Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 7-8, 2015

A Study on the Properties and Chloride Resistance of Modified Sulfur Concrete for Nuclear Power Plant and Marine Structures

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1. Introduction

Sulfur concrete is generally known to have a strong chloride and chemical resistance compared to Ordinary concrete, but because of constraints in construction, modified sulfur has had only limited applications for road pavement and repair. Only recently a type of modified sulfur that can be mixed into concrete at room temperatures has been developed by a Korean company for the first time in the world. As such, in this study, a variety of tests have been conducted to assess its physical and chemical properties and chloride resistance with an aim to use it for construction of nuclear power plant and marine structures. The mechanical, physical and chemical properties of concrete with modified sulfur have been compared and assessed against ordinary concrete. As its excellent chloride resistance and extended service life have been verified, the technology to apply modified sulfur to the construction of nuclear power plant and marine structures has been developed and secured.

2. Methods and Results

2.1 Concrete mix design for test

The concrete mix design for tests referred to that used for containment building of Shin Kori Units 3&4.

- Design basis strength [Age 91 days: 6,000psi (42MPa)]
- Slump and air content (Slump: 180 ± 30mm, air content: 50 ± 1.5%)

Based on the mix design above, concrete specimens without modified sulfur and those containing 5%, 10% and 15% modified sulfur contents relative to the weight of cement were created.

2.2 Properties assessment of concrete containing modified sulfur (5%, 10%, 15%) and an optimal mix design

In the first stage, tests were carried out on concrete specimens described in 2.1 above regarding parameters below[1]. Here, modified sulfur was melt at 80℃ before mixed into concrete.

1) Slump and slump loss (KS F 2402)
2) Compressive strength (KS F 2405)
3) Tensile strength and flexural strength (KS F 2423, KS F 2408)
4) Static modulus of elasticity (KS F 2438)
5) Concrete drying shrinkage and length change (KS F 2424)
6) Water absorption coefficient (KS F 2609)
7) Resistance to chloride ion penetration and accelerated carbonation (KS F 2711, KS F 2584)

The test result showed that concrete specimens with 5% and 10% modified sulfur contents were analyzed to show equal or better performance in all properties compared with ordinary concrete. The concrete specimen with 15% modified sulfur content failed to meet the allowance criterion for compressive strength at 91 days of age, which led to a conclusion that modified sulfur content exceeding 10% was not desirable. Meanwhile, concrete specimens with 5% and 10% modified sulfur contents had little difference in terms of improvement in properties whereas 5% sulfur concrete had significant improvement in several properties compared with ordinary concrete. Concrete containing 10% modified sulfur had a disadvantage in terms of economics since it will raise material costs of 20kg per 1㎥ when compared with 5% modified sulfur concrete.

As such, considering concrete slump (workability), compressive strength, corrosion resistance, water-proof properties and economics, an optimal mix design for modified sulfur has been analyzed to be around 5% (based on cement + FA mass) (Table 1).

Table 1. Improvement of physical and chemical properties found in modified sulfur concrete (5%) relative to ordinary concrete

Property		Ordinary concrete	Modified sulfur	Improve-ment
Slump	0 minute	225mm	235mm	4.4%
	30 minute	215mm	230mm	7%
	60 minute	155mm	215mm	38.7%
Compressive strength (Age 91 days)		6,856psi	7,126psi	4%
Tensile Strength		682psi	691psi	1.3%
Water absorption coefficient		0.277	0.165	40%
Resistance to chloride ion penetration		1,202 coulombs	831 coulombs	30%
Carbonation Depth		7.77mm	5.25mm	32%

As it is shown in Table 1, when compared with ordinary concrete, concrete specimens containing modified sulfur had the equal levels of mechanical properties including compressive strength and tensile strength, but showed about a 30% improvement in chemical resistance such as resistance to chloride ion penetration, carbonation depth (Figure 1). In addition, an addition of modified sulfur significantly reduced concrete slump loss, resulting in a decrease in loss of workability (Figure 2, Figure 3). The test on change in length induced by drying shrinkage revealed that concrete containing modified sulfur had smaller length changes relative to ordinary concrete, which will curb the creation of cracks developing as a result of drying shrinkage (Figure 4).

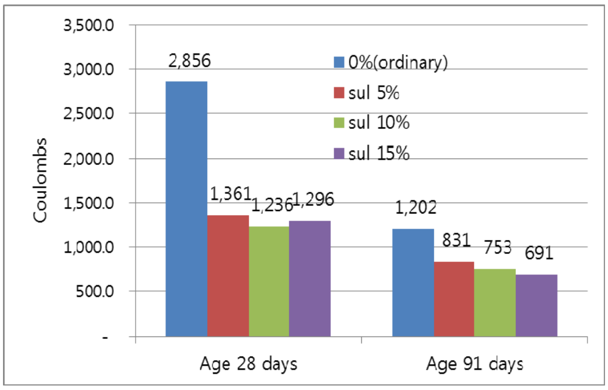

Figure 1. Resistance to chloride ion penetration with an addition of modified sulfur

