

## **Shrinkage characteristics of alkali activated slag mortar with Super-absorbent polymer**

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### **ABSTRACT**

For the reduction of carbon dioxide emission, alkali activated slag (AAS), whose main constituents are ground granulated blast furnace slag (GGBFS) with alkali activators, has been developed for various applications in construction industry. The compressive strength of alkali activated slag is currently as high as that of normal concrete, but shrinkage issue has occurred, which causes cracks on concrete structures. Thus, researchers have continued their efforts to mitigate shrinkage strains and stresses. For the reason above, in this article, two alkaline activators, liquid sodium silicate with 15M sodium hydroxide solution and sodium carbonate powder, were considered for alkali activated slag mortar, and ordinary Portland cement mortars were produced to compare with alkali activated slag. Moreover, mechanical properties such as the setting times and compressive strength of three mixtures were evaluated. Autogenous strains were evaluated using corrugated plastic molds according to ASTM C 1698, and microstructure characteristics of alkali activated slag and control mixtures were proved by conduction calorimetry and mercury intrusion porosimetry. In this study, "Superabsorbent polymer (SAP) had been used to reduce autogenous shrinkage or alkali activated slag mortars for the internal curing effect.

### **1. Introduction**

There have been tons of efforts to exploit green materials in construction industry in the world. Greenhouse gas is currently considered as a major cause occurring global warming, and thus researches on development of building materials that can reduce emission of carbon dioxide have been conducted. Research engineers have already found out several alternatives which do not generate carbon dioxide during manufacturing and are environmentally friendly. For instance, "Geopolymers" is one of the well-known alternatives, which was introduced by J.Davidovits in 1988. This is the one of inorganic composites that was hardened under low temperature from the reaction of Alumino-silicate and alkaline activators. Alumina (Al) and Silica (Si) are very plentiful in fly ash, metakalolin, and so on. Similarly, alkali activated slag is consisted of ground granulated blast furnace slag and alkaline activators, and currently, ground

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granulated blast furnace slag is used as raw materials of blast furnace slag cement or concrete admixtures. However, the researches on alkali activated slag without ordinary Portland cement have still been dominant topics because of its superior characteristics such as high early-age strength, high durability, high resistance to chemical attacks and low hydration heat. In this article, total six mixtures were provided to explain the characteristics of alkali activated slag mortars, and several experiments were conducted, such as setting time measurement, compressive strength test, autogenous shrinkage strains, and a few micro-structure analysis such as conduction calorimetry and mercury intrusion porosimetry (MIP).

## 2. Material properties and experimentation

### 2.1 Material properties used

Total six mixtures were tabulated to evaluate characteristics of alkali activated slag and cement mortars to perform various experiments in Table 1. Alkali activated slag mortars were mixed with sodium silicate and 15 mole sodium hydroxide solution (NaOH/Na<sub>2</sub>SiO<sub>3</sub>) (Mixture W and W(IC)) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) (Mixture S and S(IC)). Also, cement mortars (Mixture C and C(IC)) were prepared to compare with alkali activated slag mortars as plain mixtures.

	Activator mixture (g)	Control C	Control C(IC)	Waterglass/NaOH W	Waterglass/NaOH W(IC)	Na <sub>2</sub> CO <sub>3</sub> S	Na <sub>2</sub> CO <sub>3</sub> S(IC)
Binder	Type I cement (g)	568.6	568.6	-	-	-	-
	GGBFS (g)	-	-	568.6	568.6	568.6	568.6
Aggregate	ISO standard sand (g)	1,350	1,215	1,350	1,215	1,350	1,215
	SAP (g)	-	51.9	-	51.9	-	51.9
Activator	Water (g)	227.4	117.7	143.6	201.5	227.4	201.5
	Water, SAP (g)	-	50.2	-	50.2	-	50.2
	Waterglass (g)	-	-	93.8	93.8	-	-
	15M NaOH solution (g)	-	-	43.3	43.3	-	-
	Sodium carbonate (g)	-	-	-	-	38.9	38.9

Table 1 Mixing proportions of alkali activated slag and cement mortars

The cement used was Type I ordinary Portland cement obtained from Korea with a specific gravity of 3.15 g/cm<sup>3</sup>.

