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The Effect of Calcium Sulfate and Dolomite on the Solidification/Stabilization of Dyeing Sludge

Hyungjin Han, Sebum Kim, Sookoo Lee

Dept. of Environ. Eng., Seoul National University of Technology, Seoul

I. INTRODUCTION

A lot of municipal solid wastes have been generated due to several reasons such as development of industry and an increase of population etc. The most of solid wastes have been treated by landfills, but landfill sites are so insufficient and it is difficult to find new sites. Especially, in case of industrial wastes that contains hazardous materials, it should be handled very carefully. So the development of proper treatment methods for these kinds of wastes is needed in viewpoint of environment, techniques and economics.

Additionally, the annual growth rates of wastewater sludges such as plating sludge and dyeing sludge were raised and many studies of treatment methods and reuse have been in progress. For the industrial wastes, the generation rates in Korea were raised about 117 ton/year in 1997, 96 ton/year in 1998 and 142 ton/year in 1999, respectively as shown in Table 1.

Table 1. The quantity of industrial wastes generated in Korea. (1,000ton/year)

Year	1995	1996	1997	1998	1999
Quantity	100.3	130.9	146.8	144.0	173.8

Land disposal has been a major technology for the management of those wastes owing to its advantage on economical operation. However, limited sites and stringent standards for landfilling have brought to bear on the use of land for disposing of hazardous wastes. Furthermore, direct landfill of organic sludge will be prohibited. Especially, when industrial sludge containing heavy metals and toxic organic matters is landfilled, it might release toxic matter to ground environment of its soil and water.

In order to make the sludge acceptable for safe land disposal and reuse, solidification/stabilization technology employing various cementitious binders have been developed. It aims to improve the handling and physical characteristics of hazardous waste as well as to protect the pollutants from leaching.

This study was performed to advance the physical and chemical characteristics of specimens for the dyeing sludge from Fenton treatment process using solidifying agent such as SB series made in our laboratory. The effects of calcium sulfate and dolomite as substitute of SB constituents in stabilization and solidification were studied.

Sookoo Lee, Tel : 02-970-6624, Fax : 02-971-5776, E-mail : sookulee@duck.snut.ac.kr

Dept. of Environ. Eng., SNUT, #172 Gongneung-Dong, Nowan-Gu, Seoul, Korea, 139-743

II. MATERIAL AND METHODS

Dyeing sludge and blast-furnace slag employed in this experiments were obtained from B dyeing wastewater treatment plant located in An-san and P steel industry located in Po-hang.

The raw dyeing sludge was dried at 100~105℃ in dry oven for 2 days. After that, the sludge was ground by ball mill and screened with 25 mesh sieve. The admixture with portland cement as solidifier was SB series composed by CaO, SiO_2 and $CaCO_3$ etc. The sand as aggregate from foundry was dried and sieved under 0.8 mm. Fly ash from power plant was directly used as it was.

Table 2 shows the matrix of mixing for solidification of dyeing sludge. Calcium sulfate as retarder was added at 0, 2 and 5%, respectively and dolomite was added at 0, 3.5 and 4% for substitute of SB constituents. The standard cement mortar was prepared in accordance with KSF 2305. The dried sludge was homogeneously mixed with cement, water and other additives using a mortar mixer for 10 min. The water contents is maintained at 0.6~1.0 as W/C. After mixing, it was filled into cubical moulds of 50 mm sides for making specimens. After 1~2 days, the cured specimens were demoulded and were cured for 7, 14 and 28 days, respectively, at 25℃ and 100% humidity to set.

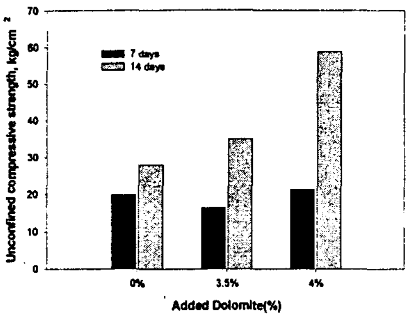
The unconfined compressive strengths was measured for the specimens of each matrices and aging time by UTM(Universal Test Machine, Instron Model 4201). Broken specimens provided samples for SEM analysis and leaching test. The elution of heavy metals were tested according to the KSLT(Korea Standard Leaching Test) which uses a hydrochloric acid. The heavy metal contents such as Cd, Cu, Cd and Zn were analyzed by AAS(Atomic Adsorption Spectrophotometer).

Table 2. Matrix of Mixing for Solidification

Test	Mixing ratios of compounded materials (%)							
	Sludge(dry)	Cement	Solidifier	CaO	Sand	Fly ash	Slag	Other
SB-1	33	12	8.5	4.5	17.5	8	16.5	-
SB-2	33	12	8.5	4.5	17.5	8	16.5	$CaSO_4$ 2%
SB-3	33	12	8.5	4.5	17.5	8	16.5	$CaSO_4$ 5%
SB-4	33	12	8.5	4.5	17.5	8	16.5	-
SB-5	33	12	8.5	4.5	17.5	8	16.5	Dolomite3.5%
SB-6	33	12	8.5	4.5	17.5	8	16.5	Dolomite 4%

III. RESULTS AND DISCUSSIONS

For the solidification of the dyeing sludge, the dried and ground sludge were used to form the specimen and mixed with cement, sand, slag, fly ash, solidifying agents, calcium sulfate and dolomite powder as additives. The experimental results of various dolomite ratios were shown in Fig.3.1. The compressive strength was increased with the ratios of dolomite added in 14 curing days. The unconfined compressive strength at 14 days were 28, 34.9 and 58.8 kg/㎠ with the various ratios, respectively. It shows that dolomite could be used as additive and the compositions of dolomite play a good role of substitute of solidifying agent compositions.



