Characteristics of seawater-resistance for Geo-polymer type of grout agent

Seon-Ju, Kim, Kyung-Sub, Cha & Tae-Hoon ,Kim
Daewoo E&C, Suwon,/Kyonggi-do, Korea
Chan-Ki, Kim
Department of civil engineering–University of Daejin, Kyonggi-do, Korea
Chae-yong, Lim
Ssangyong Cement co, Yuseong/Daejeon, Korea

ABSTRACT
In accordance with the policy of Korea government who is to nurture new recycle energy as a next generation growth power, several tidal plants are planned or designed in domestic areas including Sihwa, Inchon and Garolim. In addition, a large scale of off-shore wind power plant complex will be constructed along the southeast costal area of korea. Such structures require inevitably cofferdams so as to cut off water flowing from the seaside. However, many construction cases show that an uncompleted cut-off water system causes construction delay and additional cost. In general, Injection methods like cement paste grouting and chemical grouting are frequently adopted for reinforcement. However, the cement paste grouting is not adequate for where the ground water flows because of its longer gel time. Meanwhile the chemical grouting has long term durability problem due to eluviations. In this study, various lab tests such as eye examination, XRD test and uniaxial compressive test were carried out to evaluate seawater resistance of the developed material. By means of visual inspection, white precipitate and surface crumbling were observed. Also, a strength reduction was observed as in the existing material. As a result of XRD test, calcium carbonate was to be found as a main cause of strength reduction. However, the developed material can generate higher initial strength and secure long-term strength as well. That might be because that the developed material can derive a pozzolan reaction at the earlier stage which prevents bleeding and accelerates a reaction with cement.

RÉSUMÉ
De acuerdo con la política del gobierno de Corea, que está planificando criar las nuevas energías y energías renovables como el funete de crecimiento de próxima generación, varias centrales mareomotrices se han planicado o deseñado en áreas regionales, incluso Sihwa, Incheon y Garorim. Además, un complejo de central eólica costa afuera a gran escala se construirá a lo largo de la costa sureste de Corea. Estas estructuras requieren inevitablemente unas ataguías para cortar flujos de agua desde el mar. Sin embargo, muchos casos de construcción muestran que incompleto del sistema de corte de agua causa el retraso de la construcción y el costo adicional. En general, los métodos de inyección como la lechada de pasta de cemento y la lechada de inyección química son adoptada para refuerzo con frecuencia. Sin embargo, la lechada de pasta de cemento no es adecuado para donde agua subterránea fluye debido a que su tiempo del gel es más largo. Mientras tanto, la lechada de inyección química tiene los problemas de durabilidad a largo plazo debido a eluviación. En este artículo, varias pruebas de laboratorio como inspecciones visual, pruebas de XRD y ensayos de compresión uniaxial se llevan a cabo para evaluar la resistencia de los materiales desarrollados al agua de mar. Por medio de la inspección visual, el precipitado blanco y el desmoronamiento de la superficie se observaron. Además una reducción de la resistencia se observó como en los materiales existentes. Como resultado de la prueba de XRD, el carbonato de calcio, que es una de las causas principales de la reducción de la fuerza, se encuentra. Sin embargo, el material desarrollado puede generar una mayor resistencia inicial y garantizar la resistencia a largo plazo también. Eso podría deberse a que el material desarrollado puede obtener una reacción puzolánica en la etapa anterior que previene la exudación y acelera una reacción con el cemento.

1 INTRODUCTION

Nowadays, lots of marine construction cases show that an uncompleted cut-off water system causes construction delay and additional cost.

In general, Injection methods like cement paste grouting and chemical grouting are frequently adopted for reinforcement. However, the cement paste grouting is not adequate for where the ground water flows because of its longer gel time.

Meanwhile the chemical grouting has long term durability problem due to eluviation. In this paper, geo-polymer type of grouting agent that has better seawater resistance compared to the chemical grouting is introduced.

That is investigated by means of various tests such as eye examination homo-gel test, sand-gel test and XRD analysis.

2 GEO-POLYMER GROUT AGENT

2.1 Material properties

In order to improve durability, a geo-polymer mixture agent was produced with pozzolan and material for seawater stabilization. The raw materials for pozzolan such as fly-ash and meta-kaolin contain SiO_2 that leads pozzolan reaction with cement.

