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Green options for anti-sulfate of slag cement concrete containing pozzolans

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Abstract. This study mainly adopted densified mixture design algorithm (DMDA) with pozzolans (fly ash and slag), different fineness slag cement (1:1; MF40 and HF40) and Type I cement (E40) to construct the mixtures for w/cm=0.40, and applied ACI 211.1R and Type II cement as control group (CII40, w/c=0.40). Life cycle inventory of LEED suggested by PCA for cementitious materials (kg/m^3) contained cement use, CO_2 emission, raw materials, energy consumption, compressive strength, and immersed in different concentration Na_2SO_4 solution. Results showed cement content, CO_2 emission, raw materials and energy consumption for E40, MF40 and HF40, with respect to CII40, were 14% ~ 26%, 14% ~ 26%, 13% ~ 26% and 17%~28%. At 28 days, compressive strength(all mixtures) were greater than 41MPa. Repeatedly 25 cycles, specimens immersed in 5000ppm Na_2SO_4 solution and oven-dried at 105^{o}C, the exterior had no damage, and weight loss (*n*) and pulse velocity change (*nv*) were less than -1% and -5%. But in saturated Na_2SO_4 solution, the *n* and *nv* were ranged from -0.91% (E40) to -2.62% (MF40) and -6.7% (E40) to -10.9% (MF40). The exterior had been obviously scaling (chalking) or spalling at the second (CII40), the fifth (MF40 and HF40) and the ninth cycle (E40). The comprehensive evaluation of green options for anti-sulfate indicated that the merits of all mixtures were respectively E40 > HF40 > MF40 > CII40.

1 Sulfate attack and pozzolans

Concrete structure exposed in different concentration sulfate solution environment(submersion or immersion) were due to the chemical reaction of sulfate-attack. The reaction of hydration product of ettringite due to extreme expansion at the hardened stage is a very severe destructive ambient worldwide [1-3]. Especially, the infrastructure constructed under the ground water level were easy to suffer the aggressive ion attack. The sulfate ions concentration (in ground water) and the $Ca(OH)_2$ content in the paste of concrete played important roles, and the permeability of concrete was the same [2, 4-7]. According to ACI 318-11 [8], the suggestion of chapter 4 indicated exposure to various concentration sulfate ion, the mixture must be simultaneously considered the compressive strength, water-to-cementitious ratio, cement type used and pozzolans [9-15], etc. The effect of global greenhouse gas emission had a serious issue. After the 2015 Paris Global Climate Summit Meeting [16], internationally the carbon dioxide reduction and sustainability is in full swing taking actual action.

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The U.S. Green Building Council (USGBC) is transforming the way which design, build, maintain and operate our buildings, homes and communities [17]. LEED, or Leadership in Energy and Environmental Design, is changing the way we think about how buildings and communities are planned, constructed, maintained and operated. Leaders around the world have made LEED the most widely used third-party verification for green buildings, with around 1.85 million square feet being certified daily. LEED-certified buildings are resource efficient. They use less water and energy and reduce greenhouse gas emissions. The newest version of LEED is designed to be more flexible and improve the overall user experience including materials (Focuses on materials to get a better understanding of what's in them and the effect those components have on human health and the environment), performance-based, smart grid and water efficiency [18-20]. In Taiwan, the Architecture and Building Research Institute promoted EEWH green building evaluation system included ecology, energy saving, waste reduction (CO_2 reduction indicator and construction waste reduction indicator, non-metallic recycled material) and health [21]. LEED for Green options using life cycle inventory was according to Portland Cement Association(PCA) suggestion including the carbon dioxide emission for cement and others cementitious materials of the mix, raw materials used for manufacture process, energy consumption during manufacturing, properly engineering properties including compressive strength development and sustainable durability behaviors to analyze and assess, and applied the most proper mixture from green option for the life cycle inventory [22-24].

