Stabilization of marine dredged sediment using lime-fly ash-red mud-gypsum binder

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ABSTRACT: The aim of this study is to evaluate the strength characteristics of marine dredged sediment (MDS) and stabilized with cementless binder. In this study, the new cementless binder, tentatively named Fa-RmLG, derived from a cementitious mixture composed of fly ash (Fa), red mud (Rm), lime (L) and gypsum (G) is proposed and employed. For the stage of MDS stabilization, a pilot experimental program was first performed to find the optimum water content in mixtures. Various mixtures of MDS were then prepared with different proportions of Fa-RmLG. The settlement, pH values, leaching of heavy metals and the most important property unconfined compressive strength, were evaluated on the MDS mixtures. As a result, an extremely large increase in strength was obtained from the stabilized MDS mixtures when comparing to the unstabilized MDS ones. The proposed Fa-RmLG binder was found to be feasible to solidify MDS.

KEYWORDS: Stabilization; Marine dredged sediment; Cementless binder; Fly ash; Red mud; Lime; Gypsum.

1 INTRODUCTION

Large amounts of industrial by-products are produced annually from thermal power plants and chemical industries in South Korea. Among them, coal ash, gypsum are the main wastes produced in large quantities. The disposal of these wastes will be a big challenge in the near future for Korea to decrease the harmful environmental effects (e.g., generation of respirable particulate matter and pollution of soil and water due to leaching of heavy metals). Meanwhile, large volumes of sediments are dredged every year in Korea for harbor activities. The management of these marine dredged sediments (MDS) has become increasingly complex recently. More than ever, finding an alternative use of these materials in geotechnical applications is essential for a reduction of environmental pollution and sustainability contribution. For that purpose, it is ideal to develop a new cementless binder derived from industrial by-products (e.g., fly ash, red mud, and gypsum) for MDS stabilization. However, it is necessary to test feasibility of this solution to construction standards, environmental and human health requirements. Fly ash is a by-product of burning pulverized coal in a thermal electric power plant. In Korea, around 60% of fly ash is beneficially reused, and the largest markets for the reuse of fly ash are the cement and concrete industries. However, recent fly ashes in Korea contain relatively high content of unburned carbon particles; thus, it is expected that the amount of disposed fly ash in Korea is increasing due to the regulation of ASTM C618 (Choo et al., 2016).

Fly ash is widely used in Controlled low-strength materials for many advantages, such as good flowability, reduced segregation, bleeding, and in numerous cases, a reduced material cost (Gabr and Bowders, 2000; Pierce et al., 2002; Kim et al., 2016). In addition, fly ash is also introduced to concrete (Mustard 1959 and Siddique 2004). Red mud is the by-product of the manufacture of alumina from bauxite by the Bayer process. It is annually generated in Korea with a rate of 200,000 tons/year (Lim and Shon 2015; Do and Kim 2016). Red mud is a complex material whose chemical and mineralogical composition varies widely, depending upon the source of bauxite and the technological process parameters (Lim and Shon 2015; Do and Kim 2016). Gypsum is a by-product originating from the production of phosphoric acid by the wet process. In Korea, 30 million tons of Gypsum was accumulated as waste (Mun et al., 2007). With the high content of $CaSO_4$ (i.e., larger than 95%) in Gypsum, it is possible to be used in the production of binder (Singh and Garg 1999). With the subject of MDS stabilization, there have been a number of studies addressing this problem with various approaches (Dermatas et al., 2002; Maher et al., 2004; Zentar et al., 2008; Silitonga et al., 2010). The common point of these studies is that cement was employed fully or partially as the representative binders in MDS stabilization. From the standpoint of economics and sustainable development, this study focuses on developing the new cementless binder derived from industrial by-products as a full replacement of cement for MDS stabilization.

2 EXPERIMENTAL PROGRAM

2.1 *Materials*

The soil used in the present study is fine marine dredged sediment originating from Jeollanam-do harbor in Jeolla Province (South Korea). MDS is classified as a silty sand (SM) with 16.34% of the soil passing through a 75-µm (No. 200) sieve. The liquid limit of this soil is 29.6%. MDS was first dried in an oven at 105°C until constant weight was attained and then passed through a 4.76-mm size sieve to eliminate unnecessary large particles, such as oyster shells. The physical properties of MDS are tabulated in Table 1.

