An Approach to the Beneficial Use of Fine Sediments by Solidification: I. Leaching Properties and Intensity

Kyoungrean Kim (Korea Institute of Ocean Science and Technology/University of Science and Technology, The Republic of Korea)
Eun-Ji Won (Dept. of Marine Science and Convergent Technology, Hanyang University, The Republic of Korea)
Yehui Gang (Korea Institute of Ocean Science and Technology/University of Science and Technology, The Republic of Korea)
Kongtae Ra (Korea Institute of Ocean Science and Technology/University of Science and Technology, The Republic of Korea)

ABSTRACT: Sediments that contain high contents of fine sediments less than 75 μm and water were beneficial use followed by solidification treatment. This treatment was tested for a short period of time (within 3 days) considering the application of on-site dredging or adjacent sea area. Five solidification agents having high content of SiO_2 and Al_2O_3 were used in this research. After solidification treatment, treated materials were converted to jelly like materials depending on reaction conditions. Uniaxial compressive strength (UCS) could be possibly measured from the third day after solidification treatment. Since UCS ranged from 0.5 MPa to over 1.5 MPa, UCS met with standards of beneficial use in Korea, according to treatment conditions. Based on toxicity characteristic leaching testing, leaching blocking effect of heavy metals was more than 90%. The feasibility of solidification treatment was found for the beneficial use of sediments.
KEYWORDS: Marine sediments, fine particles, solidification, treated materials, beneficial use

INTRODUCTION

Both managing and disposing of dredged materials including contaminated marine sediments require considerable capital, time, space and environmental problems with the inclusion of pollutants (Bonomo et al., 2009). Although numerous remediation technologies were developed, the beneficial use of sediments which are dredged materials and contaminated marine sediments is still restricted (Lirer et al, 2017). Solidification has been widely used for the treatment of sediments and soil. Currently, treated materials were tested as construction materials such as brick production (Cappuyns et al., 2015), filling or cover materials and other ground materials (Siham et al, 2008; Said et al., 2015) followed by solidification treatment. Unfortunately, particles larger than 75 μm (sand) are mainly focused in the viewpoint of conventional solidification. In case of marine sediments, the contents of fine particles less than 75 μm are around 70 ~ 90% and water contents are also around 60% or more. These characteristics are apparently different from that of soil. It is very difficult to treat marine sediments, unless water treatment facilities are installed separately. Besides, conventional solidification treatment, it also needs a curing period of at least 7~8 days. Overcoming the difficulties mentioned above and developing a new application method based on solidification that can be applied directly to on-site dredging or adjacent sea areas are expected to have significant scientific, technological and economical viewpoints. The usability of marine sediments having high water contents and fine particles treated by solidification was mainly focused in this research. The results of this research could be used as preliminary data for the development of commercial scale remediation technology.

MATERIALS AND METHODS

Marine sediments were collected using a Van Veen grab in Masan Bay which is a coastal area of Changwon City located in the southeastern region of the Korean peninsula (Figure 1).

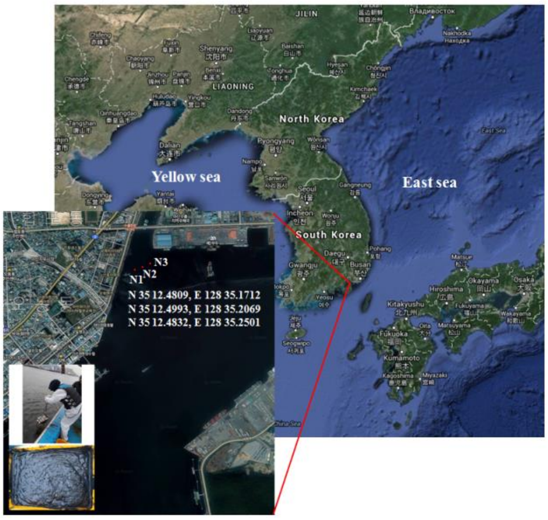

FIGURE 1. Sediment sampling site.