The structural concrete with cementitious materials included cement, fly ash, slag, silica fume and other pozzolans used widely in buildings design as specification. Cement industry has been always among the largest CO_2 emission sources. Second only to the water, concrete is the most used material in the world. Almost 5% of global CO_2 emissions are caused by cement plants, while 900 kg CO_2 is emitted to the atmosphere for producing one ton of cement (now 800 kg) [25, 26]. The basis of the carbon dioxide emission of cement includes two parts, one is from consuming the electricity, oil and others fuels to heat until about 1500 ^oC, and the other is from the raw materials (lime + clay) decomposing due to high temperature at 900 ^oC ($CaCO_3 \rightarrow CaO + CO_2$). The CO_2 emission of two parts are about the same [1,2]. Pozzolans can substitute to cement with high pollution in manufacturing process. The carbon footprint of pozzolans from post-industry production can be regarded as zero. The carbon dioxide emission all have be classified to their industrial products. Pozzolans from post-industry after high temperature treatment was included fly ash, ground-granulated blast furnace slag (Blast-furnace slag is water quenching and grinding to powder. According to PCA suggested the slag CO_2 emitted about 2% of cement [26]), silica fume, etc, above a billion metric tons in 2015 [27, 28]. Pozzolans are an important option for carbon dioxide reduction and sustainable development [29-31]. This paper focuses on an infrastructure for underground transport structure located at the Kaohsiung city in the southern area of Taiwan. The structures were exposed to groundwater containing 3000 ppm for sulfate ion concentration [32]. According to Table 4.2.1(Exposure categories and classes) of ACI 318-11(Building code requirements for structure concrete), the mix proportion applied DMDA [33] method incorporating slag cement (slag : cement=1:1; slag including medium and high fineness) and pozzolans at a w/cm of 0.40 when exposed in sulfate environments. The ACI 211.1 [34] design method was used as a control group for w/c=0.40. The life cycle inventory of cementitious materials in concrete was suggested by PCA as including cement content, CO_2 emission, raw materials, energy consumption and the properties with compressive strength and sulfate resistance [25].

2 Materials, mix proportion and experiments

2.1 Materials

The properties for cementitious materials were according to ASTM C150 as shown in Table 1. The ground granulated blast-furnace slag (produced by the China Hi-Ment Corp.) and Type F fly ash(acquired from Tai-Power Hsin-Ta Thermal Power Plant) conformed to ASTM C989 and ASTM C618 as shown in Table 1. Coarse and fine aggregates met ASTM C33 requirements were as shown in

Table 2. Water was potable water conformed to ASTM C94. The high range water-reducing agents was produced by Sika corporation and used as a high flow agent and conformed to ASTM C494 Type G.

Table 1. Properties of cementitious materials.

Item	Type I	Type II	SC^{MF}	SC^{HF}	Fly ash	$Slag^{MF}$	$Slag^{HF}$
SiO_2	21.5	22.4	-	26.8	51.2	34.0	-
Al_2O_3	4.8	4.6	-	9.2	24.3	14.7	-
Fe_2O_3	3.1	4.9	-	1.9	6.1	0.3	-
CaO	62.4	60.7	-	37.8	6.3	42.0	-
MgO	2.9	3.1	-	5.4	1.6	6.3	-
SO_3	2.1	2.0	-	0.8	0.6	0.4	-
Na_2O	0.22	0.10	-	0.44	0.15	-	-
K_2O	0.70	0.50	-	0.41	0.27	-	-
L.O.I(%)	-	-	-	-	4.9	0.3	-
Fineness(cm_2/g)	3,622	3,420	3,686	4,602	3,110	4,302	5651
G_s	3.14	3.13	3.06	3.05	2.32	2.87	2.88

MF: Medium Fineness Slag Cement (Slag : Cement(I) = 1:1);
HF: High Fineness Slag Cement (Slag : Cement(I) = 1:1).

Table 2. Properties of aggregates.

Properties	Corse Aggregate*	Fine Aggregate**
$G_s(SSD)$	2.64	2.63
$G_s(OD)$	2.63	2.62
Absorption(%)	1.1	2.2
$D_{max.}(mm)$	12.5	-
F.M.(%)	6.08	2.82
$UW_{dry}(kg/m^3)$	1,536	-

*: Crushed stone
**: River sand

2.2 Mix proportion

Table 3. Mixture proportion (kg/m^3)

Materials, kg/m^3	E40[1]	MF40[2]	HF40[3]	CII40[4]
Cement	141	71	71	548
Slag	94	165	165	-
Fly ash	140	140	140	-
Coarse Aggregate	957	957	957	845
Fine Aggregate	936	936	936	749
Water(Included HRWRA)	150	150	150	219
$UW_{concrete}$	2418	2419	2419	2361

1.Used ordinary Portland cement Type I;
2.Used medium Fineness Slag cement (Slag : Cement = 1 : 1);
3.Used high Fineness Slag cement (Slag : Cement = 1 : 1);
4.Used ordinary Portland cement Type II.

