도금공장 유해폐기물의 고형화에 관한 연구

Solidification of Hazardous Wastes from Electroplating Industry

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요 지

본 연구는 도금공장에서 생산된 슬러지를 시멘트 고형화방법을 이용하여 처리할 때 고형화에 영향을 미치는 인자들 중에 모래／시멘트 비, 물시멘트 비, 젖은 슬러지의 양, 그리고 중금속 용출방지제를 네가지의 인자로 하여 압축강도와 용출량의 변화를 살펴 보았다. 모래／시멘트 비는 Cr(VI) 용출에 가장 큰 영향을 미치는 인자이며, 물／시멘트 비는 Zn 와 압축강도에 가장 큰 영향을 미치는 인자였다. Cr(VI)는 Zn 보다 시멘트 고형화에서 leachability 가 더 적었다. 현장에서의 Cr(VI)과 Zn 그리고 압축강도를 예측하기 위한 모델을 계발하였으며, 고체화의 3급 Brick 으로의 이용을 위해 혼합조건을 제시하였다. 그리고 30g 의 건조슬러지를 고형화할 때 최적조건은 모래／시멘트 비, 물／시멘트 비, 그리고 중금속 용출방지제의 양은 각각 1, 1.5, 1.075g 이었다.

Abstract

This research evaluated factors on cement-based solidification process designed for hazardous sludge produced from electroplating industry. Four factors of sand/cement ratio, water/cement ratio, amount of wet sludge and amount of a precipitator, were investigated in terms of leachability and compressive strength of the solidified materials.

Results of triplicate tests and statistical analysis indicated that sand/cement ratio(S/C) had the greatest effect on leaching of Cr(VI) from the solidified materials while water/cement ratio(W/C) on Zn and compressive strength. Cr(VI) was fixed better than Zn by portland cement. An experimental modeing was developed to estimate leached metal concentration and compressive strength at a given condition. Proper mixing criteria were also suggested for the use of the solidified mixture as construction

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materials. In solidification of 30g dry sludge, optimal condition was studied for S/C ratio, W/C ratio and the weight of precipitator which were 1, 1.5 and 1.075g respectively.

Ⅰ. Introduction

Environmental problems caused by inadequate disposal of sludges containing heavy metals increase as the population as well as industrialization accelerates their growth rate. In 1985, one-fifth million tons of hazardous industrial wastes were generated in Korea(1). Around 30% of these materials was treated on-site and the rest was treated by consignment company. However as there is a limited capacity of controlled disposal site, most of the waste end up with improper places, that is, open dump sites. Especially hazardous sludge containing heavy metals would release toxic metals to ground environment contaminating its soil and water. As the landfill disposal method might be the most viable alternative for this waste, proper conditioning should be made before filling. One of the popular techniques to fix the waste elements is a solidification with cementitious materials. This method has long been used in radioactive waste management, but its application to industrial waste is rather new, which necessiates further researches.

In this study, four major factors including S/C ratio, W/C ratio, amount of wet sludge and dose of a precitator were investigated in order to understand and improve the solidfication process. Laboratory tests were conducted with hazardous sludge obtained from an electroplating industry-one of popular inorganic industries in Korea.

Ⅱ. Methods and Materials

2.1 Solidification Materials

Type I ordinary portland cement, sand, a precipitator and water were used for the solidification of sludge containing heavy metals. Portland cement typically contains 63% CaO, 20% SiO2, 6% Al2O3, and 3% Fe2O3 by weight. Heavy metals would be precipitated by $Ca(OH)^2$ or become enmeshed in the solid as the matrix form due to adsorption capacity of calcium silicates(2,3). Effective size, uniformity coefficient, and curvature coefficient of the sand were 0.27, 1.89, and 0.84 respectively. A commercial liquid chemical was investigated as a possible agent to react with and fix heavy metals. This chemical would be called as 'a precitator' in this paper afterward.