Collected sediments were used as samples in this research. The samples were freeze-dried (model, PVTFD10R, Ilshin, Korea) after removing impurities such as shells, gravel, and waste through a 1 mm sieve. The lyophilized sample was homogenized and used for basic characterization. Particle size analysis was conducted using a laser particle size analyzer (Mastersizer 2000, Malvern, UK). The difference between sample weights before and after freeze-drying was measured to determine water content of the original samples. Chemical oxygen demand (COD), total organic carbon (TOC) and ignition loss (IL) were analyzed according to the Korean Marine Environmental Process Test (Korea Ministry of Environment, MOMAF, 2013a). The pH was measured in the supernatant after 5 g of sediment and 25 mL of distilled water were stirred and allowed to stand for 1 h (Model No, Orion, Thermo Electron Crop., USA) (KME, 2017). To analyze the concentration of heavy metals in the sediments, high-purity (Merck, Suprapur grade) 4 mL hydrofluoric acid (HF), 2.5 mL nitric acid (HNO_3), and 0.75 mL perchloric acid ($HClO_4$) were added to 0.5 g of the ground sample in a Teflon® vessel, and then heated to 180ºC for 24 h (Windom et al., 1989). After the mixture was evaporated to full dryness, 2% HNO_3 was added to dissolve the residue in the Teflon container and finally adjusted to 10 mL. Following these procedures, the prepared liquid was diluted and measured with inductively coupled plasma mass spectrometry (ICP-MS; iCAP Q, Thermo, USA).

Prior to the addition of solidifying agents, the total heavy metal contents of the solidification agents were measured in the same manner as in the sediment method, and minerals in the agent were determined by X-ray diffraction (XRD) analysis. The wetted raw sediments were mixed with agents to produce samples of 5%, 10%, 15%, 20%, 25% and 30% sediments by weight. The samples were mixed by hand for 15 min using a spatula and the mixtures were cured in a silicon mold (9 cm × 4 cm × 4 cm) for 3 d (25ºC).

To determine the reduction efficiency of leaching heavy metals in each solidified sample, the toxicity characteristic leaching test (TCLP) was used according to the USEPA protocol (USEPA, 1992). The solidified sample was crushed to a size below 9.5

mm. One gram of the material was transferred to a polyethylene (PE) test tube and acetic acid (pH 2.88) was added to create a liquid-to-solid ratio of 20:1. The extraction occurred for 18 h in an end-over-end manner (30±2 rpm, 22ºC). The leachate was filtered by GF/A glass microfiber filters (0.45 μm) and then analyzed by ICP-MS for chromium (Cr), nickel (Ni), zinc (Zn), arsenic (As), cadmium (Cd), and lead (Pb).

Samples treated by solidification were molded in brass molds (5 cm x 5 cm x 5 cm) then cured at room temperature (20 ºC) for 3 days. Uniaxial compressive strength (UCS) was measured to test the physical properties of the cured samples. Three repetitions per sample were used and the mean value of the three measurements was used as the measurement value.

In case of the assessment of impact on water environment, the solidified sample (100 g) was placed in a polyethylene flask. Followed by this procedure, the flask was filled with 400 mL of untrapure water, and then sealed and allowed to stand for 7, 14, 21 and 28 days. After each experiment day, UCS was measured for each day. Separated liquid was filtered with GF/F glass fiber filter (0.45 μm) then analyzed for chromium (Cr), nickel (Ni), zinc (Zn), arsenic (As), cadmium(Cd) and lead (Pb) by ICP-MS.

RESULTS AND DISCUSSION

Characteristics of sediment sample. The characteristics of the sediment samples are shown in Table 1.

TABLE 1. Physicochemical characteristics of sediments from Masan Bay, Korea.

TOC(%)	COD(mg/kg)	IL(%)	pH	Water contents (%)	Particle size distribution (%)		
					>75㎛	75-32㎛	<32㎛
2.51	37.85	12.38	7.04	60.17	13.28	15.86	70.86

Characteristics of solidification agents. Five solidification agents which have a relatively higher content of SiO_2 and Al_2O_3 than conventional cement-based solidification agents were used in order to induce rapid solidification reaction such as hydration (Table 2).

TABLE 2. Characteristics of solidification agents.

