

Stabilization of mercury containing sludge by a combined process of two-stage pretreatment and solidification*

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Abstract

The stabilization of a mercury-bearing sludge, which is a typical hazardous waste of the chlor-alkali industry in the southern of Taiwan, has been performed by using a cement-fly ash solidification method. A two-stage pretreatment procedure consisting of using sodium sulfide and ferrous sulfate is employed to stabilize the solid end-product. Both the concentrations of the organic mercury in the extraction leachate (C_o) of the solids matrix, which had not been previously paid much attention to, and of the total mercury (C_t) have been examined. The results indicate that the two-stage pretreatment greatly enhances the stabilization efficiency of the solid matrix. The value of C_t can be reduced to a value lower than 1 ppb, which is well below 5 ppb (a Japanese safety regulation on Hg for the in-land sanitary landfill). No organic mercury in the extraction leachate has been detected for the combined process of the two-stage pretreatment and the solidification. Furthermore, within the ranges of experimental conditions of this work, the tendency of C_t to increase with curing time in the solidification by the process without two-stage pretreatment is greatly prevented by the two-stage pretreatment process. In addition, the 28-day compressive strength of the solid end-product can reach a value larger than 33 kg/cm², which is well above 10 kg/cm² (another Japanese regulation).

1. Introduction

Inorganic mercury compounds have been commonly used in the production of electrical goods, and in the chlor-alkali industry for the production of

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sodium hydroxide and chlorine. On the other hand, the major organic mercury compounds have been found in the use of slimicides and fungicides in the pulp and paper industry, in agriculture, and in medicine. Both inorganic and organic mercury can cause serious health effects [1]. Inorganic mercury poisoning may result in disorders of central nervous system and possibly psychoses. Primary health effects of organic mercury poisoning by methyl mercury include numbness, impaired speech, paralysis, oleformity, coma, and death. The toxicity of mercury in organic form is more serious than that of the inorganic form. The organic methyl mercury retained in bio-tissue is very stable and has a very long retention time. Thus, it may be concentrated to a very high level causing great health damages. The media most affected by the mercury poisoning are water and food. One of the most frightening disasters associated with the methyl mercury poisoning has been the "Minamata disease" which occurred earlier at Minamata Bay in Japan in the 1950s.

Solidification/stabilization (S/S) methods have long been applied to stabilize the hazardous wastes [2–8]. The methods are especially useful for the treatment of heavy metal bearing sludges and inorganics, as noted by many investigators (for example [3, 9–15]). Applications of S/S binding processes have also been found in the use of treating radioactive waste [3, 16–18]. However, the S/S technologies are only emerging for organic waste [3, 9, 19–25, 45]. Among those numerous applications, the cement-based methods employing portland cement with some additives are about the most common ones and have been widely used (for example [10, 11, 13–15, 17, 25–33]). The silicate-based methods have also been employed in some applications [9]. However, the durability of most silicate-stabilized wastes is poor. In some countries, such as the United States, the methods are usually acceptable only if some other binding agents such as cement are employed. The cement-based methods are indeed very effective. However, their uses may be pending on the cost of cement. In order to reduce the cost due to the use of cement, lime-based methods using lime with some additives to form pozzolanic concrete have been developed (for example [34–38, 32, 39]). Various reusable wastes have been used as additives in the lime-based methods. Chu et al. [34] and McDowell [38], Webster et al. [39], Knight and Rothfuss [36], Johannesmeyer and Ghosh [35], Lin [37], Liu [40], and Shah [41], added fly ash to stabilize soil, sewage sludge, flue gas desulfurization (FGD) by-product disposal, cadmium and chromium bearing sludge, metal-bearing sludge, mercury-bearing sludge, and arsenic-bearing sludge, respectively. The waste by-product lime was also employed to substitute the virgin lime in solidification processes [37, 40, 41]. The application of industrial wastes, such as fly ash (for example [13, 38]), and the by-product lime in solidification reduces the cost of raw materials. However, a great amount of total solidification agents is required for an acceptable treatment result for sludge. This would increase the cost of the final disposal of the solid end-product, and thus result in a drawback of the solidification method with a large amount of reused wastes.