2.2 Sludge Properties

Sludge was collected from the wastewater treatment plant of a TV antenna industry visited. The concentrations of total Cr, Zn and normal hexane extract in wastewater were 1.67mg/l, 3.56mg/l and 3.40mg/l, respectively. And trace amounts of copper and cyanide were detected in the wastewater. The concentrations of Cr(VI) and Zn in the sludge from wastewater treatment plant were 33148mg/kg and 4581mg/kg respectively on the basis of wet sludge. Water content and volatile solids of sludge were about 70% and 111mg/kg.

2.3 Solidification Procedure and Design

Cube moulds (50mm) made of acrylic resin were used to cast solidified samples for compressive strength test. Sand, cement, wet sludge and additional water were mixed homogeneously by hand. After mixing, the mixture was placed and compacted in the moulds. Cube moulds were covered with wet clothes to prevent the loss of moisture from samples for 24 hours and cured in a humidified curing box for 13 days.

Experiments were conducted according to a 3×3×3×3 factorial design to investigate the effect of four factors on leachability and compressive strength of solidified samples. Factors studied were sand/cement ratio, water/cement ratio, amount of wet sludge and amount of a precipitator. Experiments were conducted under the respective condition as shown in Table 1.

Triplicate samples were moulded for each of 81 conditions. Compressive strength on 14th-day after mixing was measured following the method specified in KSL 5105[4].

Table 1. Experimental Design

	Level 1	Level 2	Level 3
Water/Cement(W/C)	1.5	2.0	2.5
Sand/Cement(S/C)	1.0	1.5	2.0
Wet Sludge (g)	50	75	100
Precipitator (ml)	1.0	2.5	4.0

2.4 EP Toxicity Test

EP toxicity test[5] was used to evaluate the leaching potentials of solidified waste. After compressive strength test, the samples were crushed and screened with a 9.51mm sieve for the use of this test. The maximun amount of acid added to keep the pH at 5 ±0.2 was 80ml. Sample of 20g was placed in 320ml of distilled water before the acid addition. The samples were then placed on a shaker table with a 2.5cm stroke at 120 cycles per minute at 20°C for 24 hours. The samples were removed after shaking and filtered through a 0.45μm filter. The filtrate was analyzed by an Atomic Absorption spectrometry for Cr(VI) and Zn concentration. Collected data were statistically analyzed using ANOVA and mutiple regression methods.

Ⅲ. Results and Discussion

3.1 Compressive Strength Test

As shown in Fig. 1, compressive strength decreased by 60% when w/c ratio increased from 1.5 to 2.5. Compressive strength of solidified samples for a constant w/c ratio was decreased when the amount of sludge was increased. This might be caused by the less cement portion and the adverse effect of the sludge on hardening. Minimum strength of 20kg/cm² observed with w/c ratio of 2.5 surpassed the required strength of 10kg/cm² specified for controlled landfill[6]. As the w/c ratio of 1.5 in the experiment

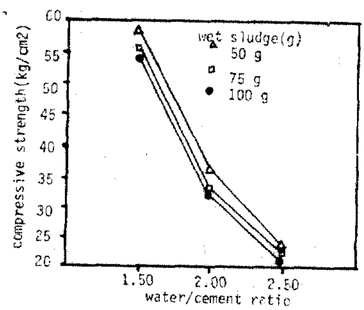

Fig. 1 W/C Ratio vs Compressive Strength(s/c : 1, precipitator. 4ml)

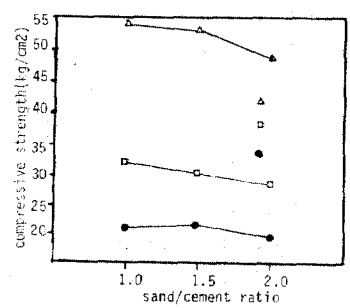

Fig. 2 S/C Ratio vs Compressive Strength (wet sludge : 100g, precipitator : 4ml)

was the possible minimum ratio due to the high water content of the sludge used, further dewatering was necessary for the lower w/c ratio and the increased compressive strength.