But they also contain Al_2O_3 ,which produces a new compound reacting with water glass. Besides, AluminoSilicateOxide($Si_2O_5Al_2O_2$) that also exist in the fly-ash and meta-kaolin reacts with water glass to produce a new type of compound which is different from CSH gel by pozzolan reaction as following equations.

$$(SiO_2O_5Al_2O_2)n + n\ SiO_2 + NaOH + H_2O \rightarrow (OH)_6\text{-Si-O-}\underset{\underset{(OH)}{|}}{\text{Al}}\text{-O-Si-}(OH)_6$$

$$\mathbf{n}(OH)_6\text{-Si-O-Al-O-Si-}(OH)_6 + \underset{\underset{(OH)_2}{|}}{\text{NaOH}} \rightarrow \text{Na-Si-O-Al-O-Si-O} + n\ H_2O$$

In grouting, a silica is growing fast by silica sodium and cations eluviated from cement or any other material to gel. In addition, calcium hydroxide produced by cement hydration, hydration due to pozzolan reaction and Geopolymerization recation can enhance strength and durability. Especially, the materials produced by pozzolan reaction and Geopolymerization have excellent durability, anti-chemIstry and anti-seawater compared to cement compound.

2.2 Standard Mix Design

Two types of solutions were used in this study. A-type is composed of water glass solution and activator, and B-type consists of water, portland cement and accelerating/decelerating agents. The activator used in A-type solution is for the improvement of reactivity and it is produced by mixing pozzolan with 8,000~20,000㎠/g of fineness and plasticizer and alkali salt powder.

Table 1. Standard mix design for geo-polymer type of grout agent

Grout agents	A-type : (200ℓ)			B-type : (200ℓ)		
	Water-glass (ℓ)	Activator (kg)	Water (ℓ)	Cement (kg)	Additive (kg)	Water (ℓ)
Short geltime agents	100	40	83	100	20	163
Long geltime agents	100	40	83	100		166

Table 2. Standard mix design for existing groutings

<table>
<tr><td rowspan="2" colspan="2">LW</td><td colspan="2">A-type : (200ℓ)</td><td colspan="4">B-type : (200ℓ)</td></tr>
<tr><td>Water-glass (ℓ)</td><td>Water (ℓ)</td><td colspan="2">Cement (kg)</td><td colspan="2">Water (ℓ)</td></tr>
<tr><td></td><td>Short</td><td>100</td><td>100</td><td colspan="2">110</td><td colspan="2">165</td></tr>
<tr><td rowspan="3" colspan="2">SGR</td><td colspan="2">A-type : (200ℓ)</td><td colspan="4">B-type : (200ℓ)</td></tr>
<tr><td rowspan="2">Water-glass (ℓ)</td><td rowspan="2">Water (ℓ)</td><td rowspan="2">Cement (kg)</td><td colspan="2">Additive(kg)</td><td rowspan="2">Water (ℓ)</td></tr>
<tr><td>Short</td><td>Long</td></tr>
<tr><td></td><td>Short</td><td rowspan="2">100</td><td rowspan="2">83</td><td>60</td><td>24</td><td></td><td>168</td></tr>
<tr><td></td><td>Long</td><td>60</td><td></td><td>24</td><td>168</td></tr>
<tr><td rowspan="3" colspan="2">MSG</td><td colspan="2">A-type : (200ℓ)</td><td colspan="4">B-type : (200ℓ)</td></tr>
<tr><td rowspan="2">Water-glass (ℓ)</td><td rowspan="2">Water (ℓ)</td><td colspan="3">Micro cement(kg)</td><td rowspan="2">Water (ℓ)</td></tr>
<tr><td>Short</td><td colspan="2">Long</td></tr>
<tr><td></td><td>Short</td><td rowspan="2">80</td><td rowspan="2">120</td><td>80</td><td colspan="2"></td><td>173</td></tr>
<tr><td></td><td>Long</td><td></td><td colspan="2">80</td><td>173</td></tr>
</table>

Meanwhile, the accelerating/decelerating agents are used to improve strength and durability, and produced with anhydrite/calcium gypsum of over 8,000 ㎠ /g fineness, pozzolan, plasticizer and stabilizer.