Table 1. Physical properties of marine dredged sediment (MDS)

Properties	MDS
Maximum dry density (g/cm^3)	1.502
Optimum Moisture Content (OMC) (%)	17.55
Liquid limit LL (%)	29.6
Plastic limit PL (%)	N.P
Specific gravity	2.69
D_{50} (mm)	0.1
Particles < 75 µm (%)	16.34
Color	Dark green

The particle size distribution curve of MDS is shown in Fig. 1 obtained by using both sieve analysis test and hydrometer test. In this study, in order to develop the new cementless binder (Fa-RmLG), fly ash, red mud, lime, and gypsum were employed. Class F Fly ash with a specific gravity of 2.3 produced from a cogeneration plant in Jeolla Province (South Korea) conforming to ASTM C618 was used. The red mud collected from Bayer process in Jeolla Province (South Korea) was passed through sieve number 60. From the production of phosphoric acid by the wet process, gypsum wastes were first ground to powder and then subjected to the temperature of 110-

120°C to drive off water of crystallization and finally produce calcium sulfate hemi-hydrate ($CaSO_4 \cdot 1/2H_2O$). The specific gravity of gypsum used in this study was 2.32. The particle size distributions of fly ash, lime, red mud, and gypsum are given in Fig.1, obtained by using the Helium-Neon Laser Optical System (ISO 13320). The X-ray florescence (XRF) MiniPal 2/PANanalytical (Netherlands) was used to determine the chemical compositions of all binder materials shown in Table 2

Table 2. Chemical compositions of fly ash (FA), lime (L), gypsum (G), and red mud (RM) by weight (%).

Compound	FA	G	L	RM
CaO	1.99	51.43	80.01	7.10
SiO_2	56.88	1.65	1.87	15.12
Al_2O_3	21.52	0.32	0.93	19.87
SO_3	-	39.08	0.22	0.72
MgO	0.92	-	3.69	0.37
Fe_2O_3	6.34	0.30	0.75	22.21
TiO_2	1.21	-	-	5.24
K_2O	1.58	-	0.31	0.11
Na_2O	0.49	0.20	0.11	14.92
Loss of ignition	8.73	6.24	11.84	13.68

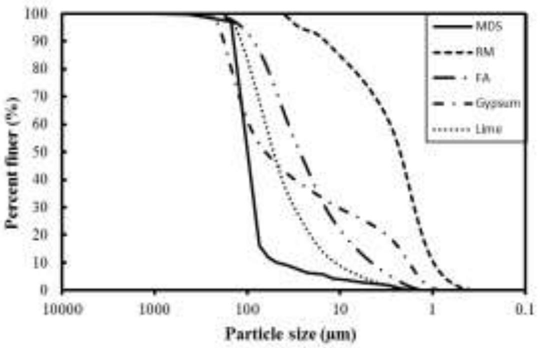

Fig. 1. Particle size distributions of MDS, RM, FA, L, and G

2.2 *Mixture proportions and test procedures*

Table 3 and 4 show the mix proportions of various stabilized MDS mixtures. In the proportions, the labels ''MDS'' and ''Fa-RmLG'' indicate marine dredged sediment and the new cementless binder, respectively. Two phases corresponding with two mix proportions were performed in this study. The first phase was to determine the optimum water content of control mixture. For that purpose, the various amounts of water were added to the MDS mixture. In the second phase, the control mixture was produced with MDS, Fa-RmLG binder, and the optimum water content, which was obtained from the first phase. Subsequently, mixtures Fa-RmLG1, Fa-RmLG2, Fa-RmLG3, Fa-RmLG4 were designed by changing the ratios of red mud to gypsum (Rm/G) from 5.00 to 2.00, 1.00, 0.50, and 0.20, respectively, (i.e., other weight fractions were fixed).

Table 3. Mix proportions of phase 1

Mix code	Rm/G[a]	Weight fraction[b]					
		Water	MDS	New Cementless binder			
				Fa	Rm	L	G
MDS1	5.00	0.46	1.00	0.47	0.17	0.14	0.03
MDS2	5.00	0.51	1.00	0.47	0.17	0.14	0.03
MDS3	5.00	0.56	1.00	0.47	0.17	0.14	0.03
MDS4	5.00	0.61	1.00	0.47	0.17	0.14	0.03
MDS5	5.00	0.67	1.00	0.47	0.17	0.14	0.03