From the above mentioned solidification applications, it can be seen that both cement- [28, 30, 31, 33] and lime-based [40] methods have found use in the stabilization of mercury-bearing sludge. Oshikata [30] performed the solidification of a mined slag sludge. He reported that the compressive strength of the solid end-product can reach a value of 26 kg/cm^2 , and that the concentration of the total mercury in the extraction leachate (C_i) of the solid matrix can be reduced to a value of 7 ppb. The investigation of ROCBEP [31] used Na_2S and FeS for the pretreatment step before solidification. The results indicated that the C_i , with the dosages of 7–10 times of the theoretical amount of Na_2S , may be lower than 5 ppb (a requirement of Japanese regulation on Hg). The pretreatment using FeS was not effective. In the studies of Ho [28] and Tseng [33], the values of C_i were about 7–31 ppb which did not meet the Japan regulation of 5 ppb. The experiments of Liu [40] employed Na_2S , and $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2S_4 as pretreatment agents, and water glass (soluble silicate) as cementation additives, respectively. With a molar ratio ($\text{Na}_2\text{S}/\text{Hg}$) of Na_2S to Hg of 15, a weight ratio (F/BPL) of fly ash (F) to by-product lime (BPL) of 3, a weight ratio $((\text{F} + \text{BPL})/\text{S})$ of (F + BPL) to mercury sludge (S) of 20, 7% $\text{Na}_2\text{S}_2\text{O}_3$, and a curing time of 28 days, the value of C_i may be reduced to as low as 0.36 ppb. When (F + BPL)/S equals 6, the other conditions held the same, C_i is about 3.1 ppb. These results were promising. However, the volumes of the solid end-products were increased to about 6–20 times of those of the original sludges.

One of the most important findings of the previous investigations on solidification of the mercury-bearing sludges is that the value of C_i surprisingly increased with curing time (t_c) when one compared the concentrations of the extraction leachates of the solids matrices having curing times of 7, 14, and 28 days, respectively. The deterioration of end-products with time has also been noted for most silicate-stabilized wastes. Besides, in our previous studies not much attention had been paid to the concentration of the organic mercury in the extraction leachate (C_o) of the solids matrix. The present work is therefore aimed at the prevention of an increase of C_i with t_c , and the effective reduction of C_o . Further, in order to take the advantages of the cement-based methods as well as the waste utilization, a cement-fly-ash solidification method is considered.

2. Experimental

2.1 Materials

The mercury bearing sludge (S) was obtained from an abandoned typical chlor-alkali plant in the southern Taiwan. The type I portland cement (C) was made by Taiwan Cement Co. The fly ash (F) was supplied by a typical coal-fired power plant located in the middle part of Taiwan. Sodium sulfide (Na_2S) and ferrous sulfate (FeSO_4) were purchased from Hayashi Pure Chemical Ind. Ltd., and Kokusan Chemical Work, Ltd., respectively. Some compositions and

TABLE 1

Some compositions of mercury bearing sludge, cement, and fly ash

Sample	Water content (%)	pH	Mercury content of sample (mg Hg/kg sample) (dry basis)		Mercury concentration of leachate ^a (mg/l, ppm)	
			Total mercury	Organic mercury	Total mercury, C _t	Organic mercury, C _o
Sludge (S)	62.6 (0.05) ^b	10.2 (0.05)	1203.9 (99.9)	12.38 (0.85)	0.662 (0.012)	0.055 (0.001)
Cement (C)	—	12.0	0.081 (0.002)	—	0.003	—
Fly ash (F)	54 ^c	10.8 ^c	—	—	0.009	<0.002

Sample	Metal content, (mg metal/kg sample, dry basis)											
	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Na	Ni	Pb	Zn
S	490	72932	3.89	13.62	27.24	4248	576	755	170461	38.92	66.16	387
C	—	—	—	—	—	—	—	—	—	—	—	—
F	—	—	—	—	—	—	—	—	—	—	—	—

Sample	Metal concentration of leachate ^a , (mg/l)											
	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Na	Ni	Pb	Zn
S	0.29	217.3	0.09	0.07	0.06	0.56	49.76	3.99	6785	0.32	0.49	0.04
C	0.25	2084	0.05	0.54	0.03	0.49	236.3	0.03	49.54	0.23	0.48	0.02
F	0.05	314.8	0.02	0.05	0.03	0.03	0.26	3.24	16.53	0.13	0.24	0.02

^aThe leachate is obtained by U.S. EPA-EP (U.S. Environmental Protection Agency-Extraction Procedure) test.