Ground granulated blast furnace slag with large amount of silica and alumina in amorphous state was one of the industrial by-products, which was obtained from iron

steel factory in Korea. Its specific gravity was 2.89 g/cm<sup>3</sup> with a value of Blaine specific area, 4330 cm<sup>2</sup>/g. The chemical compositions were described in Table 2.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	LOI	SUM
OPC	34.0	16.4	0.50	37.2	6.29	0.45	1.33	2.71	0.17	99.05
GGBFS	21.2	4.64	2.91	61.9	1.87	1.22	0.29	2.31	2.48	98.82

Table 2 Reactant chemical compositions, % by mass

The sand used was natural and siliceous ISO standard sand, whose maximum grain size was 2 mm with 2.6 g/cm<sup>3</sup> of a specific gravity. The particle-size distribution complied with the requirement of ISO 679:2009, and absorption value of was be less than 0.2 %.

Sodium silicate, which was also called “waterglass”, was liquid state of alkaline activator used in mixture W and W(IC), whose mole ratio SiO<sub>2</sub>/Na<sub>2</sub>O (*M<sub>s</sub>*) was 3.03 with 28.2 % of SiO<sub>2</sub> and 9.3 % of Na<sub>2</sub>O by total weight. The specific gravity of sodium silicate measured was 1.405 g/cm<sup>3</sup>.

99% purity of sodium hydroxide powders, the other alkaline activator for mixture W and W(IC), was dissolved to create a solution of 15M concentration in water for mixture W and W(IC). This solution was produced to control a molar ratio of activator and more details will be discussed in 2.2 *Experimentations*. 1.435 g/cm<sup>3</sup> of the specific gravity of the 15M NaOH solution was measured using a specific gravity meter.

Sodium carbonate powder was 99.5 % pure and the only alkaline activator in mixture S and S(IC). The specific gravity of the powder was 2.536 g/cm<sup>3</sup>.

A chemical admixture, super-plasticizer, was used to improve the workability of mortar mixtures, and approximately 0.5% to 1.0 % of binder weights were added during mortar mixing.

Superabsorbent polymers were polymers, which can absorb and retain a vast amount of water. Hydrogels were created after SAP dry powders had absorbed water and then swelled, and they were utilized to reduce shrinkage strains and prevent cracks on mortars in the article. SAP containing water was substituted for 10% of ISO standard sand.

## 2.2 Experimentations

Material proportions by weight of the mortar mixtures were 0.4:1.0:2.37, water, binder and sand, respectively. Water/binder ratio was fixed as 0.4, and SiO<sub>2</sub>/Na<sub>2</sub>O (*moduli, M<sub>s</sub>*) of Na<sub>2</sub>SiO<sub>3</sub> and NaOH solution was 1.2. Alkaline activators were manufactured to contain 4% of Na<sub>2</sub>O by weight of binder in liquid activator for mixture W and W(IC), and mixture S and S(IC) also contained 4% of Na<sub>2</sub>O by binder weight. The amount of additional water in mixtures with SAP had been reduced due to surface moistures on SAP swelled.

Automatic concrete setting test machine was operated to evaluate setting times of alkali activated slag and cement mortars, and specimens were casted in molds (15cm diameter with 15cm height cylinder), and test method complies with ASTM C 403.

Test specimens for compressive strength of alkali activated slag and cement mortars were casted in triple mortar molds (40mm by 40mm by 160mm). Four sets per each mixture were produced for compressive strength test at ages of 1, 3, 7 and 28 days. Universal testing machine (UTM) in Korea Conformity Laboratories had been operated to measure compressive strength of mortars manufactured according to ASTM C 109. All mixtures were cured in the water tank for the high compressive strengths of mortar specimens.

Corrugated PE-molds with two specially shaped end plugs and approximately 440mm reference bar were utilized to measure autogenous shrinkage strains of all mixtures for almost 500 hours according to ASTM C 1698. As soon as the specimens were cased, they were immediately sealed with end plugs and placed in the steady temperature and humidity room at 20 °C and 50%.