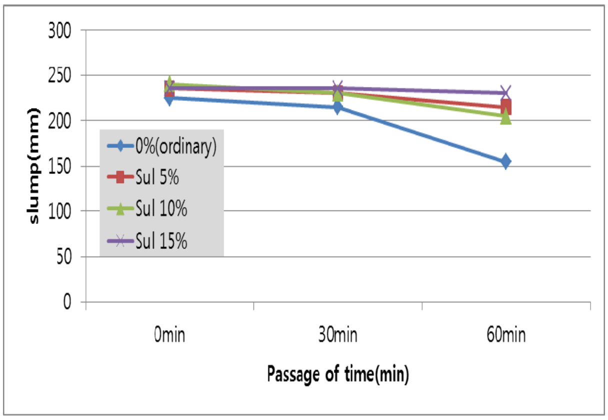

Figure 2. Changes in slump with passage of time

Ordinary 5% modified sulfur

Figure 3. Comparison of slump in ordinary concrete and 5% modified sulfur concrete after 60 minutes

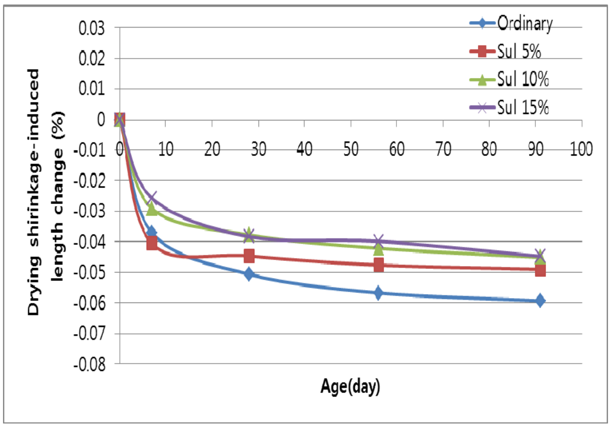

Figure 4. Drying shrinkage-induced length change after adding modified sulfur

2.3 Chemical resistance and service life assessment of modified sulfur concrete

In the second stage of study[2], concrete specimens with 5% modified sulfur content relative to the weight of cement, which was assessed to be the optimal mix in the first stage of the study, were created to test chemical resistance and service life using concrete parameters. In the first stage, modified sulfur was melt at the temperature of 80℃, whereas in the second stage, modified sulfur powder (Figure 5) recently developed by Hanmi E&C for the first time in the world was mixed with concrete. This modified sulfur powder addresses the problem which prevented modified sulfur from being used for the construction of large scale structures because it had to be melted for mixing. The modified sulfur powder allows a direct injection into a batch plant along with other admixtures to form concrete without prior processing.

Figure 5. Modified sulfur powder

2.3.1 Chemical resistance test on modified sulfur concrete

A chemical resistance test was performed by placing concrete specimens into 5% sulfuric acid solution. The test lasted for two months. For comparison, ordinary concrete specimens were also built to test under the same conditions. The test showed that when specimens were immersed in fresh water, at one- and two-month age, their compressive strength was normal and their weight underwent little change. Meanwhile, when specimens were immersed in 5% sulfuric acid, the compressive strength and weight of all specimens decreased. Yet, those containing modified sulfur had compressive strength decreased at rates 18% slower than ordinary concrete specimens two months after they were put in 5% sulfuric acid solutions(Table 2, Figure 6), while weight reduction showed little difference.

Table 2. Compressive strength and weight changes after two months from placing in sulfur acid solution

Condition	Mix Type	Compressive strength (Age 28 days, MPa)	After two months		
			Compressive strength (MPa)	Change rate of Compressive strength (%)	Change rate of weight (%)
5% sulfuric acid	Ordinary	46.9	28.3	60.3	- 5.59
	Modified sulfur (5%)	45.7	36.1	79.0	- 4.89

Ordinary 5% modified sulfur

Figure 6. Concrete specimens after two months from placing in sulfur acid solution

2.3.1 Service life assessment (Chloride ion diffusion coefficient and Life-cycle 386 program analysis)

A chloride ion diffusion coefficient test was carried out in accordance with NT BUILD 492T (Concrete, Mortar and Cement-based Repair Materials) and its result is shown in Table 3.

Table 3. Chloride ion diffusion coefficient

Mix type	Chloride ion diffusion coefficient (×10-12 ㎡/sec)		
	n1	n2	Average
Ordinary	15.3	16.62	15.96
5% modified sulfur	4.92	5.2	5.06

As the table above demonstrates, the chloride ion diffusion coefficient for modified sulfur concrete is one third of that for ordinary concrete, which shows that chloride resistance of modified sulfur concrete is very high. The service life of concrete structures (time before concrete begins to experience corrosion induced by external salinity influence) exposed to saline environment was assessed by exposure case deploying the Life-cycle 365 Program, and the result is described in Table 4 and Figure 7.