Agent	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	others	IL	Sum	Loss
A	26.8	9.5	54.6	3.00	1.78	1.33	0.64	97.6	2.43
B	5.74	19.4	41.3	1.32	1.24	1.13	0.93	71.0	29.0
C	20.9	4.65	63.1	2.14	3.21	1.69	1.98	97.6	2.37
D	14.3	10.1	49.4	3.02	2.70	1.88	16.4	97.8	2.20
M	57.7	4.33	0.76	0.01	0.50	5.37	31.2	99.9	0.14

Initial formulation test

The order of initial formulation treated by five solidification agents were as follows: ①M, ②D, ③C, ④A, B (Figure 1)

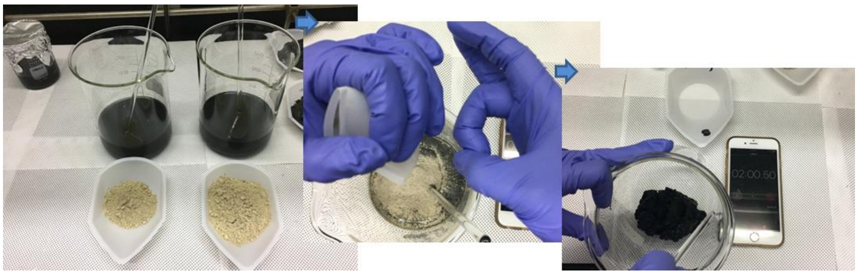

FIGURE 1. Initial formulation test.

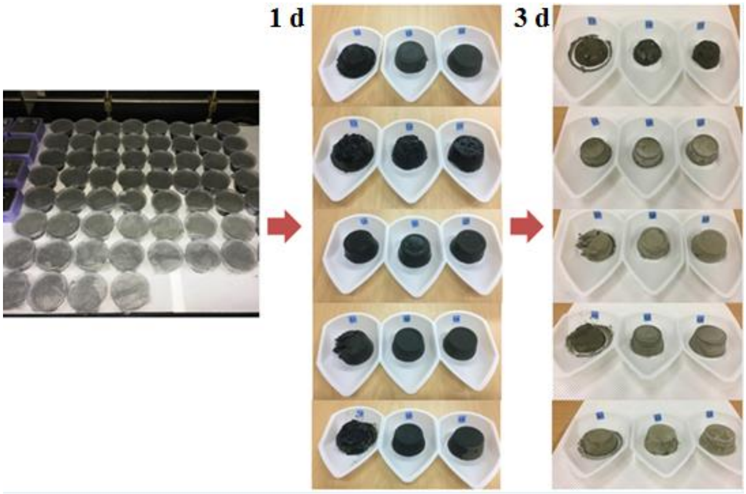

FIGURE 2. Change of treated materials depending on time.

TCLP Results. The TCLP results of solidified samples which cured 3 days followed by solidification treatment are shown in Figure 3. Leaching blocking effect of heavy metals was around 90% or more at most reaction conditions. Besides TCLP results may meet environmental standards.

FIGURE 3. TCLP results of solidified samples

Specification	Metal of TCLP leachate (mg/L)							Agent conc.
	Cr	Ni	Cu	Zn	As	Cd	Pb	wt %
Agent A	0.03	0.063	0.59	0.67	0.070	0.0010	0.007	5
	0.12	0.118	1.03	0.10	0.083	0.0008	0.008	10
	0.50	0.420	2.00	0.07	0.051	0.0007	0.005	15
Agent B	0.01	0.015	0.05	0.10	0.029	0.0009	0.007	5
	0.05	0.020	0.27	0.06	0.019	0.0006	0.007	10
	0.05	0.017	0.32	0.07	0.017	0.0007	0.004	15
Agent C	0.19	0.137	1.25	0.09	0.120	0.0013	0.010	5
	0.65	0.468	3.06	0.07	0.070	0.0014	0.007	10
	0.57	0.578	3.72	0.10	0.030	0.0015	0.011	15
Agent D	0.12	0.053	0.54	0.12	0.060	0.0029	0.012	5
	0.76	0.093	1.64	0.22	0.070	0.0026	0.036	10
	0.62	0.084	1.58	0.11	0.040	0.0018	0.015	15
Control	0.02	0.759	0.32	32.5	0.125	0.1213	0.083	

Solidification agent selection. When solidification agents C and D were used, the concentration values of all heavy metals in solidified materials were higher than that of sediment samples. Thus, solidification agent A and B were selected based on environmental stability.