There were various types of experiments and test methods to evaluate micro-structure of alkali activated slag and cement mortars, and conduction calorimetry and mercury intrusion porosimetry were selected to conduct microstructures of alkali activated slag and cement mixtures.

### 3. Result and discussion

#### 3.1 Setting times

Setting times in the experiments were evaluated according to test methods, ASTM C 403 and ASTM C 266. Since rapid setting occurs during casting mixtures W and W (IC), automatic concrete setting test machine was not able to measure accurate setting times. Thus, W series mixtures were complied with ASTM C 266. The other specimens, mixture S and C series, followed ASTM C 403, which was the test method to measure setting time with automatic concrete setting test machine. Initial and final setting times of all mixtures were presented in Table 3. Somewhat longer setting times were discovered in the mixtures with SAP, but the difference between mixtures with SAP and without SAP can be neglected because of small gaps.

		<b>C</b>	<b>C(IC)</b>	<b>W</b>	<b>W(IC)</b>	<b>S</b>	<b>S(IC)</b>
Setting time	Start (SST, min)	277	336	10	12	62	62
	Initial (FST, min)	487	516	57	72	272	272

Table 3 Time of settings for six mixtures

#### 3.2 Compressive strength

The compressive strength in Figure 1 showed control mixture C and C(IC) at the ages of 1,3,7 and 28 days. In early ages, compressive strength of non-internal curing mixture was slightly higher than that of internal curing mixture, but after 28 days,

compressive strength of both mixtures were reversed. Internally-cured specimen was 52MPa, which was larger value than 51MPa for cement mortar without internal curing.

Fig 2 also indicated similar test result with previous data that compressive strength of the mixture without SAP was lower than that of the mixture with SAP at 28 days. The mixture W and W(IC) showed the highest compressive strengths among all mixtures provided. At 28 days, the compressive strength of W mixture with SAP was 57MPa, and that without SAP was 54MPa.

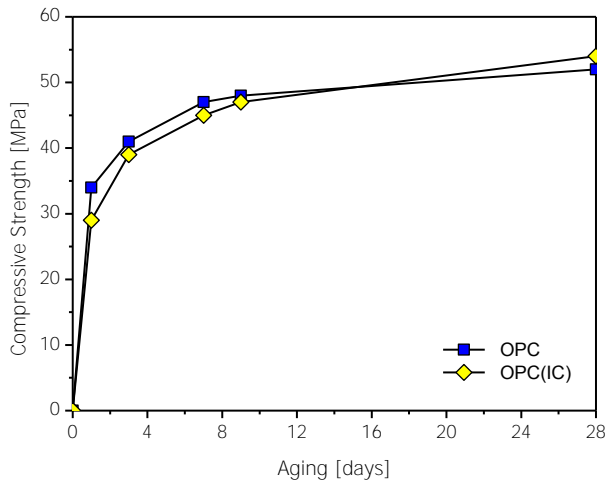


Fig 1 Compressive strengths of mixture C and C(IC)

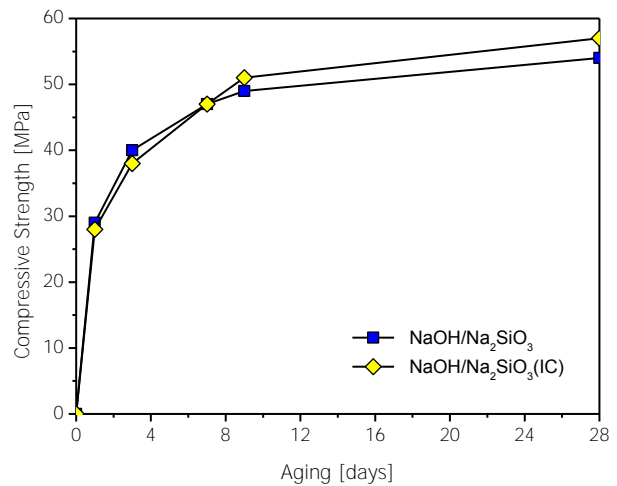


Fig 2 Compressive strengths of mixture W and W(IC)

For sodium carbonate mixtures, relatively lower early compressive strength compared to other mixtures were exhibited in Fig 3. However, 38 to 42MPa of compressive strengths at 28 days had been obtained, so the additional activators needed to be applied for higher compressive strengths of the specimens.