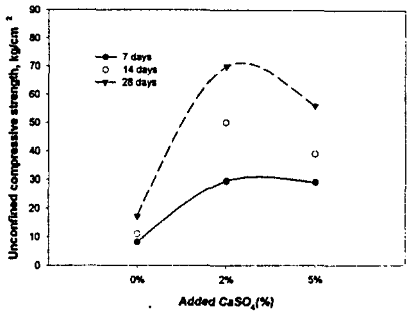


Fig.3.1 Change of UCS with each contents of Dolomite

Fig.3.2 Change of UCS with each contents of Calcium Sulfate

When calcium sulfate was used, the unconfined compressive strengths with various addition ratios were shown in Fig.3.2. Without adding of calcium sulfate, the specimens were cracked by rapid hydration reaction and heat. This cracking problem could be solved by adding calcium sulfate which took the role of retardation. The maximum compressive strength was illustrated at 2% of calcium sulfate as about 70 kg/㎠ at 28 curing days. It was due to the decrease of capillary gaps owing to production of ettringite crystal in specimens added solidifying agents and calcium sulfate. In case of 5 and 7%, compressive strengths were lower than that of 2% because of softening the specimens by over adding.

Experimental results of leaching test in raw dyeing sludge and waste sand was shown in Table 3.1. Cd is higher concentration than any other heavy metals in raw dyeing sludge and in case of waste sand. heavy metal concentration is lower or not detected on the whole. The main heavy metal contained in raw dyeing sludge was Fe and its contents show 27.8%.

Table 3.1 The concentration of heavy metals for raw Dyeing sludge and Waste sand. (mg/L)

Items	Cd	T-Cr	Zn	Cu
Sludge	21.7	0.03	0.39	0.16
Waste sand	0.02	ND	ND	0.057

* ND : Not detected

Table 3.2 shows the experimental result of elution concentration in specimen with calcium sulfate added at 7%. As compared with raw sludge, most of the concentrations were lower than regulation limits. It means that high compressive strength could decrease the elution concentration of heavy metals

The micro-structures of specimens with the low and high compressive strengths were analyzed by Scanning Electron Microscope. Fig. 3.3 shows and Fig. 3.4 illustrated the photos for the broken specimens for each cases.

Table 3.2 Leaching tests of solidified samples for the heavy metals. (mg/L)

Sample \ Item	Cu	Fe	Cd	T-Cr	Zn
Standard	3	None	0.3	(Cr^{6+} 1.5)	None
Sample	0.104	0.015	ND	ND	0.0857

* ND : Not detected

As shown in figure, a large number of crystalline products were appeared in the specimen with calcium sulfate. It is shown that the crystalline products were developed by a number of fibers interlock between the particles. It was thought that calcium sulfate could take a role to help the formation of these kind dense structure. In compared with two photos, the role of calcium sulfate can improve the quality of products to have high compressive strength and quite lower leaching concentration of heavy metals.

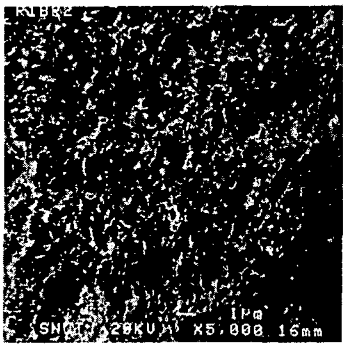


Fig.3.3 SEM photo for the low strength specimen

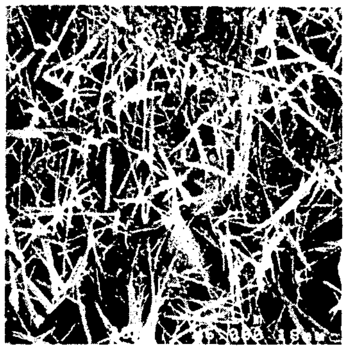


Fig.3.4 SEM photo with calcium sulfate

Ⅳ. CONCLUSIONS

From the experiments of the effect of calcium sulfate and dolomite of solidifying agents in the solidification/stabilization of the dyeing sludge, the following conclusion were obtained.

1. When calcium sulfate as retarder was used at 2%, unconfined compressive strengths could be increased up to 70 kg/㎠ which was about 4 times compared with no addition of calcium sulfate. The role of calcium sulfate can improve the quality of products to have high compressive strength and quite lower leaching concentration of heavy metals.
2. Dolomite could be used to increase the compressive strength in the range of 3-5%, which was about 34.9 and 58.8 kg/㎠ with 3.5% and 4% in 14 curing days, respectively.
3. From the results of leaching test, the main heavy metal of raw dyeing sludge was Fe and the elution concentrations of heavy metals for the specimen with calcium sulfate were much lower than the limit of the Korean Standard.