This paper applied Densified mixture design algorithm(DMDA) [35] method and a w/c(m)=0.40 to acquire the cement, slag, fly ash, sand, stone and water (with SP) amount as per kg/m^3 (E40). Slag cement (1:1) of different fineness (medium and high fineness shown in Table 1) was used to substitute the cement content of E40 for acting as MF40 and HF40. Finally, using ACI 21.1-12 [36] method with Type II cement designed as a control group(CII40). The mixture proportions were shown in Table 3.

2.3 Experiment

Experiments including compressive strength according to ASTM C31 with 10cmφ×20cmH which were curing in saturated lime water and 5000ppm Na_2SO_4 solution, and performed the tests at 7, 28, 56 and 182 days. Anti-sulfate was with 10cmφ×20cmH specimens cured in saturated lime water 28 days, then, respectively immersed in 5000ppm and saturated sulfate solution for 24 hours, and oven-dry at 105°C for 24 hours (ASTM C88-13), that was one cycle and repeatedly 25 cycles to measure the weight loss (*n*, ASTM C127), longitudinal pulse velocity variance(*nv,* ASTM C597) and exterior changes. The calculations were as shown in Formula 1-3, and the deterioration of exterior surface due to scaling or spalling was observed.

$$n = \frac{W_2 - W_{12}}{W_1} \times 100\% \tag{1}$$

Where, W_1: Weight for oven-dry 24 hours at 105°C;
W_2: Weight for immersing in a solution for 24 hours, after which the specimen was taken out and dried the surface.

$$v = \frac{L}{\mu_s}(m/s) \tag{2}$$

Here, L: Averaged length of specimen(*m*)
μ_s : Transferring time from both ends(•10^{-6} *second*).

$$nv = \frac{v_{lw} - v_{ppm}}{v_{lw}}(\%) \tag{3}$$

Here, v_{lw}: Velocity for curing in saturated lime water;
V_{ppm}: Velocity for immersed in *x* ppm Na_2SO_4 solution, and took out and dried the surface.

3 Results and discussions

3.1 Cement use

With respect to the CII40 group being 100%, the cement content of E40, MF40, and HF40 were as shown in Table 4. The reduction rate for E40, MF40, and HF40 were 26%, 14%, and 14%, respectively. The cement content of mixtures designed with the DMDA method were 74%~86% less than that of CII40. Incorporation of pozzolans and slag cement in the mixtures allowed a dramatic reduction in the amount of cement. However, it still must be compared with other performances. Pozzolans regarded as post-industrial recycled products are very useful mineral admixtures and ecological materials in concrete. According to suggestions by the PCA, the life cycle inventory for various mixtures of cementitious materials including cement, slag cement, and other pozzolans were compared to CO_2 emissions, raw materials, energy consumption, and engineering design indexes containing factors such as compressive strength and anti-sulfate property as shown in Tables 5-7.

Table 4. The amount of various cementitious materials in concrete mixtures per kg/m^3.

Materials, kg/m^3	E40	MF40	HF40	CII40
Cement	141	71	71	548
Slag	94	164	164	-
Fly ash	140	140	140	-
Rate(%)	26	14	14	100

3.2 CO_2 emission

PCA had performed that CO_2 emission of cement manufacture were 927 kg/per 1000 kg, GGBFS 2% emission of cement, and fly ash and silica fume (both carbon footprint as 0%, because of the CO_2 emission were owing to their front-products of electricity and steel). Calculation results indicated that E40, MF40, and HF40, with respect to CII40 equal to 100%, were 26%, 14%, and 14%, respectively. The mixtures that added pozzolans and slag cement significantly were 74% ~ 86% less than that of CII40. It was apparent that the reduction in the amount of cement was also accompanied by a reduction in CO_2 emissions. Concrete used DMDA mix method incorporating a higher pozzolans content (E40, MF40, and HF40) could be more carbon reduction.

Table 5. CO_2 emission for cementitious materials in concrete mixtures(kg/m^3).