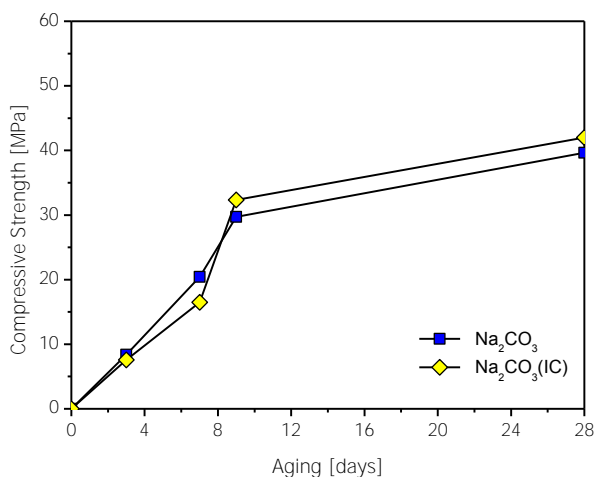


Fig 3 Compressive strengths of mixture S and S(IC)

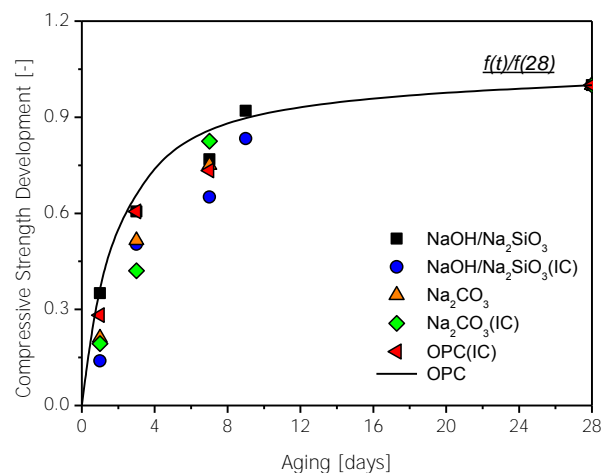


Fig 4 Compressive strengths development of all mixtures with and without internal curing

The ratio of compressive strengths at each age to at 28 days was plotted in Fig 4 in the previous page according to ACI equations. Equations that ACI recommended were provided as follow.

$$(f'_{c})_t = \frac{t}{\alpha + \beta t} (f'_{c})_{28} \quad (1)$$

$$(f'_{c})_t = \frac{t}{\frac{\alpha}{\beta} + t} (f'_{c})_u \quad (2)$$

Compressive strength development values dotted for all mixtures were mostly below the curve of Eq.1 of cement mortar without superabsorbent polymer. It means that  $\alpha$  and  $\beta$  of ground granulated blast furnace slag, the coefficients determined from cement types and by curing methods, can be considered higher than those for ordinary Portland cement.

### 3.3 Autogenous shrinkage

Autogenous shrinkages of alkali activated slag and cement mortar mixtures were evaluated according to ASTM C 1698. All data provided were collected from the time right after the final setting had ended. (Fig 5)

Total shrinkage strains of control mixture C was less than 120 micro-strains, and test results were relatively lower than those of waterglass/NaOH and sodium carbonate based alkali activated slag mixtures. As shown in Fig 6, total autogenous strains with internal curing had decreased to 10 micro-strains, and even expansion in autogenous strain curve was obtained. This shows that SAP had an important role in reduction of shrinkage strains of cement mortars.