[a] Rm/G denotes the red mud-to-gypsum ratio

[b] Material weight fraction per weight of total MDS

Table 4. Mix proportions of phase 2

Mix code	Rm/G[a]	Weight fraction[b]					
		Water	MDS	New Cementless binder			
				Fa	Rm	L	G
Control	5.00	0.51	1.00	0.47	0.17	0.14	0.03
Fa-RmLG1	2.00	0.51	1.00	0.47	0.14	0.14	0.07
Fa-RmLG2	1.00	0.51	1.00	0.47	0.10	0.14	0.10
Fa-RmLG3	0.50	0.51	1.00	0.47	0.07	0.14	0.14
Fa-RmLG4	0.20	0.51	1.00	0.47	0.03	0.14	0.17

[a] Rm/G denotes the red mud-to-gypsum ratio

[b] Material weight fraction per weight of total MDS

For unconfined compressive strength test, 50 × 100 mm cylindrical specimens were cast in plastic molds and then stored inside a curing chamber that maintained a temperature of 25°C and 100% relative humidity immediately adjacent to the cylinders for the desired testing periods of 3, 7, and 28 days. Each strength test was carried out wit three cylindrical specimens and then the average was recorded. Finally, the strengths of all proposed MDS mixtures were conformed to the strength requirement as reported in ACI 230 (1997).

Regarding the environmental effects of the MDS mixtures, corrosivity evidenced by pH values and the concentration of heavy metals were performed with the leachate of MDS specimens. The corrosivity was studied by measuring the pH of leachate collected from MDS specimens, according to the method employed by Razak et al., 2009 to determine whether a satisfactory corrosivity resistance can be obtained with the proposed MDS mixtures. A solid waste exhibits corrosivity if a representative sample of the waste is aqueous and has a pH value less than or equal to 2 or greater than or equal to 12.5. However, this range is not applicable to the corrosion or passivity of all materials (Razak et al., 2009). The toxicity of all MDS specimens was studied by measuring the concentration of heavy metals in the leachate by using Inductively coupled plasma optical emission spectrometer apparatus. Samples used in pH tests were employed in this test. The settlement of MDS mixtures was measured by the reduction in a vertical direction of 100 × 300 mm cylinder samples at a certain time. The percentage reduction of the vertical dimension of MDS specimens was then calculated.

3 RESULTS AND DISCUSSION

3.1 *Compressive strength of unstabilized MDS*

The standard proctor compaction curve of natural MDS was obtained in accordance with ASTM D698. One of the most important parameters of natural MDS is the optimum moisture content at which the maximum dry unit weight is attained from this curve. The unstabilized MDS mixtures were prepared by compacting natural MDS at the optimum water content (OMC=17.55%) and maximum dry density (γ_{dmax}=1.502 g/cm^3). A small unconfined compressive strength (UCS) (i.e., below 0.1 MPa) of the unstabilized MDS revealed that the natural MDS in this study would not be used for any purpose of construction without stabilization.

3.2 *Compressive strength of MDS stabilized by Fa-RmLG binder*

Fig. 2&3 illustrate the average unconfined compressive strengths for various MDS mixtures stabilized by Fa-RmLG binders. There were increments in compressive strength of all MDS mixtures due to the hydration process of the cementitious mixture composed of fly ash (Fa), red mud (Rm), lime (L) and gypsum (G), which gradually completed with curing ages. Most interestingly, an extremely large increase in strength was obtained from the stabilized MDS mixtures when comparing to the unstabilized MDS ones. The reaction of pozzolanic material fly ash activated by lime and red mud is believed to form the C–S– H gel. When mixed with water, lime, and red mud release OH– ions. Then, these ions hydrolyzed on the surface of fly ash, and finally, the Si, Al, and Ca species are dissolved to form C–S–H gel through polymerization (Lee et al., 2013). In addition, in the new cementless binder Fa-RmLG, the presence of gypsum reacted with alumina oxide in the fly ash, red mud, and calcium oxide in lime to form ettringites. These ettringites then filled up the pores in the specimens and eventually help in the hardening and strength development of MDS mixtures (Yang et al., 2008).