^bNumbers in parentheses are standard errors.

^cData of Liu [40].

properties of mercury-bearing sludge, cement, and fly ash are listed in Table 1. The other compositions of fly ash are referred to in Liu [40], i.e.: loss on ignition of 3.27%; (SiO₂ + Al₂O₃ + Fe₂O₃) of 86.08%; CaO, MgO, K₂O, and Na₂O of 4.1, 1.08, 2.25, 0.43%, respectively; portion passing No. 325 sieve of 17%. Table 2 lists some restrictions on the concentrations of mercury in the extraction leachates. A comparison of the results of Tables 1 and 2 indicates that the mercury-bearing sludge under the examination in this study is indeed a hazardous waste.

TABLE 2

Some restrictions on concentrations of mercury in extraction leachates

Country making regulation	Highest permissible concentration of mercury (mg/l, ppm)	
	Total mercury, C_t	Organic mercury, C_o
USA	0.2 ^a	—
Japan	0.005 ^b	NDB ^c
Taiwan, R.O.C.	0.25 ^a	NDB ^c

^a A regulation on Hg for characterizing the hazardous waste.

^b A regulation on Hg for the in-land safety sanitary landfill of waste disposal.

^c Denotes “not detectable”.

2.2 Apparatus

The major experimental apparatus used in this study include: ASTM C305-82 HOBART mixer; CNS 1230 A3043 solidification sample mould; ASTM C191 Vicat needle; curing box; compressive strength testing machine (Mori Testing Machine, Japan); shaker; tumbling mixer; and Perkin-Elmer HGA-400 AA (atomic absorption) analyzer. Detailed description can be found in Jann [42].

2.3 Procedures

The solidification test procedures are illustrated in Fig. 1. The sample of mercury-bearing sludge is pretreated by adding some properly chosen chemicals, followed by solidification treatment. Tests of the setting time and of the curing are then proceeded. The measurement of the compressive strength (P_{cs}) of the cylindrical solid sample and the standard U.S. extraction procedure (EP) [43] are conducted to evaluate the performance of solidification product. Atomic absorption (AA) analysis is used to determine the total mercury as well as the organic mercury concentrations of the extraction leachates of the solid matrices.

The molar ratios of pretreatment agent to the total mercury content of sludge are about 5 to 25 for Na_2S and 5 for FeSO_4 , respectively. The pretreatment times are about 5 to 30 minutes for Na_2S , and 30 minutes for FeSO_4 , respectively. For solidification treatment, the ratios of C, F, and S under examination include:

$C/F/S = 50/0/50, 30/15/45, 25/25/50, 60/0/40, 40/20/40, \text{ and } 30/30/40$. The curing time ranges from 14 to 126 days. The rate of pressure increase during measurement of P_{cs} is maintained at 1.50 mm/min. The acid used for the leaching test on the solid matrix is 0.5 N acetic acid. The extraction (leaching) time is about 24 to 28 hours. The measurement of the total mercury using the cold-vapor atomic absorption (AA) analysis at a wavelength of 253.7 nm is according to the U.S.