When the s/c ratio increased from 1.0 to 2.0, the compressive strength was slightly decreased by 10% in three different ratios of w/c ratio (Fig. 2). Samples with s/c and w/c ratios of 2.0 and 2.5 presented the minimum test result of 20kg/cm^2.

Effect of the precipitator on the strength was found insignificant.

3.2 Leachability Test

Leaching of both Cr(VI) and Zn from samples with different w/c and s/c ratios showed the same tendency as shown in Fig. 3 and 4. As the w/c and s/c ratios increased to 2.0 and 2.5 respectively, both metals were leached more. However there was no distinct variation of leachability with the s/c of 1.0, 1.5 and the w/c of 1.5, 2.0. When the w/c ratio is excessively high, the degree of hydration and crystallization became greater. As the curing time passes, the water evaporates out leaving capillary pores inside the solidified sample. Accordingly the permeability of the samples increased resulting in enhanced leachability. It can be summarized that high s/c and w/c ratios might result in improper mixture for a stable solidification.

As might be expected, increased amount of sand was detrimental in keeping the metals. Fig. 5 showed that leaching of Cr (VI) increased from 2.5 to 8.7mg/l as the s/c ratio increased from 1.0 to 2.0. When the sample contained 100g of sludge, Zn also presented the same tendency as shown in Fig. 6. It was natural that with the sludge increase, leached concenteation of Cr(VI), and Zn increased.

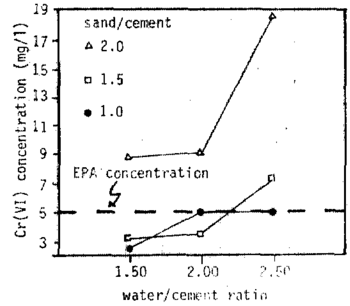

Fig. 3 Leached Cr(Ⅵ) vs W/C Ratio(wet sludge : 100, precipitator : 4ml)

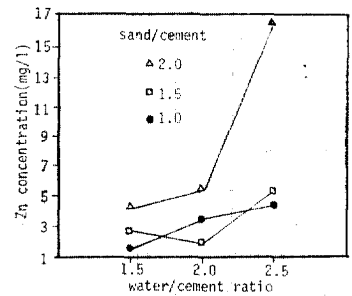

Fig. 4 Leached Zn vs W/C Ratio (wet sludge : 100 g, precipitator : ml)

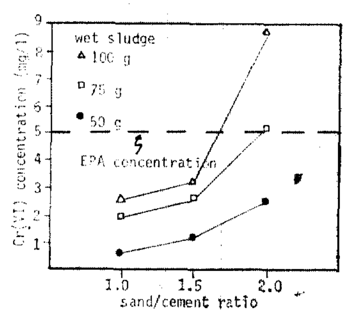

Fig. 5 Leached Cr(Ⅵ) vs S/C Ratio (w/c : 1.5, precipitator : 4ml)

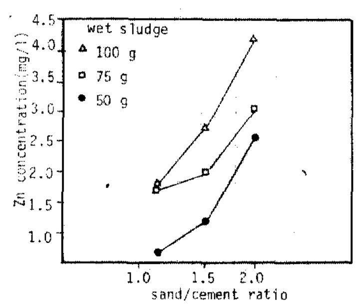

Fig. 6 Leached Zn vs S/C Ratio(w/c : 1.5, precipitator : 4ml)

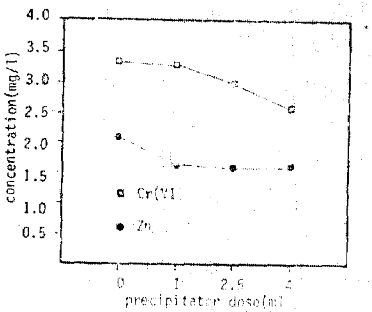

Fig. 7 Cr(VI) and Zn vs the Precipitator Dose(wet sludge : 100g, w/c : 1.5)

