder specimen

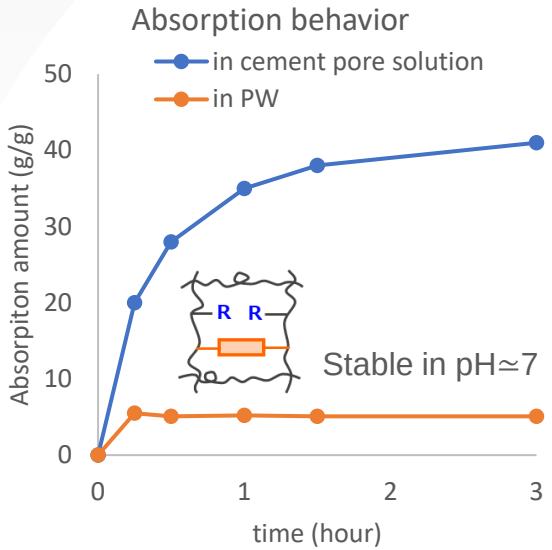
Sensor : strain gauge
Curing condition : sealed



Potential as admixture for 3D concrete printing

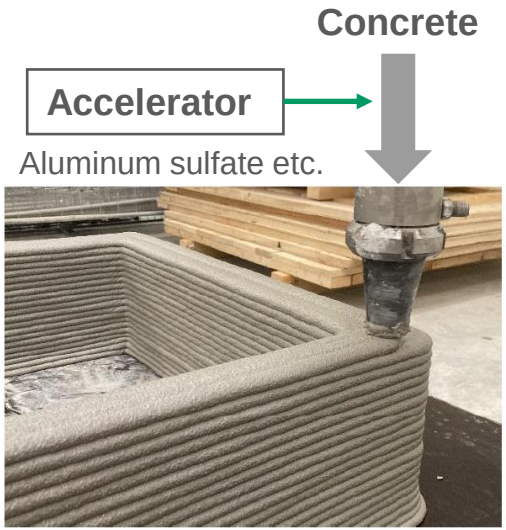
● **SAP dispersion liquid (water based)**

- SAP type: N-SAP III
- Conc. of SAP = ca.18%



● **3D concrete printing**

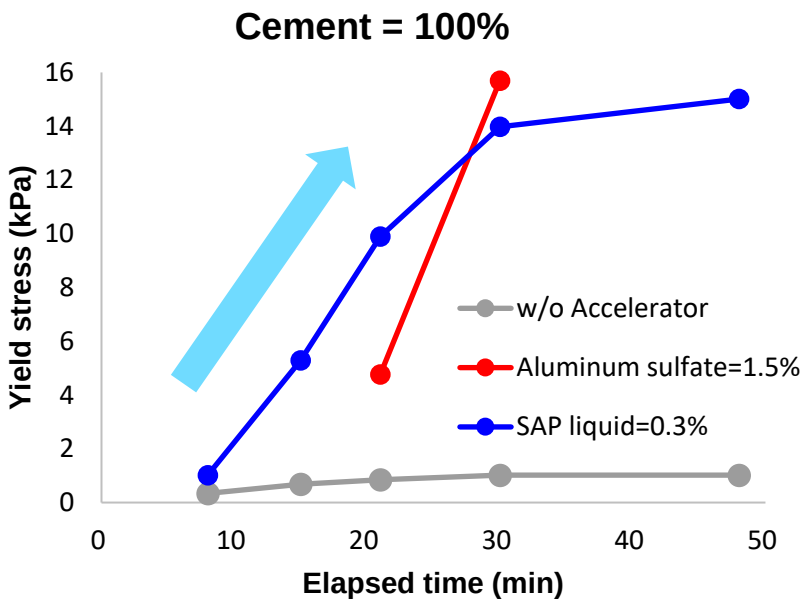
"2K printing system" has a secondary mixing step where an accelerator is added just before extrusion.



Mortar test results for 3D concrete printing

● Portland cement mix

- W/C=30%, cement = 900g, water = 270g Sand = 1350g, Dosage of PCE = 0.5%/cement
- Yield stress was measured by using vane shear instrument.



● Low carbon mix

- W/B=30%, cement = 315g, Calcined clay = 132g, Limestone = 277g, water = 218g, Sand = 1350g, Dosage of PCE = 0.7%/cement
- Penetration resistance test