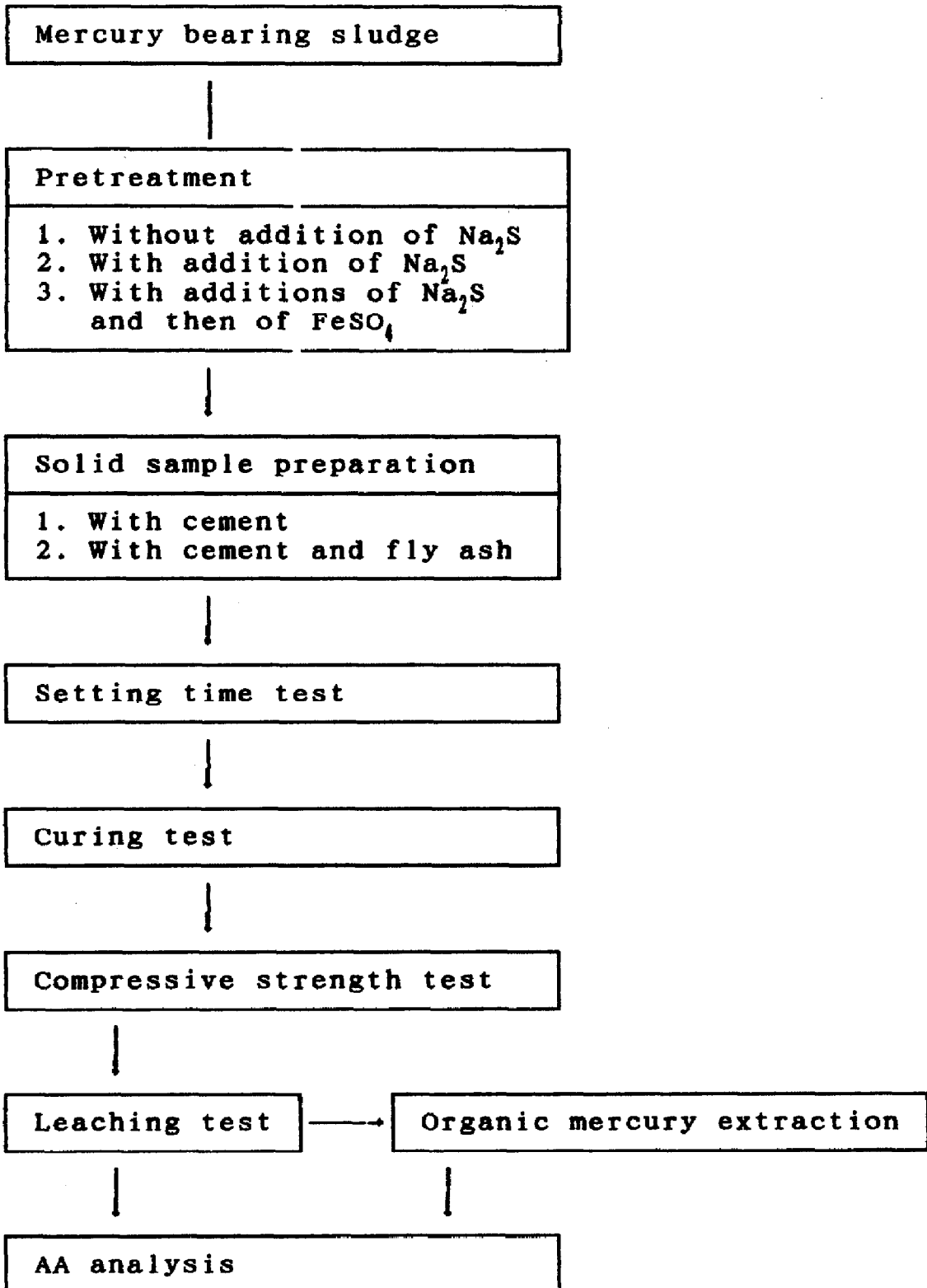


Fig. 1. Procedures for solidification test of mercury bearing sludge.

Water Pollution Control Federation (WPCF) standard methods for the examination of water and wastewater [44]. The chemicals needed for AA analysis of total Hg include H_2SO_4 , HNO_3 , KMnO_4 , $\text{K}_4\text{S}_2\text{O}_8$, $\text{NH}_2\text{OH}\cdot\text{H}_2\text{SO}_4$, NaCl , SnCl_2 , and HCl . The organic mercury contained in the leachate from leaching test of solid matrix is extracted by using organic solvent of benzene after the addition of HCl into the leachate. This is followed by extraction of the organic phase with a cysteine acetate solution made from 1 g cysteine hydrochloride monohydrate, 0.744 g sodium acetate trihydrate, and 12.5 g anhydrous sodium sulfate in 100 ml deionized water. The aqueous phase containing the mercury is then measured for Hg. The result is used for the back-calculation of the organic mercury in the original sample. To perform the Hg concentration measurements using the cold vapor AA analysis, a calibration curve with concentrations in the ppb range is constructed first according to the WPCF standard method [44]. With standard solutions of 1, 2, 5, 15, and 20 ppb Hg, a typical linear regression plot of concentration versus absorbance was determined (with a correlation coefficient of 0.996). For an unknown sample having a concentration below 1 ppb, an estimation is made by extrapolation from 1 ppb to zero concentration. This then gives the estimation of some organic mercury concentrations with values less than 1 ppb, as reported in the present work. More details are given by Jann [42].