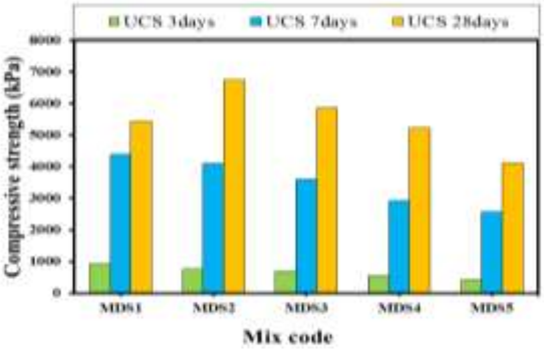

Fig. 2. UCS of the stabilized MDS mixtures of phase 1

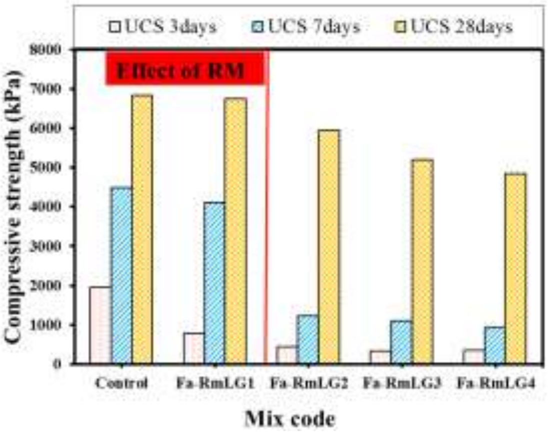

Fig. 3. UCS of the stabilized MDS mixtures of phase 2

In particularly, Fig. 2 summarizes the average of unconfined compressive strengths for mixtures of MDS1, MDS2, MDS3, MDS4, and MDS5. It was found that the 28-day strength of MDS mixtures decreased with an increase in water content except for one of mixture MDS1. The 28-day strength of MDS2 showed the highest value when compared with others. MDS2 mix was, therefore, recommended as the control mixture for the second phase of this work. Fig. 3 shows all compressive strengths of the stabilized MDS mixtures of phase 2. The 3-day and 7-day strengths varied in ranges of 347–1950.9 kPa and 921.9–4485.3 kPa, respectively. At the age of 28 days, the strengths of all proposed MDS mixtures ranged from 4843.9 to 6844.4 kPa, much higher than the strength of the natural MDS despite the full replacement of Portland cement in MDS stabilization. Therefore, it can be concluded that the proposed Fa-RmLG binder might be used to solidify MDS if the environmental effects are considered.

Furthermore, it was found that the compressive strength was a function of the red mud to gypsum ratio (Rm/G) (i.e., strengths decreased with a corresponding decrease in the Rm/G ratio, regardless of curing ages). It can be seen the redundant presences of Al_2O_3 (19.87%) and Na_2O (14.92%) and CaO (7.1%) in red mud from its chemical compositions. Calcium hydroxide released from red mud and calcium hydroxide produced from lime, could react with the alumina left in red mud to produce calcium aluminates (CA and possibly C_3A_5) (Ribeiro et al., 2011). Therefore, the strengths of Rm/G-reduced mixtures were smaller than those of the control mixtures owing to a loss of strength contribution of red mud, which led to some loss in strength.

Finally, it is worth noting that red amount in the new cementless binder notably affected to early strengths of the stabilized MDS mixtures. The 3-day and 7-day strengths of the mixtures containing a high amount of red mud (e.g., control and Fa-RmLG1) were very high. Especially, the strengths of control mixture were 1950.9 kPa (3-day strength) and 4485.3 kPa (7-day strength). It is much higher than those of other mixtures Fa-RmLG2, Fa-RmLG3, and Fa-RmLG4). A highly alkaline environment released by red mud might be a reason explaining for a development in early strengths. This finding is consistent with previous studies on red mud utilization (Kalkan 2006; Qiu and Qi 2011).

3.3 *Settlement*

Table 5 presents the settlement of various MDS mixtures. The initial heights of the fresh MDS mixtures including Control, Fa-RmLG1, Fa-RmLG2, Fa-RmLG3, Fa-RmLG4 were 299.6 mm, 301 mm, 299 mm, 301 mm, 299.5 mm, respectively. As a result, most of the settlement of fresh MDS mixtures finished within approximately 24 h after placing. Most MDS mixtures showed very small settlements with a maximum settlement of 4.74 mm. In particular, the final settlement of Fa-RmLG1 mixture showed the highest value of 4.74 mm followed by 4.72 mm (Control), 4.58 mm (Fa-RmLG3), 4.50 mm (Fa-RmLG2), 4.44 mm (Fa-RmLG4).