The standard mixing ratio was presented in Table 1. The results of tests were compared with those of the existing materials, of which standard mixing ratio were also presented in Table 2.

3 TEST

3.1 Surface observation

In order to investigate the durability of the material under the seawater condition, specimens with dimensions of 40mm×40mm×160mm were prepared right before gelling and aged under fresh water and seawater conditions for 6 months. Then, surface variation was examined

3.2 Homogel compressive test(KS L ISO 679)

Uniaxial compressive tests were carried out based on the standard strength test for cement, KS L ISO 679. Specimens were prepared with dimension of 40mm×40mm×160mm.

The specimens were cured in the seawater condition. The tests were performed on the specimens with 3day, 7day, 28day, 90day and 180day curing.

3.3 Sandgel compressive test(KS F 2314)

Sandgel compressive strength tests were carried out based on standard strength test for soil, KS F 2314. In this test, the injection material is injected to a model ground.

The mechanical properties of the model ground are presented in Table 3. Unlike the specimen of homogel test, little reference is available for sandgel test. Therefore, a special injection device has been manufactured as shown in FIGURE.1.

And so has a mould that dimensions are 7cm in diameter and 24cm in height. Using this device and the mould , a model ground was prepared.

During preparation, the front and back side of the mould were capped.

Then the model grounds were separated from the mould and cured in the water for 3days, 7days, 28days, 90days respectively.

Table 3. Engineering properties of soil

Model ground	Dr (%)	G_s	γ_d (g_f/cm^3)	N (%)	K (cm/sec)	Grain size distribution		
						D_{10}	D_{30}	D_{60}
Engineering properties of Jumunjin sand	70	2.64	1.56	40.1	7.1 x 10^{-2}	0.92	1.11	1.40


Figure 1. Sandgel compressive strength test

3.4 XRD test

XRD analysis was performed to verify the cause of strength reduction under condition of seawater curing.

Since the grouting material is apt to be eluviated rapidly in the air the analysis was carried out on a piece of specimen.

The piece of specimen was obtained from the surface of a homogel specimen.

Each specimen was cured for 3days, 7days and 28days respectively.


Figure 2. XRD principles and equipment

4 DISCUSSION

4.1 Surface observation

As shown in Figure. 3, surface variation of specimens were examined under seawater conditions for 6 months.

Form of all specimens were maintained when observed with naked eye.

But in case of LW, SGR , surface was constricted, in particular SGR was weak enough to break even hand rub at all conditions which means strength is extremely low. In case of MSG, Form of specimen was good, but surface was constricted.

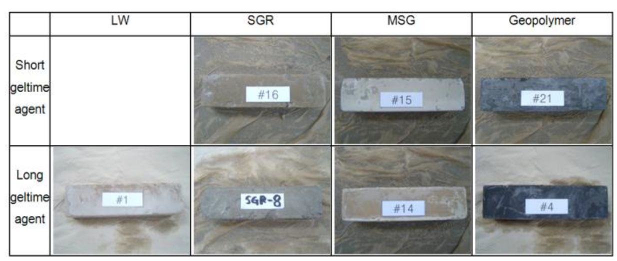


Figure 3. Surface variation of specimens under seawater

4.2 Homogel compressive test

Figure. 4 and 5 show the variations of long term strengths of the new material and the existed materials under fresh/seawater conditions.

In case of the geo-polymer type of material, both long gel time and short gel time specimens appear to have strength increase.

Especially, the strength of a short gel time specimen appears to increase up to 13.1MPa after 6 month later. For the existed materials, the strength appears to be reduced after 28days curing, and this phenomenon seems to be more clear at the long gel time specimens.

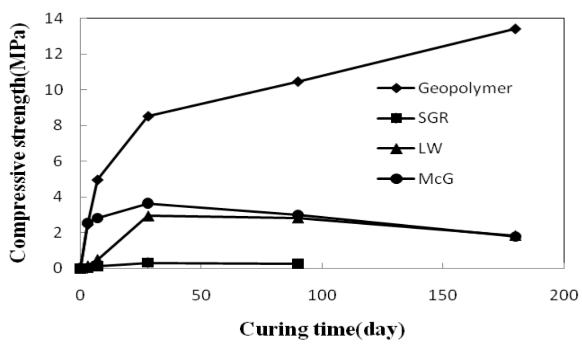
In case of SGR, the strength is less than 1MPa which is relatively very small compared to any other materials.