Fig 5 Test specimens of corrugated PE molds after the experiments

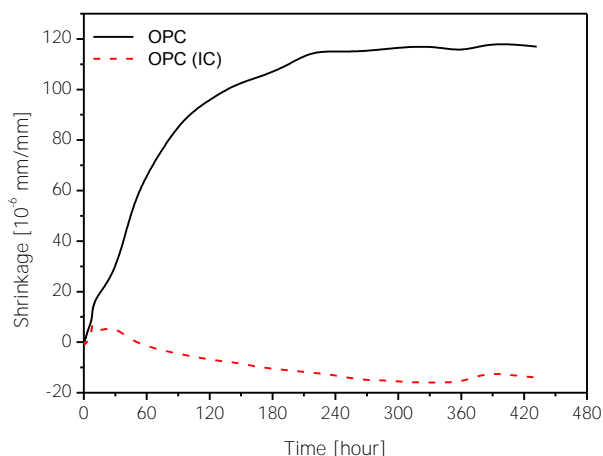


Fig 6 Autogenous shrinkage strains of mixture C and C(IC)

Mixture W and W(IC) caused huge autogenous strains, and more than total 1100 micro-strain strain was measured when it was not cured internally. However, shrinkage of mixture with SAP was dropped from 1100 to 300 micro-strains, which was a huge shrinkage strains reduction.

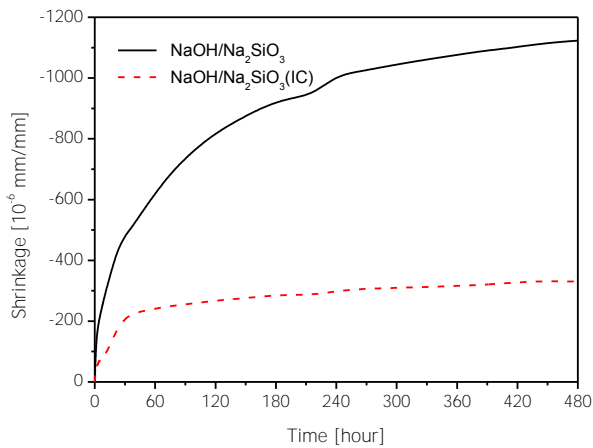


Fig 7 Autogenous shrinkage strains of mixture W and W(IC)

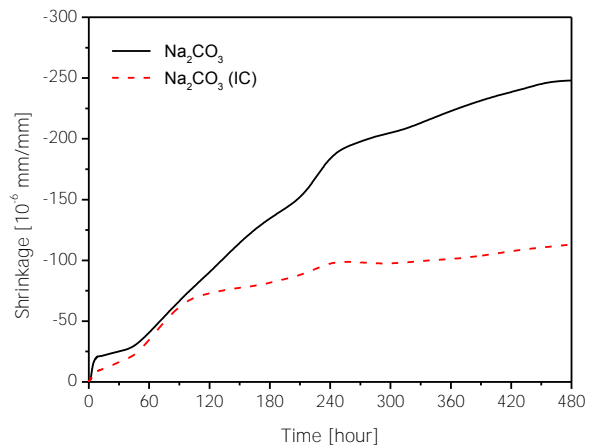
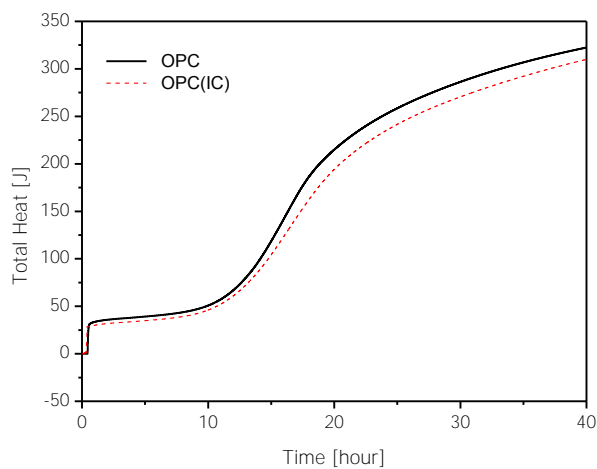


Fig 8 Autogenous shrinkage strains of mixture S and S(IC)