Table 5. Settlement of various MDS mixtures

Mix ID	Settlement (mm)						
	1 h	2 h	8 h	24 h	2 d	3 d	5 d
Control	2.82	3.5	4.37	4.66	4.7	4.72	4.72 (1.58%)
Fa-RmLG1	2.95	3.38	4.18	4.7	4.72	4.74	4.74(1.57%)
Fa-RmLG2	2.68	3.26	4.14	4.48	4.5	4.5	4.5 (1.51%)
Fa-RmLG3	2.68	3.14	4.18	4.3	4.58	4.58	4.58 (1.52%)
Fa-RmLG4	2.60	3.27	4.22	4.39	4.44	4.44	4.44 (1.48%)

3.4 *Environmental effects*

The pH values of the stabilized MDS mixtures were measured from leachate collected from MDS specimens and tabulated in Table 6. The pH values of leachate were measured at 7, 14, 21, and 28 days. As a result, the pH values of leachate ranged from 10.58 to 11.66 and the leachate of all MDS specimens occurred within 21 days after placement. It was found that the leachate (i.e., pH of leachate at 28 days) were primarily alkaline due to the hydroxide released from the hydration process. However, the range was still smaller than 12.5, which is the limitation of corrosivity for the alkaline specimens. Furthermore, it is also worth noting that the pH values slightly decreased with a reduction of red mud amount probably due to a decrease in the amount of OH^{-} released from aluminum and sodium hydroxides in red mud.

Table 6. pH values of various MDS mixtures

Mix ID	pH values			
	7 days	14 days	21 days	28 days
Control	10.64	11.54	11.57	11.65
Fa-RmLG1	10.66	11.42	11.61	11.63
Fa-RmLG2	10.64	11.50	11.63	11.64
Fa-RmLG3	10.65	11.51	11.63	11.66
Fa-RmLG4	10.58	11.50	11.58	11.58

Table 7. Results of leachable substances in leachate

Element	Concentration (mg/l)					Limits
	Fa-RmLG1	Fa-RmLG2	Fa-RmLG3	Fa-RmLG4	Fa-RmLG5	
Ni	0.0018	0.0038	0.0244	0.0760	0.0471	5
Cu	0.0269	0.0227	0.0333	0.0273	0.0526	100
As	0.0535	0.1041	0.1093	0.1217	0.0917	5
Cd	<0.001	<0.001	0.0017	0.0018	0.0018	1
Pb	<0.001	0.0010	0.0012	0.0026	0.0022	5
Zn	0.0073	0.0033	0.0163	0.017	0.0137	100
Mn	<0.001	<0.001	<0.001	<0.001	<0.001	50
Cr	0.0029	0.0041	0.0047	0.0035	0.0033	5

The test results of heavy metals in leachate collected from MDS specimens are listed in Table. 7. Heavy metals are elements with metallic properties and an atomic mass of > 20. The most common contaminants of heavy metal are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). Accumulation of heavy metals often results in soil/water degradation and ecosystem malfunction. Moreover, heavy metals enter food chains from polluted soil, water, and air, and consequently cause food contamination, thus posing a threat to human and animal health. As a result, the concentrations of all elements including Ni, Cu, As, Cd, Pb, Zn, Mn, Cr were below than the regulatory levels specified in Code of Federal Regulation of US governments (40 CFR 268.40). Therefore, the hardened stabilized MDS specimens were classified as non-hazardous.

4 CONCLUSION

The stabilization of marine dredged sediment using the new cementless binder Fa-RmLG derived from a cementitious mixture composed of fly ash (Fa), red mud (Rm), lime (L) and gypsum (G) was investigated. Based on the obtained results, three main conclusions can be drawn as following:

The unconfined compressive strengths of all MDS mixtures stabilized with the new cementless binder Fa-RmLG increased significantly when comparing to the unstabilized MDS ones. In addition, it was found that the compressive strength was a function of the red mud to gypsum ratio (Rm/G) (i.e., strengths decreased with a corresponding decrease in the Rm/G ratio, regardless of curing ages).

It is worth noting that red mud amount in the new cementless binder Fa-RmLG notably affected to early strengths of the stabilized MDS mixtures. The more amount of red mud used, the higher early strengths observed.

Most of the total settlement of fresh MDS mixtures took places within 24 h. The settlement of all MDS mixtures was very small, with a maximum of only 4.74 mm. A very small settlement is one of the requirements for in-service properties of soil stabilization in pavement construction.

In terms of environmental impacts, it was found that the hardened stabilized MDS specimens were classified as non-hazardous since both results of corrosivity and heavy metals leachate were in the acceptable ranges.

5 ACKNOWLEDGEMENTS

This research was supported by a grant (No 17-RDRP-B076564-04) from Regional Development Research Program funded by Ministry of Land, Infrastructure and Transport of Korean government.

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