For the long gel specimens after 90days, there were too much cracks to estimate the strength. In case of McG that the strength after 6 month which is 1.78MPa becomes a second of what obtained in 28day which is 3.64 MPa, although the initial strength appears to be high.

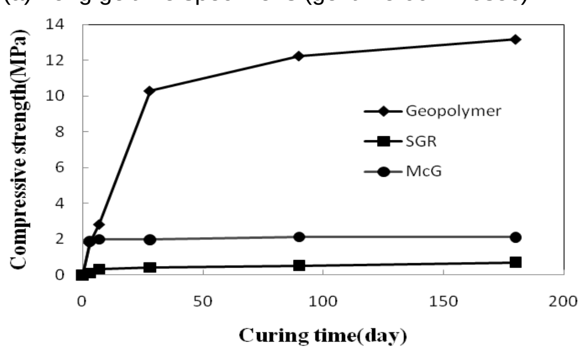
Meanwhile, for the specimens cured in the seawater, all the specimens after 180 days seem to have very low strength so as that the surface can be ripped away by bare hands. In contrast, the specimens with geo-polymer type appear to have relatively good status in both short and long gel time.

The uniaxial compressive strength indicates about 13.3MPa. From this observation, it may be concluded that geo-polymer type of material remains good quality in seawater

The writers would like to acknowledge the contribution of a number of individuals to the paper.



(a) Long geltime specimens (gel time 60~120sec)



(b) Short geltime specimens (gel time less then 10sec)

Figure 4. Variations of strengths under fresh water

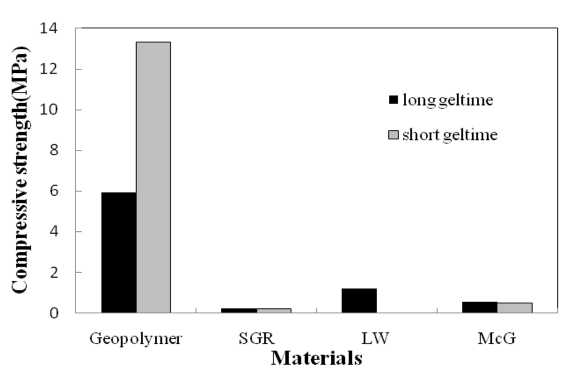


Figure 5. Long term strengths of the specimen cured for 180days under seawater

4.3 Sandgel compressive test

Since sandgel uniaxial compressive strength test should be performed on a specimen which is obtained from a model ground injecting a material within certain gel time, long gel time material was used.

The model ground was prepared with coarse sand and relative density of 70%.

Likewise, two groups of specimens were prepared and each group was cured in different water condition.

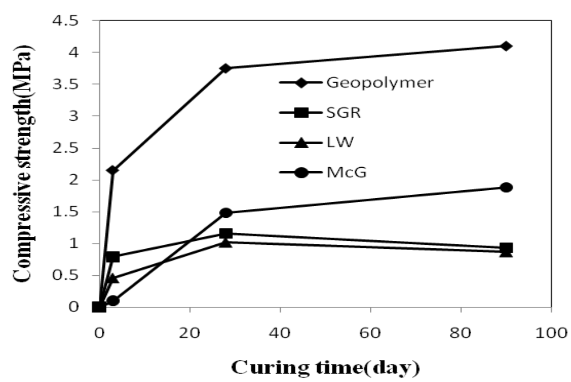
Figure 6. shows the results of uniaxial compressive tests. When geo-polymer type of material is cured in fresh water, a continuous strength increase was observed after 28days.

However, the existed materials except McG show a strength reduction.

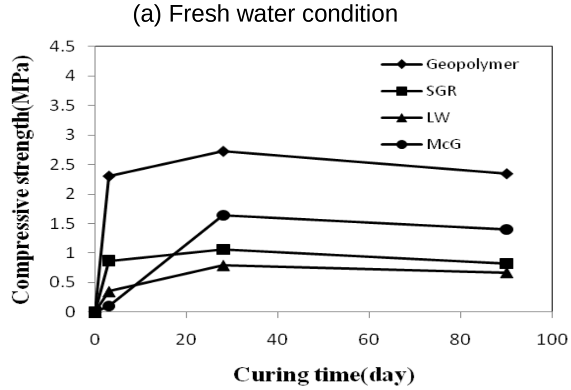
For the McG material, the strength seems to increase but estimated less than the geo-polymer type material.