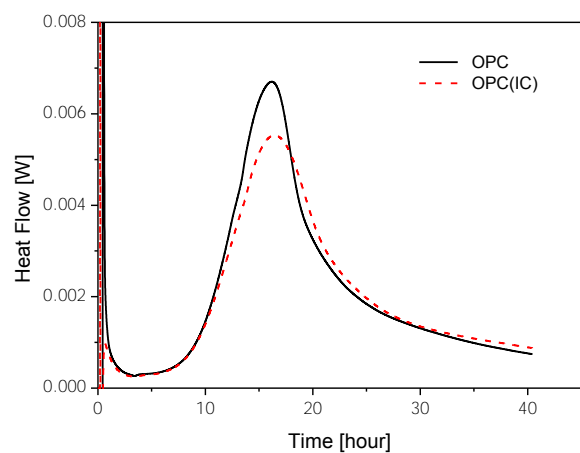
Autogenous shrinkages of mixture S and S(IC) were plotted in Fig 8. The shrinkage strains were almost equally increased during the first 100 hours, but rapid strain increase in mixture S has shown after 100 hours. Although shrinkage strain in mixture S(IC) also had increased, the slope of curve in mixture S was relatively gradual.

### 3.4 Conduction calorimetry

Early age hydration behavior and heat of hydration were measured in order to evaluate hydration heat trend of ground granulated blast furnace slag and ordinary Portland cement by conduction calorimeter.



(a) Total heats for mixture C and C(IC)



(b) Heat flow for mixture C and C(IC)