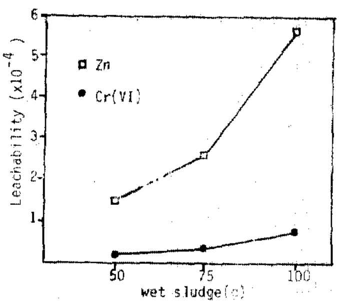

Fig. 8 Leachability of Zn and Cr(VI) (w/c : 1.5, sc : 1, precipitator : 4ml)

The precipitator did not significantly contribute in preventing metals from leaching out as shown in Fig. 7. Addition of 4ml of the liquid chemical decreased the Cr(VI) and Zn concentrations in leachate by only 20%. Therefore, it was required to investigate its use for the solidification purpose in terms of economy and efficiency of the precipitator.

In Fig. 8, the estimated leachability of Cr(VI) and Zn were depicted. Leachability was defined as the ratio of leached concentration to the total concentrationincluded in a solidified sample. Results in the figure indicated that Cr(VI) was more stabilized than Zn in this respect.

US EPA set the standard concentrations for Cr(VI) and Zn as 5mg/l and 500mg/l, respectively. In all investigated cases, leached Zn concentrations were well below 500

Table 2. Conditions for Leaching more than 5mg/ml Cr(VI)

Case	Sand/ Cement	Water/ Cement	Wet Sludge (g)	Precipitator (ml)
1	1.0	2, 2.5	100	1, 2.5, 4
2	1.5	2.5	75, 100	1, 2.5, 4
3	2.0	1.5, 2, 2.5	50, 75, 100	1, 2.5, 4

mg/l. However leached concentration of Cr (VI) was not low enough in all tests, and Table 2 suggested a design guide for proper mixture of the hazardous waste.

3.3 ANOVA Analysis for 3×3×3×3 Factorial Design

Many experiments involve a study of effects of two or more factors. It can be shown that, in general, factorial designs are most efficient for this type of experiments. Factorial design means that in each complete trial or replication of the experiment all possible combinations of the levels of factors are investigated. The effect of a factor is defined to be the change in response produced by a change in the level of interest in the experiment. In some experiments, the difference in response between the levels of one factor is not the same at all levels of the other factors. When this occurres, it is an interaction between the factors.

To estimate the effects of main and interaction, this experiment was conducted by 3×3×3×3 factorial design with three levels and triplication of test runs. The order in which the 3×3×3×3 observations were taken was selected at random, so that this design was a completely randomized design.

The observations may be described by a following linear statistical model.

$$\begin{aligned} Y_{ijklp} = {} & u + a_i + b_j + c_k + d_l \\ & + (ab)_{ij} + (ac)_{ik} + (ad)_{il} + (bc)_{jk} \\ & + (bd)_{jl} + (cd)_{lk} + (abcd)_{ijk} \\ & + (abd)_{ijl} + (acd)_{ikl} + (bcd)_{jkl} \\ & + (abcd)_{ijkl} + e_{ijklp} \end{aligned}$$

$i, j, k, l, p = 1, 2, 3$

$e_{ijklp} : N(0, \sigma_E^2)$, independently,

where a, b, c and d represent the effects of s/c, w/c, the weight of wet sludge(g) and the precipitator(ml) while u is the overall mean effect.

Items of ab, ac, ⋯, $abcd$ represent the effect of interaction between these factors. The last item e_{ijklp} is a random error component.

To estimate both main and interaction effects, the analysis of variance (ANOVA) was perfomed with the SPSS/PC package(7). Results of ANOVA were shown in Table 3, 4 and 5.

At 5% significance level, the decreasing order of significant effect for compressive strength was b, a, c, d, (ab) and (bd). For Cr(VI) concentration in leachate, the order of significant effect was a, b, c, (ab), (ac), d, (abc), (bc), (bd) and (abd). For Zn concentration in leachate, the order of significant effect was b, a, c, (ab), (ac), (bc), (abc) and d.