Materials, kg/m^3	E40	MF40	HF40	CII40
Cement	131	66	66	508
Slag	1.7	3.0	3.0	0
Fly ash	0	0	0	0
Total	132.7	69.0	69.0	508.0
Relative Value(%)	**26**	**14**	**14**	**100**

CO_2 Emission of cement: 927 kg/1000 kg of cement;
CO_2 Emission of slag: 2% of 927 kg/1000 kg of cement;
CO_2 Emission of fly ash: None.

3.3 Raw materials

Cement is an industry for higher natural resource requirements. The main raw materials including limestone and clay (weight, 3:1) for the manufacturing process consume a large amount of natural resources. With reference to PCA reports, the raw materials required to produce 1,000 kg of cement consume more than 1,613 kg of natural materials. For the nature was an intrusive destruction, air pollution and consumption of ecological resource were very serious problems. The consumption of raw materials (limestone and clay) for cement in kg/m^3 were shown in Table 6. With respect to CII40 being 100%, E40, MF40, and HF40 were 26%, 13%, and 13%, respectively. Mixtures designed with the DMDA method showed that the raw material consumption of cementitious materials significantly decreased by 74% ~ 87%. For the cement industry, both pozzolans and slag cement play an effect in ecology.

Table 6. The raw materials used for cementitious materials in concrete(kg/m^3).

Materials, kg/m^3	E40	MF40	HF40	CII40
Cement	227	115	115	884
Slag	-	-	-	-
Fly ash	-	-	-	-
Total	227	115	115	884
Relative Value(%)	**26**	**13**	**13**	**100**

Raw materials: 1613 kg/1000 kg of cement

3.4 Energy consumption

The PCA literature states that the energy consumption for cement manufacturing is 4.8 GJ/1,000 kg of cement, and grinding process consumed for granulated blast-furnace slag was 14% of cement per 1,000kg. Since the energy consumption was due to their front-products, electricity and steel, fly ash, and silica fume were regarded as being zero. According to Table 7, the energy consumption of cementitious materials in the mixtures, with respect to CII40 being 100%, were 28% (E40), 17% (MF40), and 17% (HF40). E40, HF40, and HF40 used the DMDA method, and compared to CII40, consumed 72 ~ 83% less energy for the cementitious compounds. The expected effect on energy saving of CII40 which adopted the ACI 211.1 method was much less.

Table 7. Energy consumption for cementitious materials in concrete mixture(kg/m^3).

Materials, GJ/t(1000kg)	E40	MF40	HF40	CII40
Cement	0.677	0.341	0.341	2.631
Slag	0.063	0.110	0.110	-
Fly ash	0	0	0	-
Total	0.740	0.441	0.441	2.631
Relative Value(%)	**28**	**17**	**17**	**100**

Cement Energy Consumption: 4.8 GJ/1000 kg Cement;
Slag Energy Consumption: 14% of 4.8 GJ/per 1000 kg cement.

3.5 Compressive strength effect

The life cycle inventory (front four items) was used to assess the effect of design and production for cementitious materials in the mixtures. The hardened properties and anti-sulfate durability were used to evaluate and predict service performance. This study measured the compressive strength by curing in saturated lime water and immersing in a 5,000 ppm sulfate solution.

The compressive strength development (7d, 28d, 56d, and 182 days) for curing in saturated lime water and 5,000 ppm sulfate solution were as shown in Table 8. At 28 days, E40, HF40, and HF40 showed compressive strengths of 47 MPa and 48MPa, 43 MPa and 45 MPa, and 48 MPa and 47 MPa, respectively. Meanwhile, those of CII40 were 47 MPa and 47 MPa. The variance of two curing ambient were less than 5%. All the mixtures were suitable in environments exposed to high concentrations of sulfate solution (ACI 318-13). Meanwhile, at 182 days, the compressive strengths of E40, MF40, HF40, and CII40 were 71 MPa and 72 MPa, 62 MPa, and 63 MPa, 67 MPa and 66 MPa, 62 MPa and 62 MPa, respectively. The amount of cement for CII40 was too high to increase the compressive strength. Pozzolans and slag cement for anti-sulfate concrete had a very important effect in lowering the heat of hydration and refining the microstructure to be denser to improve long-term properties. The compressive strength ratios at 182 days, with respect to CII40 being 100%, were 115% and 113% for E40, 100% and 102% for MF40, 108% and 105% for HF40 as shown in Table 9. E40 with pozzolans increased the compressive strength. MF40 and HF40 incorporating pozzolans and slag cement indicated an increased fineness and a better strength enhancement. The finer blast-furnace slag grinding following water quenching was a useful application for ecology and carbon reduction.