3. Results and discussion

Table 1 indicates that the concentration of the total mercury in the extraction leachate (C_i) of the mercury-bearing sludge is about 0.66 ppm. This value substantially exceeds the permissible value of 0.2 ppm (as listed in Table 2), a U.S. regulation on Hg for characterizing the hazardous waste. In addition, its corresponding concentration of organic mercury (C_o) is about 0.055 ppm. These results reveal that the mercury-bearing sludge considered in this investigation is a hazardous waste and, thus, supports the necessity of treating and disposing it in a safe way, such as by solidification.

Table 3 presents the effects of the ratio of cement (C), fly ash (F), and sludge (S) on the compressive strength (P_{cs}) of the cylindrical solid sample. It is seen that the cases of C/F/S = 50/0/50, 30/15/45, and 25/25/50 cannot meet the requirement that $P_{cs} \geq 10 \text{ kg/cm}^2$ after a 28-day curing time (t_c). For the cases of C/F/S = 60/0/40, 40/20/40, and 30/30/40, values of P_{cs} are satisfactory. Evidently, a sufficient amount of binding materials is needed for solidification so as to provide sufficient binding strength and thus to achieve an acceptable level of the compressive strength. The fly ash, due to its pozzolanic property, may substitute a portion of cement for the use in solidification. In order to maintain a satisfactory value of P_{cs} while reducing the use of cement, one should choose C/F/S = 30/30/40 for further application. With C/F/S = 30/30/40, the volume increase of treated sludge is about 1.5 times of that of the original sludge.

TABLE 3

Effects of ratio of cement (C), fly ash (F), and sludge (S) on compressive strength (P_{cs})^b of cylindrical solid sample^a

Compound	(C + F)/S ^c					
	50/50			60/40		
C	50	30	25	60	40	30
F	—	15	25	—	20	30
S	50	45	50	40	40	40
t_c (days)	28	< ^f	<	275% ^d (17%) ^e	92.4%	100%

^a Dimensions of cylindrical solid sample: height = 10 cm, diameter = 5 cm.

^b Unit of P_{cs} = kg/cm².

^c Ratios are on dry basis.

^d Percentages represent relative values of P_{cs} of specific cases with respect to that (29.5 kg/cm²) of case without pretreatment with C/F/S = 30/30/40 and t_c (curing time) = 28 days.

^e Numbers in parentheses are standard errors.

^f Denotes cases with P_{cs} < 10 kg/cm².

The effects of the ratio of cement, fly ash, and sludge on the concentration of total mercury in the extraction leachate of the solids matrix are listed in Table 4. At a t_c of 28 days, the values of C_t with (C + F)/S = 60/40 are generally smaller than those with (C + F)/S = 50/50. This indicates that a larger amount of binding materials of (C + F) gives a higher binding/encapsulation strength and enhances the stabilization efficiency of solidification. The stabilization may thus reduce the release of mercury from the solids matrix. Furthermore, the ability of stabilizing mercury in the solids matrix is generally greater for cement than for fly ash. All cases at t_c = 28 days meet the strict Japanese regulation, i.e., C_t < 5 ppb. However, as t_c increases from 28 days to 126 days, the values of C_t tend to increase and may exceed 5 ppb in some cases. The prevention of the increasing tendency of C_t with t_c is thus very desirable.