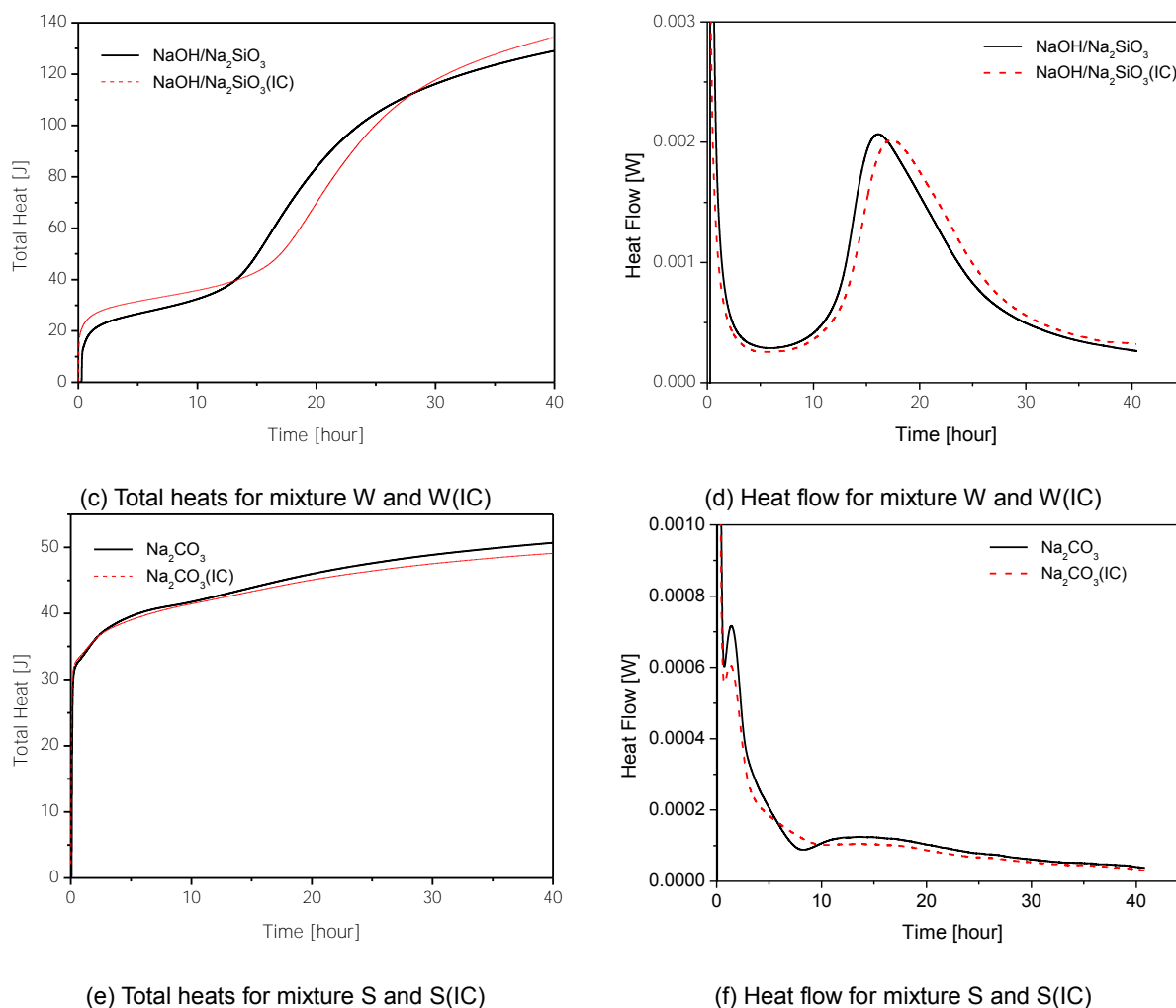


Fig 9 Total heats cumulated and heat flow for the mixtures

The conduction calorimetry was performed to investigate the existence of surplus water on SAP swelled because the surface water on SAP could influence on the mixing water and water/binder ratio. Since experiment result shows no significant difference between mixtures with SAP and without SAP, it could be considered that appropriate mixing water was added in the mixtures as shown in (b), (d) and (f) of Fig 9.

The gap between two peak values on mixture C and C(IC) could be considered as allowable ranges because of the identical time on peak heat flow. Slag based mixtures showed almost the same heat flow curves and they were not influenced by additional water inside and outside of SAP. Relatively low peak heat flows were exhibited in mixture S and S(IC), and they released peak heat at the early stage, which is faster than the other mixtures did. Also, mixtures with SAP radiated heat later than those without SAP, and this means that surplus water was added in the mixtures.



### 3.5 Mercury Intrusion Porosimetry (MIP)

Porosity significantly influences on mechanical property of concretes or structures because it related to durability and compressive strength. Mercury intrusion porosimetry (MIP) was conducted to investigate pore volumes intruded by mercury with respect to pore diameter for pore volumes in the mortars. The range of pore diameter measured was from 100,000 nm to 5 nm, and maximum pressure intruded was 33,000 psia during high pressure analysis. At the age of 9 days, pore volumes of all mixtures with SAP were reduced more than 10 percent as shown in Fig 10.