3.4 Experimental Modeling by Multiple Linear Regression

To project compressive strength and leached metal concentrations experimental modeling were delveloped. From the previous effect analysis, main effect was found to be more significant than interaction effect, so that at specific condition, only main effects were considered. That is, weights of sand, cement, dry sludge, precipitator and water were considered in developing each model for compressive strength, Cr(VI), and Zn concentrations in leachate by multiple linear regression using the SPSS/PC package.

The observations were described by multiple linear regression model.

$$Y = b_0 + b_1 x_{1i} + b_2 x_{2i} + b_3 x_{3i} + b_4 x_{4i} + b_5 x_{5i} + e_i$$

$i = 1, 2, 3, 4, 5$

$e_i : N(0, \sigma_E^2)$, independently,

where x_1, x_2, x_3, x_4, and x_5 represent regression variables for sand, cement, dry sludge, precipitator and water respectively.

Table 3. Analysis of Variance for 14th-Day Compressive Strength

Source of Variation	Sum of Square	Degree of Freedom	Mean Square	F	Significance of F
a	750.789	2	375.395	93.886	0.0
b	40055.335	2	20027.668	5008.927	0.0
c	213.213	2	106.607	26.662	0.0
d	63.767	2	31.883	7.974	.000
ab	125.042	4	31.261	7.818	.000
ac	35.799	4	8.950	2.238	.067
ad	23.933	4	5.983	1.496	.206
bc	24.248	4	6.062	1.516	.200
bd	46.470	4	11.617	2.906	.023
cd	14.208	4	3.552	.888	.472
abc	53.814	8	6.727	1.682	.106
abd	38.113	8	4.764	1.191	.307
acd	19.266	8	2.408	.602	.775
bcd	17.406	8	2.176	.544	.822
abcd	83.572	16	5.223	1.306	.199
Residual	647.740	162	3.998		
Total	42212.717	242	174.433		

Table 4. Analysis of Variance for Cr(VI) Concentration in Leachate

Source of Variation	Sum of Square	Degree of Freedom	Mean Square	F	Significance of Square
a	2529.538	2	1264.769	1295.862	0.0
b	1040.761	2	520.380	533.173	0.0
c	580.228	2	290.114	297.246	0.0
d	24.552	2	12.276	12.578	.000
ab	274.067	4	68.517	70.201	0.0
ac	134.273	4	33.568	34.394	0.0
ad	8.405	4	2.101	2.513	.077
bc	28.749	4	7.187	7.364	.000
bd	16.282	4	4.071	4.171	.003
cd	8.815	4	2.204	2.258	.065
abc	90.067	8	11.258	11.535	0.0
abd	30.521	8	3.815	3.909	.000
acd	14.157	8	1.770	1.813	.078
bcd	17.274	8	2.159	2.212	.029
abcd	30.693	16	1.918	1.965	.018
Residual	158.113	162	.976		
Total	4986.496	242	20.605		

Table 5. Analysis of Variance for Zn Concentration in Leachate

Source of Variation	Sum of Square	Degree of Freedom	Mean Square	F	Significance of F
a	439.574	2	219.787	949.692	0.0
b	639.038	2	319.519	1380.630	0.0
c	308.723	2	154.361	666.990	0.0
d	2.660	2	1.330	5.746	.004
ab	192.499	4	48.125	207.945	0.0
ac	156.622	4	39.156	169.190	0.0
ad	1.579	4	.395	1.706	.151
bc	130.211	4	34.553	149.301	0.0
bd	1.718	4	.430	1.856	.121
cd	1.584	4	.396	1.711	.150
abc	177.925	8	22.241	96.101	0.0
abd	1.831	8	.229	.989	.447
acd	2.711	8	.339	1.464	.174
bcd	3.674	8	.459	1.984	.051
abcd	4.247	16	.265	1.147	.317
Residual	37.492	162	.231		
Total	2110.089	242	8.719		