Table 3. The ratio of heavy metals of treated materials (15% addition) based on control.

Specification	Cr	Ni	Cu	Zn	As	Cd	Pb
Control(mg/kg)	52.6	15.7	68.5	284	9.25	1.07	59
A/Control	1.04	1.18	0.92	0.88	0.94	0.93	0.83
B/Control	1.15	1.08	0.79	0.8	0.9	0.77	0.84
C/Control	1.18	1.09	1.38	1.2	1.39	1.16	1.04
D/Control	1.34	3.91	3.95	1.76	0.88	4.71	1.85

Uniaxial compressive strength. UCS of solidified samples could be measured a third day followed by solidification treatment (Figure 3.). On the contrary, conventional solidification with cement component needs to cure time at least 7 days. In Korea, UCS standards for beneficial use are set as follows. UCS standard is 0.5 MPa or more in the case of filling materials for ground (S1) and 1.5 MPa or more for the solidified materials of sewage sludge (S2). Therefore, solidified materials may use filling materials for ground and be effectively utilized for other ground purposes.

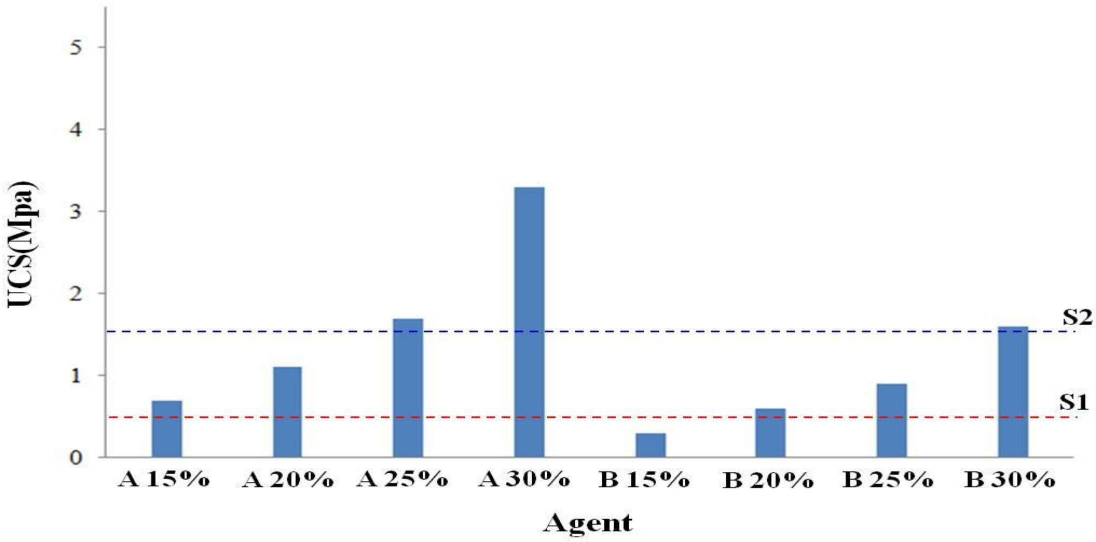

FIGURE 3. Uniaxial compressive strength depending on reaction conditions.

Stability test in water

From the results of stability testing in water, the UCS of solidified materials rapidly increased from 2.12 MPa to 5.67 MPa for the first 7 days. After the period, it increased gradually to 8.88 MPa and then remained above 8 MPa until 28 days. It is considered that the effect of solidified materials on the water environment is negligible since the change of shape or strength was not found when exposed to the water environment for 28 days.