Table 5 shows the effects of the ratio of cement, fly ash, and sludge on the concentration of organic mercury in the extraction leachate of the solids matrix. It is observed that the values of C_o are either very low or not detected. The leaching results indicate that the possible organic mercury pollution problem associated with mercury-bearing sludge can be effectively reduced or prevented by solidification/stabilization.

The effects of sodium sulfide pretreatment on the concentration of total mercury in the extraction leachate of sludge are listed in Table 6. The purpose of the pretreatment is to enhance the stabilization efficiency of the combined process with the subsequent solidification step. The data of Table 6 indicate that a pretreatment with a pretreatment molar ratio (PMR) of Na₂S/Hg of about 15 results in a maximum reduction of C_t of sludge. It is expected that an

TABLE 4

Effects of ratio of cement, fly ash, and sludge on concentration of total mercury in extraction leachate (C_t)^a of solids matrix

Compound	(C + F)/S					
	50/50			60/40		
C	50	30	25	60	40	30
F	—	15	25	—	20	30
S	50	45	50	40	40	40
Curing time t_c (days)						
28	127% ^b	146%	191%	79% (8%) ^c	90.6%	100%
63	309% (4%)	403% (10%) > ^d	613% (21%) >	191%	242% (6%)	270% (7%)
126	761% (20%) >	1075% (74%) >	1944% (221%) >	290% (10%)	253% (17%)	555% (22%) >

^a Unit of C_t = ppb ($\mu\text{g/l}$).^b Percentages represent relative values of C_t of specific cases with respect to that (1.29 ppb) of case without pretreatment with C/F/S = 30/30/40 and t_c = 28 days.^c Numbers in parentheses are standard errors.^d Denotes cases with $C_t > 5$ ppb (equivalent to 5 ppb/1.29 ppb = 388%), but still < 200 ppb (equivalent to 200 ppb/1.29 ppb = 15504%).

* Other notations and conditions are the same as in Table 3.

TABLE 5

Effects of ratio of cement, fly ash, and sludge on concentration of organic mercury in extraction leachate (C_o)^a of solids matrix

Compound	(C + F)/S					
	50/50			60/40		
C	50	30	25	60	40	30
F	—	15	25	—	20	30
S	50	45	50	40	40	40
Curing time, t_c (days)						
28	—	—	—	ND ^b	ND	0.015 ^a
63	0.03 (0.00) ^c	0.038 (0.003)	0.01 (0.01)	—	ND	0.13
126	ND	ND	ND	ND	ND	—

^a Unit of C_o = ppb ($\mu\text{g/l}$).^b ND denotes "not detected".^c Numbers in parentheses are standard errors.

* Other notations and conditions are the same as in Table 3.

TABLE 6

Effects of sodium sulfide pretreatment on concentration of total mercury in extraction leachate (C_i)^a of sludge.

Pretreatment time, t_p (min)	PMR ^b of Na ₂ S/Hg				
	5	10	15	20	25
5	372.8 ^a [44] ^c	217.6 [67]	163.4 [75]	352.5 [47]	494.1 [25]
10	322.8 [51]	170.1 [74]	145.2 [78]	311.0 [53]	422.3 [36]
20	286.3 [57]	134.2 [80]	127.1 [81]	280.2 [58]	381.6 [42]
30	260.4 [61]	113.5 [83]	106.9 [84]	253.4 [62]	348.7 [47]

^a Unit of C_i is ppb ($\mu\text{g/l}$).

^b Pretreatment molar ratio (PMR): Molar ratio of pretreatment agent to total mercury content of sludge.

^c Numbers in [] denote the percentages of reduction of C_i of sludge with pretreatment with respect to that without pretreatment; unit is %. C_i of sludge without pretreatment is about 661.5 ppb.

increasing use of Na₂S would generally help the formation of HgS, a low soluble mineral product, by the reaction of S²⁻ with Hg²⁺. The formation of low soluble HgS will greatly reduce the leachability of mercury from the solids matrix. However, an excessive amount of Na₂S might enhance the further side reaction of HgS with S²⁻ to form the highly soluble HgS₂²⁻ ion. This would be detrimental to the stabilization of HgS. Thus, there may exist an optimal dosage of Na₂S for the pretreatment. At a pretreatment time (t_p) of 30 minutes, the percentage of reduction of C_i of sludge with Na₂S pretreatment with a PMR of Na₂S/Hg of 15 was found as large as 84%.