Table 8. Compressive strength development (curing in saturated lime water/5000ppm Na_2SO_4 solution).

Compressive Strength(MPa)	E40	MF40	HF40	CII40
7 days	34/36	29/33	31/35	40/37
28 days	47/48	43/45	48/47	47/47
56 days	54/55	55/55	56/56	54/54
182 days	71/70	62/63	67/66	62/62

Table 9. Strength ratio with respect to CII40 as 100%(curing in saturated lime water/5000ppm Na_2SO_4 solution).

Compressive Strength(%)	E40	MF40	HF40	CII40
7 days	85/97	73/89	78/95	100/100
28 days	100/102	92/96	100/100	100/100
56 days	100/102	102/102	104/104	100/100
182 days	115/113	100/102	108/105	100/100

3.6 Sulfate resistance effect

In order to ensure that the effect for mixtures immersed in different concentration sulfate solution, this study was according to ASTM C88-10 repeated exposure to the wet-dry extreme environment to observe the exterior and measure the difference for weight loss and longitudinal pulse velocity. Specimens were immersed in a solution for 24 hours and oven-dried for 24 hours at 105°C, and this cyclic process was repeated for 25 cycles. The exterior was observed to gage whether scaling, spalling, or nothing occurred. Upon oven-drying, the weight and longitudinal pulse velocity of the specimens were measured. Test results were as shown in Table 10.

3.6.1 Exterior changes

The specimens were immersed in a 5,000 ppm Na_2SO_4 solution and oven-dried, with this process being repeated for 25 cycles. Upon careful examination of the external surface, the exteriors of all the mixtures were observed to be neither damaged nor had defects. The ASTM C88-10 method showed that the force of expansion developed from the sulfates during multiple immersions was somewhat similar to the expansion of water during freezing. Oven-drying the specimens at 105 °C was similar to freezing and immersing them in the sulfate solution was similar to a sulfate attack at an ambient temperature. The method was constructed at extreme exposure environments to accelerate the speed of destruction.

However, when the specimens were immersed in a saturated solution of Na_2SO_4, the exteriors displayed differences among the surfaces. Mix CII40 underwent scaling from the second cycle; MF40 and HF40 began spalling significantly after the fifth cycle; and E40 commenced slight spalling (just like tiny pitting) during the ninth cycle. From the exterior observation, the mixtures showed that E40 had the best anti-sulfate resistance performance due to the compressive test and immersion in saturated sulfate solution, while MF40 and HF40 were superior to CII40 [35].

3.6.2 Weight loss

The specimens during the extreme test process, especially during oven-drying at 105°C and the chemical reaction of the sulfate attack to form ettringite induced scaling, spalling, and weight loss as shown in Table 10. Following immersion in a 5,000 ppm solution of Na_2O_4, the weight loss rates (n) of the mixtures were less than -1% after the 25 cycles. At -1%, CII40 had the highest weight loss rate and no exterior abnormalities. Other mixtures also had the same behaviors, and E40 had the smallest n value as shown in Figure 1. Following immersion in the saturated solution of Na_2SO_4, n_{E40}, n_{MF40}, n_{HF40}, and n_{CII40} were 0.91% (24 cycles), -2.62% (20 cycles), -2.12% (24 cycles), and -2.05% (24 cycles), respectively. The test results showed that n_{E40} was less than -1%, and the others were all greater than -2%. A value of -2.62% was recorded for n_{MF40} as shown in Figure 1. E40 had the smallest n value due to weight loss.

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Table 10. The weight loss and pulse velocity change for specimen with various mixtures.