Obtained experimental models were as follows:

i) compressive strength

$$Y=1.56x_2+0.33x_3+0.4x_4+0.19x_5-61.688$$

($R=0.98$, significance of $F=0.0$)

ii) Cr(VI) concentration in leachate

$$Y=-0.475x_2+0.175x_3-0.24x_4+0.094x_5+15.89$$

($R=0.79$, significance of $F=0.0$)

iii) Zn concentration in leachate

$$Y=-0.258x_2+0.13x_3-0.082x_4$$

$+0.024x_5+10.751$

$(R=0.70$, significance of $F=0.0)$

Ⅳ. Engineering Application

4.1 Application as Construction Materials

Solidified wastes could be considered for an application as construction materials. Compressive strength standard for brick was listed in Table 6[8]. Solidified wastes within a strength higher than 40kg/cm² and leaching concentration less than 5mg/l Cr(VI) might be used as third-grade bricks. Table 7 represents the recommended mixture conditions for wastes and solipifying agents for the use as third grade bricks.

However, the impact on public health and environment should be assessed before its use.

Table 6. Compressive Strength Standard(KSF 4002)

	1st Grade Brick	2nd Grade Brick	3rd Grade Brick
Compressive Strength(kg/cm²)	80	60	40

Table 7. Mixing Conditions Recommended for the 3rd Grade Brick

Sand/Cement	Water/Cement	Wet Sludge (g)	Precipitator (ml)
1	1.5	50, 75, 100	1, 2.5, 4
1.5	1.5	50, 75, 100	1, 2.5, 4

4.2 Optimization of Sludge Solidification

To minimize the volume of solidified waste and cost, optimization of sludge solidification was performed by linear programming method. Basic data were summarized in Table 7. Linear programming for optimization was as follows[9].

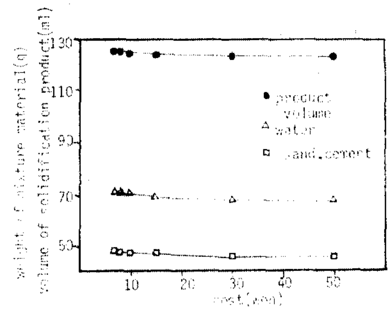

Fig. 9 Weight of Mixture Material and Volume of Solidification Product

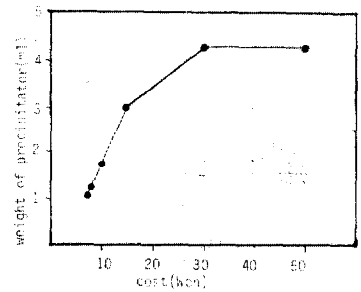

Fig. 10 Weight of Precipitatorvs Solidification Cost

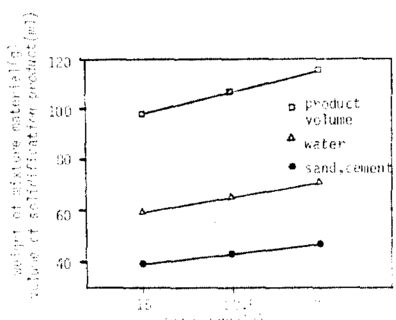

Fig. 11 Weight of Mixture and Volume of Solidification Product

Minimize Volume $0.377x_1+0.318x_2$ $+(\text{Sludge Volume})+0.94x_4+x_5$ 1)

Constraint

Table 8. Density and Unit Cost of Solidification Materials

	Sand	Cement	Wet Sludge	Precipitator	Water
Density(g/cm³)	2.65	3.14	1.11	1.075	1
Unit Cost(Won/g)	0.00645	0.075	—	4	—

$-0.475x_2+0.175x_3-0.240x_4$
$+0.095x_5+15.89<5ppm$ 2)

$-0.258x_2+0.130x_3-0.082x_4$
$+0.024x_5+10.751<500ppm$ 3)

$1.560x_2+0.330x_3+0.400x_4$
$+0.190x_5-61.688>10kg/cm^2$ 4)

$x_2>0.3x_5$ 5)

$x_2>x_3$ 6)

$0.94x_4>0.03x_3$ 7)

$104>x_1>39$ 8)~9)

$61>x_2>34.5$ 10)~11)