For instance, the strength of the McG material after 90days is about 3MPa which is only third of the geo-polymer type material. In the meantime, when cured in seawater, all the materials show strength reduction after 28days.

That might be because cement compound reacts with SO_4^{-3} in seawater to cause micro cracks. Consequentially, the geo-polymer type material has a higher strength compared to the existed materials in both fresh and seawater conditions



(a) Fresh water condition



(b) Sea water condition

Figure 6. Variations of long term strengths of the sandgel specimen(long gel)

4.4 XRD analysis

On the basis of XRD analysis, it is deduced that the initial strength enhancement and overall strength reduction of seawater cured material is induced by ettringite and carbonation.

However, as shown in Figure. 7 and 8, ettringite was detected at all the specimens regardless of water condition, which means that ettringite itself has no affection on the strength reduction. In other words, ettringite produced in both fresh and sea water reacts with SO_4^{-3} in seawater to expand and lead a temporary strength enhancement.

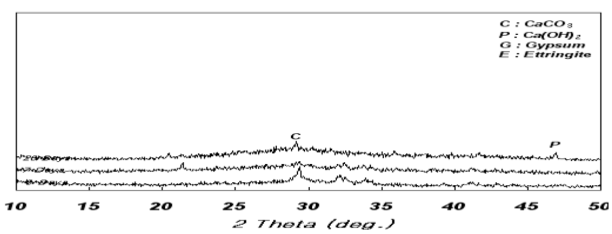
However, continuous reaction of the ettringite causes expansion crack which leads a strength reduction. In addition, calcium carbonate was detected in the all specimens cured in seawater, which indicates that carbonation is in progress

When concrete contacts with alkali chloride or sea water, portlandite elution from concrete accelerates and generates more voids in cement paste.

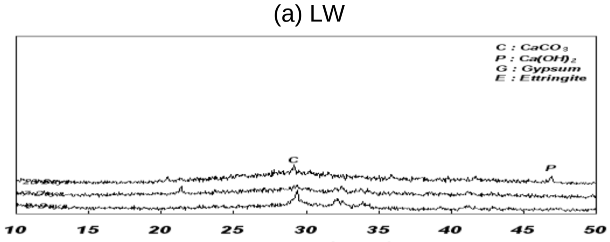
Dissolved calcium ions become white precipitate by carbonation. Figure. 9 shows a specimen covered by white precipitate. Figure. 10 represents the result of XRD analysis on this precipitate. Figure. 10(a) represents the white precipitate while Figure. 10(b) represents calcium carbonate.

As shown in the FIGURE, the peak point of the white precipitate seems to be almost the same as that of calcium carbonate.

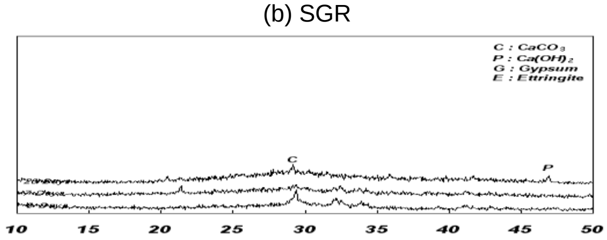
It means that primary constituent of the white precipitate is calcium carbonate.