	5000ppm Na_2O_4 solution					Saturated Na_2O_4 solution				
Mix	n %	N cycles	V m/s	n	nv %	n, %	N (cycles)	V m/s	n	nv %
E40	-0.55	19	4500*	12	-1.7	-0.91	24	4280	22	-6.5
MF40	-0.62	7	4400*	25	-2.7	-2.62	20	4030	11	-10.9
HF40	-0.71	9	4480*	25	-4.4	-2.12	24	4250	11	-9.3
CII40	-1.00	24	4300*	15	-2.6	-2.05	24	3945	5	-10.7

*: The ultrasonic pulse velocity of specimens cured in lime water, at 28days, were respectively 4576, 4524, 4685 and 4474m/s.

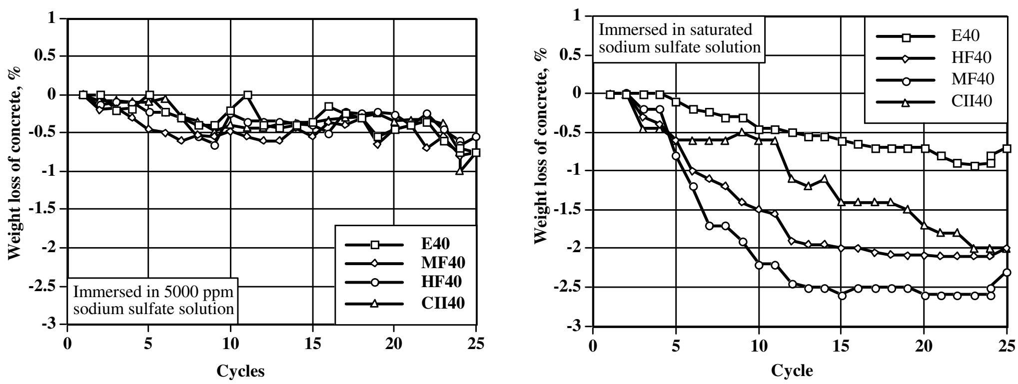

Figure 1. Weight loss development due to immersion in a 5,000 ppm saturated solution of Na_2SO_4 and oven-drying repeatedly for various mixtures.

3.6.3 Ultrasonic pulse velocity(UPV) variance

The ultrasonic pulse velocity (UPV) transferred through the longitudinal direction of a specimen to detect interior defects such as (micro)cracks, voids, and honeycombs, can indirectly measure the quality of concrete. Moreover, according to Whitehurst [37] in his nondestructive testing concrete review, the pulse velocity for good and excellent concrete quality reported the UPV ranges from 3,660 m/s to 4,570 m/s. In Table 11 and Figure 2, specimens immersed in the 5,000 ppm Na_2SO_4 solution showed that the lowest UPV (see Figure 2, left) for E40, MF40, HF40, and CII40 were 4,500 m/s, 4,400 m/s, 4,480 m/s, and 4300 m/s, respectively; meanwhile, in the saturated Na_2SO_4 solution, the UPV dropped down to 4,280 m/s, 4,030 m/s, 4,250 m/s, and 3,945 m/s, respectively. The specimens cured in lime water at 28 days were 4,576 m/s (E40), 4,524 m/s (MF40), 4,685 m/s (HF40), and 4,474m/s (CII40). Repeatedly immersed in 5,000 ppm Na2SO4 solution and oven-dry; and repeatedly immersed in saturated and oven-dried ambient. The variance was -1.7%, -2.7%, -4.4%, -3.9% and -6.5%, -10.9%, -9.3%, -11.8%. The nv values were less than 5% for specimens repeatedly immersed in the 5,000 ppm Na_2SO_4 solution and oven-dried. Mixtures designed with pozzolans, slag cement, Type II cement, w/cm=0.40, and compressive strength, could have an improved anti-sulfate property.