Since the presence of S²⁻ might also lead to reaction with HgS to form HgS₂²⁻, it may be feasible to apply a second-stage pretreatment after the first-stage pretreatment of Na₂S, aiming at a reduction of C_i in the solids matrix end-product with long curing times. The second-stage pretreatment chemicals under consideration, on the one hand, should not inhibit the reaction of Hg²⁺ with S²⁻ to form HgS. These, on the other hand, should be capable of consuming the residual S²⁻ or the S²⁻ ions that are possibly produced during curing of the solid end-product so as to prevent the further reaction of HgS with S²⁻ to form HgS₂²⁻. The salt FeSO₄ seems to meet these criteria, as its Fe²⁺ may consume the excessive S²⁻, with a reaction affinity lower than Hg²⁺, to form solid FeS of low solubility (but not as low as that of HgS). Referring to the results of Table 6, one finds that the percentages of reduction of C_i of sludge at a t_p of 30 minutes with values of PMR of Na₂S/Hg of 15 and 10, respectively, are about the same. Thus, if one chooses

TABLE 7

Effects of various pretreatments on compressive strength (P_{cs})^b of cylindrical solid sample^a; (C + F)/S^c = 60/40. C/F/S = 30/30/40

Curing time (days)	Na ₂ S/Hg:FeSO ₄ /Hg ^c		
	0:0	15:0	15:5
28	100%	126% ^d	112%
63	145%	191%	153%

^a Dimensions of cylindrical solid sample: height = 10 cm, diameter = 5 cm.

^b Unit of P_{cs} = kg/cm².

^c Ratios are on dry basis.

^d Percentages represent relative values of P_{cs} of specific cases with respect to that (29.5 kg/cm²) of case without pretreatment with C/F/S = 30/30/40 and t_c (curing time) = 28 days.

^e Pretreatment molar ratio (PMR): Molar ratio of pretreatment agent to total mercury content of sludge; pretreatment times for each chemical are 30 min.

* Other notations and conditions are the same as in Table 3.

a PMR of Na₂S/Hg of 15 in the first-stage pretreatment and a PMR of FeSO₄/Hg of 5 (viz. 15 - 10) in the second-stage pretreatment, one may then maintain the effectiveness of Na₂S to form HgS and also the capability of FeSO₄ to capture any surplus S²⁻.

Table 7 lists the effects of the various pretreatments on P_{cs} of the cylindrical solid end-product. For the cases at C/F/S = 30/30/40, t_{p1} = 30 min, (pretreatment time of first stage) and t_{p2} = 30 min, (pretreatment time of second stage) all the processes without pretreatment, and with pretreatments of Na₂S alone or both (Na₂S + FeSO₄) yield solid end-products with acceptable values of P_{cs} .

The effects of the various pretreatments on C_i and C_o of the solids matrix are presented in Tables 8 and 9, respectively. The process with one-stage pretreatment only using Na₂S is but moderately effective in preventing the tendency of C_i increase with t_c . The relative percentages of C_i of the solids matrices at a t_c of 63 days for the processes without pretreatment, and with pretreatments of Na₂S only or both (Na₂S + FeSO₄), to that at a t_c of 28 days for the process without pretreatment, are about 270%, 153%, and 42%, respectively. The comparison of these three processes indicates that the two-stage pretreatment with both Na₂S and FeSO₄ gives the best stabilization efficiency. The values of C_i of the solids matrices with the two-stage pretreatment for a t_c of 42 and 63 days, respectively, are about the same, and are very much lower than the Japanese regulation of 5 ppb. The values of C_o of the solids matrices also meet the Japanese regulation with organic mercury not being detected at all. These results presented here indicate the need of pretreatment prior to the solidification of mercury-bearing sludge, and support the effectiveness of the proposed

TABLE 8

Effects of various pretreatments on concentration of total mercury in extraction leachate (C_t)^a of solids matrix; (C + F)/S = 60/40, C/F/S = 30/30/40

Curing time, t_c (days)	$\text{Na}_2\text{S}/\text{Hg}:\text{FeSO}_4/\text{Hg}^c$		
	0:0	15:0	15:5
14	37.4% ^b (5.8%) ^d	18.2% (4.5%)	5.3%
28	100%	31.6% (6.3%)	26.3% (5.3%)
42	178% (9%)	149% (4%)	41.1% (3.2%)
63	270% (7%)	153% (5%)	41.6% (2.1%)

^a Unit of C_t = ppb ($\mu\text{g}/\text{l}$).