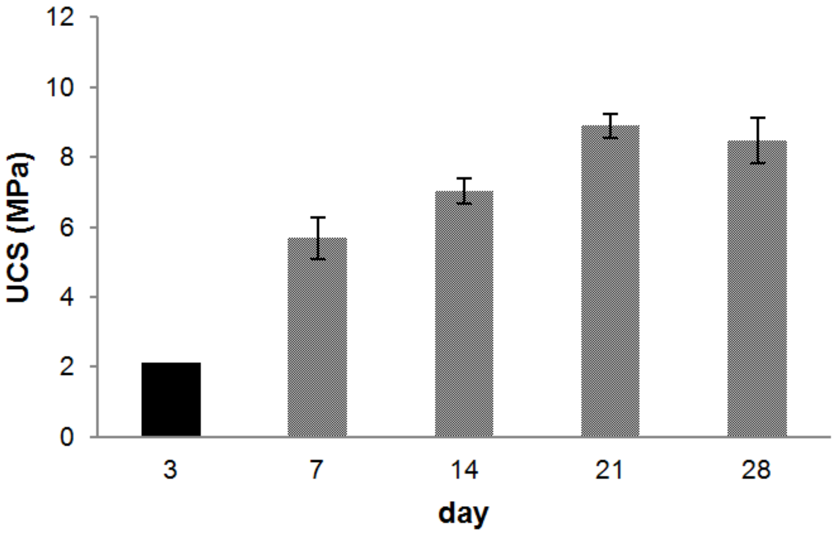

FIGURE 4. Change of uniaxial compressive strength of solidified sample in water.

Disscusion. Based on experimental results, treated sediments were to meet domestic environmental standards for beneficial uses such as superficial, landfill or filler materials. Initial formulation change could be possible within 3 h. Unlike the initial curing period of at least 7 days for conventional solidification, short formulation change and intensity are acceptable for the properties and conditions of treated materials as adequate usable materials. Even under certain conditions, the intensity was above 1.5 Mpa. Followed by solidification, as the result of the leaching test, the blocking effect of heavy metals was about 99%. Therefore, a new concept of solidification treatment in this research could be applied for the solidification of marine sediments which have high contents of fine particles and water. This technology could also be applied as a unit treatment process or one of the treatment processes in a remediation system for beneficial use of marine sediments including contaminated marine sediments. The results of this research could be successfully applied not only to remedy contaminated marine sediments but also to treat dredged materials, sediments or soils and deep-sea mine tailings.

CONCLUSIONS

The following conclusions were drawn from this research.

1. A new concept of solidification could be applied to solidification of marine sediments which have high contents of fine particles and water.
2. Solidification agent and treatment process need to be optimized for beneficial use of marine sediments.
3. It is necessary to set environmental standards depending on each beneficial use purpose.
4. Except chemical environmental standards of treated materials, the impact on the ecosystem including marine life needs to be considered for the future.
5. This approach could be applied to a unit process or a process in a remediation system and could be applied not only to sediments but also to soil or deep sea mine tailings.

ACKNOWLEDGEMENTS

This research was supported by Korea Institute of Ocean Science and Technology

(PE99568 and PE99616), Korea.

REFERENCES

Bonomo, L., Careghini, A., Dastoli, S., De Propris, L., Ferrari, G., Gabellini, M. and Saponaro, S., 2009. “Feasibility studies for the treatment and reuse of contaminated marine sediments”. *Environmental Technology*, 30(8): 817-823.

Cappuyns, V., Deweirt, V. and Rousseau, S., 2015. “Dredged sediments as a resource for brick production: Possibilities and barriers from a consumers’ perspective”. *Waste Management*. 38:372-380.

Lirer, S., Liguori, B., Capasso, I., Flora, A. and Caputo, D., 2017. “Mechanical and chemical properties of composite materials made of dredged sediments in a fly-ash based geopolymer”. *Journal of Environmental Management*, 191:1-7.

Said, I., Missaoui, A. and Lafhaj, Z., 2015. “Reuse of Tunisian marine sediments in paving blocks: factory scale experiment”. *Journal of Cleaner Production*, 102:66-77.

Siham, K., Fabrice, B., Edine, A. N. and Patrick, D., 2008. “Marine dredged sediments as new materials resource for road construction”. *Waste Management*, 28(5):919-928.