But the result of immersion for saturated sulfate solution ambient had significantly different, either high concentration accelerating sulfate attack or due to oven-dried at 105 ^oC. The deterioration, with respect to curing in saturated lime water, showed all nv values to be above 5%. Meanwhile, MF40 and CII40 had values above 10%: nv_{MF40} (-10.9%) and nv_{CII40} (-11.08%) as shown in Table 10 and Figure 2 (right). Repeatedly, the extremely exposed ambient with chemical attack of Na_2SO_4 and oven-dried influenced the exterior integrity and interior compactness. These factors were due to incongruous force of wet-dry and expansion-attraction between the paste and aggregates. From the results, nv_{E40} of -6.5% was the lowest among the mixtures. The variables in mixtures were C_3S and C_3A content. In Table 11, with respect to CII40 as 100%, E40, HF40 and MF40 which displayed C_3S and C_3A amount were much less than CII40, and hydration products of CH were much fewer. Pozzolanic reaction of these mixtures (excluded CII40) with oven-dry process accelerated the compactness of interior structure. The cement paste for CII4 mix was even higher than others. The objects of suffered attack were more widely, and the water amount was higher enough to loosen the unit weight (see Table 3). The UPV for before and later experimental results extended the minimum values, but was completely greater 3,660 m/s. The mixtures in this study displayed that interior quality were better. E40 had a better anti-sulfate attack performance. The order of sulfate resistance in terms of decreasing performance was E40, HF40, MF40, and CII40. In the study, the mixtures with DMDA method incorporating pozzolans, slag cement and lower water-to-cementitious ratio might be a viable approach.

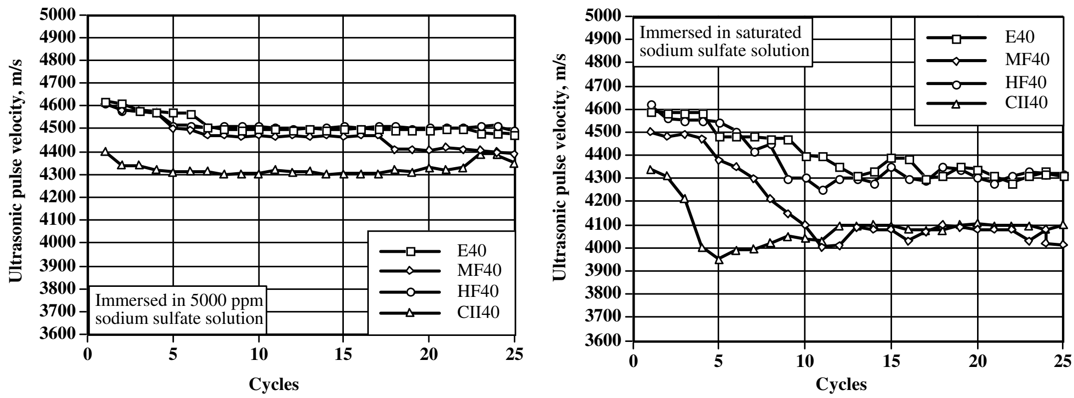

Figure 2. Ultrasonic pulse velocity development of immersed in 5000ppm and saturated solution of Na_2SO_4 and oven-dry repeatedly for various mixtures.

Table 11. The weight and ratio for clinker composition in the mixtures.

Mix	E40	MF40	HF40	CII40
Cement(kg/m^3)	141	71	71	548
$C_3S^{\#}$	30.7	15.4	15.4	205.5
$C_2S^{\#}$	78.0	39.0	39.0	215.9
$C_3A^{\#}$	10.7	5.4	5.4	21.4
$C_3S(\%)^*$	15.0	7.5	7.5	100.0
$C_2S(\%)^*$	36.1	18.1	18.1	100.0
$C_3A(\%)^*$	50.1	25.1	25.1	100.0

#: The component ratio of C_3S, C_2S and C_3A are referenced in Table 1.
*: With respect to CII40 as 100%.

3.7 Assessment of green index

Results of life cycle inventory for concrete mixtures with various pozzolans are given in Table 12. The MF40 and HF40 mixtures displayed a higher carbon reduction than E40. From the view point of cement content, CII40 had a large amount of cement used in the mixture, Type II cement was more expensive than Type I, and the properties were not better as expected. The results of CO_2 emissions, raw materials, and energy consumption were similar to cement used. The differences for compressive strength cured in saturated lime water and immersed in a 5,000 ppm solution of Na_2SO_4 were all below 5%. The mixtures in this study with various design methods could be applied in extreme sulfate attack environments. The effect of repeatedly immersing in the 5,000 ppm solution and oven-drying for 25 cycles had similar results. For repeatedly immersing in the saturated Na_2SO_4 solution and oven-drying for 25 cycles, E40 showed the best performance, others were HF40, MF40, and CII40. These mixtures met the requirements for environments with serious sulfate exposure. Integrating carbon reduction, hardened properties, and durability, E40 and H40 with the DMDA method containing a large amount of pozzolans enhanced the long-term properties and anti-sulfate performance.