^b Percentages represent relative values of C_t of specific cases with respect to that (1.29 ppb) of case without pretreatment with C/F/S = 30/30/40 and t_c = 28 days.

^c Pretreatment molar ratio (PMR): Molar ratio of pretreatment agent to total mercury content of sludge; pretreatment times for each chemical are 30 min.

^d Numbers in parentheses are standard errors.

* Other notations and conditions are the same as in Table 3.

TABLE 9

Effects of various pretreatments on concentration of organic mercury in extraction leachate (C_o)^a of solids matrix; (C + F)/S = 60/40, C/F/S = 30/30/40

Curing time, t_c (days)	$\text{Na}_2\text{S}/\text{Hg}:\text{FeSO}_4/\text{Hg}^c$		
	0:0	15:0	15:5
14	ND ^b	ND	ND
28	0.015 ^a	ND	ND
42	0.04	ND	ND
63	0.13	ND	ND

^a Unit of C_o = ppb ($\mu\text{g}/\text{l}$).

^b ND denotes "not detected".

^c Pretreatment molar ratio (PMR): Molar ratio of pretreatment agent to total mercury content of sludge; pretreatment times for each chemical are 30 min.

* Other notations and conditions are the same as in Table 3.

two-stage pretreatment and solidification process for stabilization efficiency. Although the maximum time span of the curing tests performed in this investigation were up to only 126 days (4.5 times the 28 days needed for characterization of the hazardous wastes), the advantage of using a second-stage pretreatment with chemical addition of FeSO_4 is evident. Within the

ranges of the experimental conditions used in this work, the tendency of C_t to increase with t_c is indeed greatly prevented by the combined process. However, concerning the durability and the possible deterioration rate of solid end-products at even much longer times, one should note that further long-term studies on durability are called for.

As for the cost of adding the second-stage pretreatment in the combined process, one may note that, in general, the variable cost of pretreatment agents contributes only a small portion of the total cost of raw materials essential for stabilization/solidification processes [29, 37, 40]. Since the amount of the common industrial chemical of FeSO_4 added in the second stage is only one-third of that of Na_2S employed in the first stage, the use of FeSO_4 would not cause a significant increase of the cost of the combined process.

4. Concluding remarks

1. The mercury-bearing sludge considered in this study is a hazardous waste. Its contents of inorganic as well as organic mercury should be treated by some proper technique, such as solidification.

2. There exists a tendency of the concentration of the total mercury in the extraction leachate (C_t) of the solids matrix to increase with curing time (t_c) during solidification for the process without the two-stage pretreatment.

3. The pretreatment with sodium sulfide can reduce the value of C_t of the sludge. The optimal value of the pretreatment molar ratio (PMR) of $\text{Na}_2\text{S}/\text{Hg}$ is about 15.

4. A comparison of the results of the three solidification processes, respectively, without pretreatment, with one-stage pretreatment of Na_2S , and with two-stage pretreatment of Na_2S and FeSO_4 , indicates that the two-stage process yields the best stabilization efficiency.

5. With values of PMR of $\text{Na}_2\text{S}/\text{Hg}=15$ and $\text{FeSO}_4/\text{Hg}=5$, and a mixing ratio of cement/fly ash/sludge = 30/30/40, the compressive strength of the solid end-product and the concentrations of the total and of the organic mercury in the extraction leachate of the solids matrix all meet the strict Japanese regulation for the in-land safety sanitary landfill.

6. Within the ranges of experimental conditions of this work, the tendency of the increase of C_t with t_c is greatly reduced by the proposed combined process of the two-stage pretreatment and the solidification.

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