$4.3>x_4>1.075$ 12)~13)

$130>x_5>58.5$ 14)~15)

$2.5>x_5/x_2>1.5$ 16)~17)

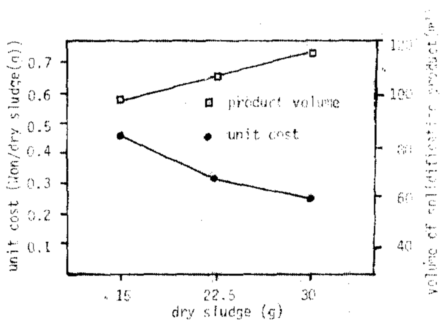

Fig. 12 Unit Cost and Volume of Solidification Product vs Dry Sludge

$2>x_1/x_2>1$ 18)~19)

$0.00645x_1+0.075x_2+4x_4$
<Material total Cost (Won)

$x_1,\ x_2,\ x_3,\ x_4,\ x_5>0$ 20)

First, optimization for solidification of 30g dry sludge are presented in Table 9 Cost and the volume of solidified waste were 7.34 Won and 125.4ml respectively.

Fig. 9 and 10 show the variation of the volume of solidified waste and the weight of materials, when cost was increased from 7.34 Won to 50 Won. The volume of solidified waste was reduced by 2.1ml and the increase of the cost might be largely caused by the increase of the precipitator, as the weight of precipitator was increased from 1.075g to 4.3g.

Table 10 represents slack variable and dual price for solidification of 30g dry sludge. Critical constriants for optimization were equation 3, equation 12, equation, 17, equation 19 and equation 20. Dual price means the volume variation of solidified waste with incremental of 1 unit in costants at rightside of constriant. Plus and minus

Table 9. Optimum Solution at 30g of Dry Sludge

x_1(Sand)	x_2(Cement)	x_3(Precipitator)	x_5(Water)	Cost	Volume
47.6g	47.6g	1.075g(1ml)	71.3g	Won 7.34	125.4ml

Table 10. Slack Variables and Dual Prices (Dry Sludge : 30g, Cost : Won 7.34)

Equation	Slack Vari	Dual Price	Equation	Slack Vari	Dual Price
2	26.4	0	3	0	6.6
4	496.0	0	5	0.1	0
6	26.2	0	7	17.6	0
8	8.6	0	9	56.4	0
10	13.1	0	11	13.4	0
12	0.0002	0	13	3.2	0
14	12.8	0	15	58.7	0
16	47.6	0	17	0	−1.6
18	47.6	0	19	0	−0.4
20	0	0.2			

means the volume reduction and increase of solidified waste. Conclusively, it is most realistic to reduce W/C ratio and S/C ratio but the use of precipitator in solidification was not desirable.

Secondly, optimization of 15g, 22.5g and 30g dry sludge was performed. Fig. 11 and 13 show the variation of the amount of materials, the volume of solidified waste and unit cost. When the volume of solidified waste was increased from 98.1ml to 125.4 ml, unit cost was reduced from 0.456 Won to 0.245 Won.

V. Conclusions

Based on the results obtained, the following conclusions were made.

i) Cr(VI) and Zn concentrations in leachate were decreased with decreasing sand/cement and water/cement ratios and increasing amount of the precipitator.

ii) The 14th-day compressive strength were increased, when sand/cement and water/cement ratios as well as wet sludge portion were decreased.

iii) In ANOVA analysis, sand / cement ratio had the greatest effect on leaching of Cr(VI). Water/cement ratio had the greatest effect on leaching of Zn and on compressive strength.

iv) Cr(VI) was stabilized better than Zn in cementitious solidification.

v) Experimental models by multiple linear regression were developed to estimate compressive strength, Cr(VI), and Zn concentrations in leachate.

vi) In solidification of 30g dry sludge, optimal condition was for S/C ratio, W/C ratio and precipitator were 1, 1.5 and 1.075 g respectively.

vii) The use of precipitator and sand for solidification was not economically and practically essential.

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