Table 12. The comprehensive evaluation of green options for different mixtures(%).

Parameter(%)		E40	MF40	HF40	CII40
Cement use		26	14	14	100
CO_2 Emission		26	14	14	100
Raw Materials		26	13	13	100
Energy Consumption		28	17	17	100
Compressive Strength	28 days(N*)	100	92	100	100
	28 days(a*)	102	96	100	100
	56 days(N*)	100	102	104	100
	56 days(a*)	102	102	104	100
	182 days(N*)	115	100	108	100
	182 days(a*)	113	102	105	100
Sulfate resistance (cycles, deterioration)	28 days(1**)	➢ 25	➢ 25	➢ 25	➢ 25
	Exterior damage	None	None	None	None
	n (1**)	-0.55	-0.62	-0.71	-1.00
	nv (1**)	-1.7	-2.7	-4.4	-2.6
	28 days(2***)	9	5	5	2
	Exterior damage	Initial spalling	Initial spalling	Initial spalling	Initial chalking
	n (2***)	-0.91	-2.62	-2.12	-2.05
	nv (2***)	-6.50	-10.90	-9.30	-10.70

N*: Cured in 5000ppm solution of Na_2SO_4.
a*: Cured in saturated lime water.
1**: Repeatedly immersed in 5000ppm solution of sodium sulfate and oven-dried.
2***: Repeatedly immersed in saturated solution of sodium sulfate and oven-dried.

4 Conclusions

In this study, mixture proportions adopted a densified mixture design algorithm (DMDA) method, a water-to-cement (w/cm) of 0.40, various amounts of pozzolans, and slag cement of different fineness values (E40, MF40, and H40). The ACI design method acted as a control group (CII40). Experiments conducted included compressive strength and repeated immersion in 5,000 ppm and saturated Na_2SO_4 solutions. Green options for anti-corrosion of the life cycle inventory of Leadership in Energy and Environmental Design (LEED) suggested by the Portland Cement Association (PCA) included CO_2 emissions, raw materials consumption, energy consumption, compressive strength, and immersion effect of the Na_2SO_4 solution (variance of weight loss and pulse velocity). Analysis and test results were as follows:

1. The cement content for E40, MF40, and HF40 were 26%, 14%, and 14%, respectively, with respect to CII40 being 100%.
2. CO_2 emissions for E40, MF40, HF40, and CII40 were 133 kg/m^3, 69 kg/m^3, 69 kg/m^3, 508 kg/m^3, respectively. A mix proportion incorporating the correct amount of pozzolans and slag cement can greatly decrease cement use and reduce CO_2 emissions.
3. Raw materials for cement manufacturing for E40, MF40, HF40, and CII40 were 26% 13%, 13%, and 100%, respectively. The effect of pozzolans used in the mixture can decrease the ecological impact.

4. Energy consumption of cement manufacturing for E40, MF40, and HF40 were 28%, 17%, and 17%, with respect to CII40 being 100%. The mixtures incorporating pozzolans showed energy saving benefits.
5. After 28 days, curing in saturated lime water and the 5,000 ppm sulfate solution showed no visible change in the compressive strength and all mixtures were suitable in extreme sulfate solution environments.
6. Specimens were repeatedly immersed in 5,000 ppm and saturated Na_2SO_4 solutions, and were oven-driing at an ambient temperature of 105°C. Results showed that the exterior had no change in the 5,000 ppm Na_2SO_4 solution. All the mixtures were properly designed. In the saturated Na_2SO_4solution, exterior damage appeared in the second cycle (CII40, initial scaling), the fifth cycle (MF40 and HF40, initial spalling), and the ninth cycle (E40, initial spalling).
7. After repeated immersion in the 5,000 ppm Na_2SO_4 solution, all weight loss variance (n) values were less than 1%, and the ultrasonic pulse velocity variance (nv) values were less 5%. After repeated immersion in the saturated Na_2SO_4 solution, n values ranged from -0.91% (E40, the smallest) to -2.62% (MF40, the largest); meanwhile, nv values ranged from -6.7% (E40, the smallest) to -10.9% (MF40, the largest).
8. The comprehensive evaluation of green options for anti-sulfate performance of the mixtures in serious sulfate exposure environments indicated the following: E40 > HF40 > MF40 > CII40.

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