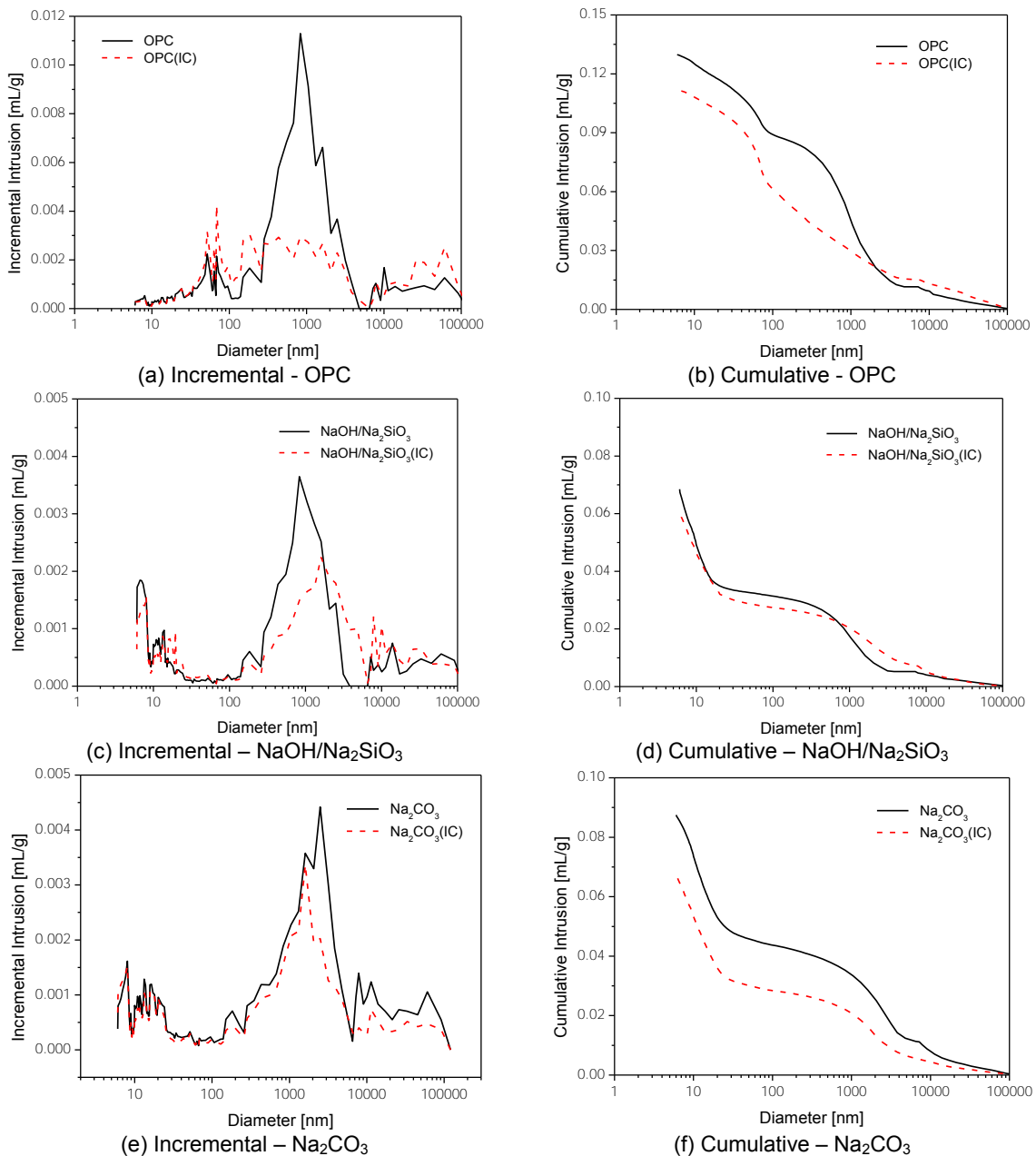


Fig 10 Incremental and cumulative intrusion data corresponding to pore-diameter at age of 9 day

## 4. Conclusion

Experiments on the effect of the internal curing using SAP have been conducted, and following conclusions can be drawn:

1. Setting times of alkali activated slag mortars were relatively shorter than that of cement mortars. Also, the addition of SAP made setting time of mortar mixtures slightly longer, but it was not a critical issue because it has not influenced on water/binder ratio or the compressive strengths.

2. Compressive strengths of alkali activated slag with sodium silicate and sodium hydroxide mixtures were the highest among all mixtures, and SAP played a crucial role in determining the strength of mortars. Alkali activated slag with sodium carbonate exhibited lower compressive strength, and early age strength need to be developed.

3. Alkali activated slag mortars caused more shrinkage strains than ordinary Portland cement mortars, so shrinkage reduction should be considered. For the reason stated, SAP was substituted of SAP for 10% of aggregates and it greatly reduced autogenous shrinkage strains in alkali activated slag and cement mortars with fixed water/binder ratio.

4. Hydration process of ground granulated blast furnace slag and cement was measured in watt (W) range, and the similar experiment results of total heat and heat flow between mixtures with SAP and without SAP were drawn.

5. Decreases in porosities were measured over 20% when SAP was used, which means that porosities of slag based mortars contained small amount of pores in specimens with SAP. Consequently, the compressive strengths were directly related to porosities of the mortars.

## ACKNOWLEDGE

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