Table 4. Service life prediction using the Life-cycle 365 Program

Type		Cover depth (㎜)	chloride ion concentration in concrete surface (kg/㎥)	chloride amount (kg/㎥)	Chloride ion diffusion coefficient ($\times 10^{-12}$ ㎡/s)	Service life (years)	Rate of Service life increase (%)
Ordinary	Case 1-1	40	13.0	1.2	15.96	10.7	-
	Case 1-2		9.0			11.8	-
	Case 1-3		4.5			14.8	-
	Case 1-4		2.0			23.4	-
	Case 1-5	80	13.0	1.2	15.96	18.8	-
	Case 1-6		9.0			21.0	-
	Case 1-7		4.5			27.7	-
	Case 1-8		2.0			49.3	-
5% Modified sulfur	Case 2-1	40	13.0	1.2	5.06	16.8	157
	Case 2-2		9.0			19.0	161
	Case 2-3		4.5			25.4	172
	Case 2-4		2.0			57.1	244
	Case 2-5	80	13.0	1.2	5.06	46.1	245
	Case 2-6		9.0			53.3	254
	Case 2-7		4.5			75.0	271
	Case 2-8		2.0			141.9	288

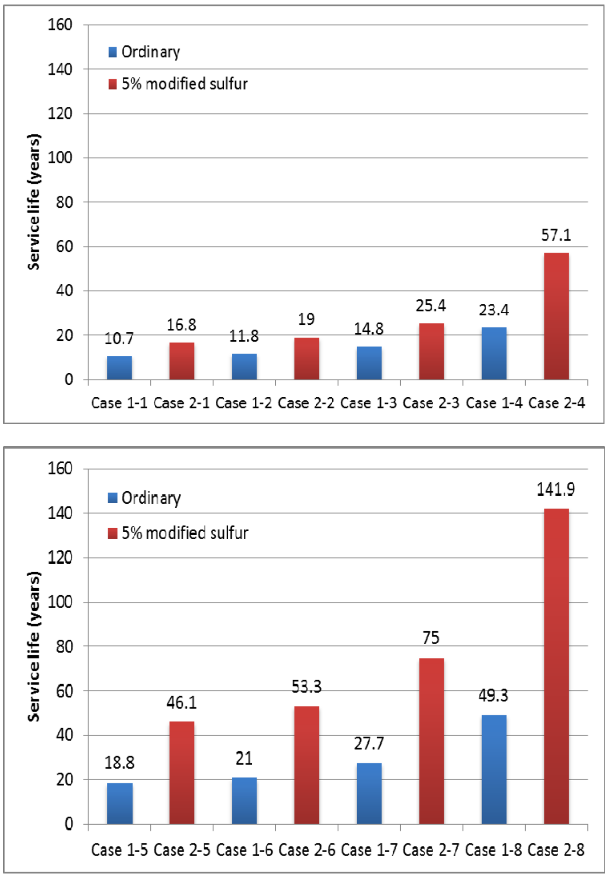

Figure 7. An analysis of service life with changes in parameters (cover depth, chloride ion concentration in concrete surface, chloride ion diffusion coefficient)

As the figure above shows, assuming that concrete cover is 40mm and 80mm in depth, it has been concluded that modified sulfur concrete(5%) has 1.5 to 2.8 times higher durability compared to ordinary concrete. As the chloride ion diffusion coefficient, which affects durability the most, for modified sulfur concrete is one third of that for ordinary concrete, chloride penetration is blocked and, as a result, corrosion of steel in structures is delayed.

3. Conclusions

Recently, modified sulfur concrete has been applied for road pavement and repair works in more than 20 sites including highway and airport in Korea. Also, in the U.S., Federal Highway Administration and Virginia Department of Transportation are implementing tests to apply modified sulfur to bridge road pavement, and the modified sulfur concrete has been recognized for its good performance. Based on these cases, this study carried out tests on physical, mechanical and chemical properties of concrete after adding modified sulfur by building concrete specimens based on the concrete mix design employed to construct the Shin-Kori Units 3&4 containment building. Multiple tests were performed particularly for chemical resistance, a factor directly related to concrete service life.

As a result, it has been verified that concrete with 5% modified sulfur content relative to cement weight has equal mechanical properties (compressive strength, tensile strength, etc.) and much better workability (slump change) and chemical resistance (resistance to chloride ion penetration, concrete carbonation) compared with ordinary concrete. Based on this, it has been concluded that an addition of modified sulfur can double the service life of concrete.

In general, studies demonstrate that a significant amount of slag should be mixed into concrete to raise chemical resistance (but with decreasing mechanical properties). Considering this, this study is unparalleled. In particular, a study on related technology developed modified sulfur powder that can be mixed with cement in a batch plant, which enhances workability and economics. Therefore, in future, this technology can be applied to those structures requiring hundreds of years of service life including nuclear power plants, marine structures and spent fuel storage facilities with great advantages expected.

Acknowledgement

This study is part of "Development of Design and Construction Technology for High strength, Light Weight, Chloride Resistant Concrete Structure," a research project of KEPCO E&C.

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