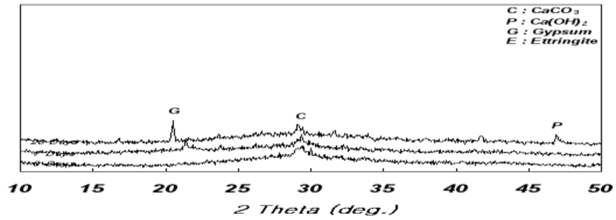
(a) LW



(b) SGR

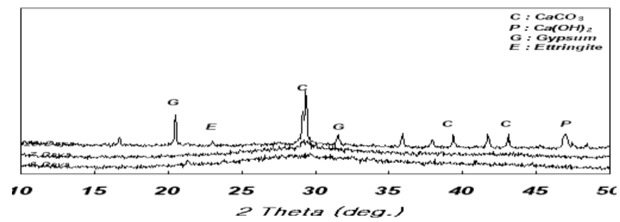


(c) McG

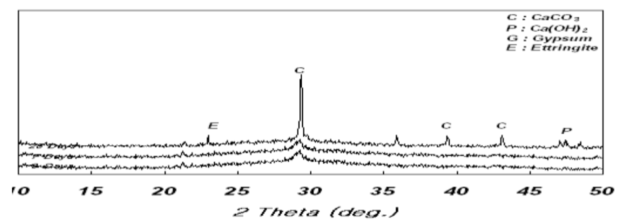


(d) Geopolymer

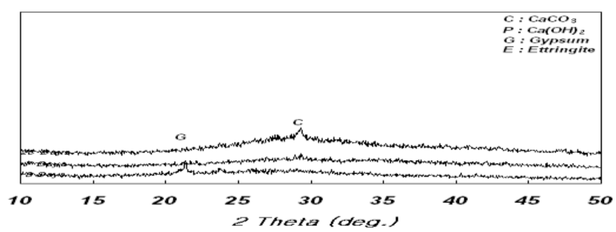
Figure 7. XRD results under fresh water



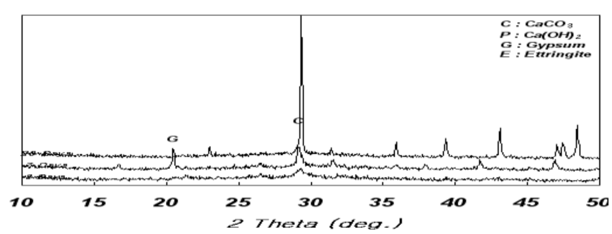
(a) LW



(b) SGR



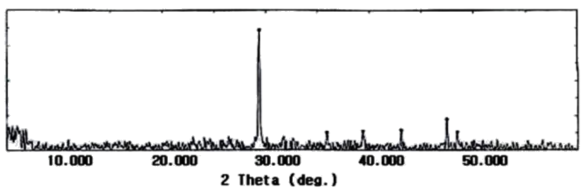
(c) McG



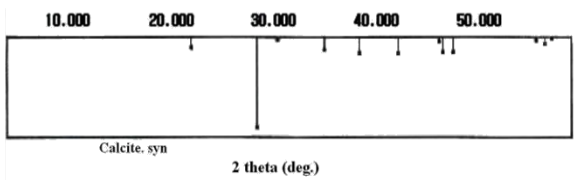
(d) Geopolymer

Figure 8. XRD results under sea water

Figure 9. White precipitate from homogel under sea water



(a) White precipitate



(b) Unique node of Calcium carbonate

Figure 10. XRD analysis

5 DISCUSSION

Visual inspection, sandgel and homogel uniaxial compressive strength tests and XRD analysis were conducted to evaluate seawater resistance of geo-polymer type grouting material and compared with the existed materials.

Throughout the experimental approach, following conclusions were derived.

1) under seawater conditions for 6 months, form of all specimens were maintained when observed with naked eye. But in case of LW, SGR , surface was constricted, in particular SGR was weak enough to break even hand rub at all conditions. which means strength is extremely low.

In case of Geopolymer, form of specimen was good and surface wasn't constricted.

2) Geo-polymer type material generates rapid initial strength when cured in fresh water. In addition, the strength appears to be much higher than those of the existed when cured in sea water.

3) A continuous strength increase is observed in geo-polymer type material cured in fresh water. In contrast, when cured in seawater, all the materials appear to have strength reduction after 28days.

However, the strength of geo-polymer type material is much higher by from 1.7times up to 18.8 times compared to any other materials.

That is because the geo-polymer type material may produce a better durable and dense hydrate by pozzolan react after cement hydration.

4) On the basis of XRD analysis, continuous reaction of the ettringite causes expansion crack which leads a strength reduction.

Calcium carbonate was detected in the all specimens cured in seawater, which indicates that carbonation which portlandite elution from concrete accelerates and generates more voids in cement paste is in progress.

However, the developed material can generate higher initial strength and secure long-term strength as well than existing material.

That might be because that the developed material can derive a pozzolan reaction at the earlier stage which prevents bleeding and accelerates a reaction with cement.

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