Lime and Lignite Fly Ash as Cement Replacement in Hazardous Waste Solidification Process: Case Study of Spent Fluorescent Lamp

ความสามารถของปูนและเถ้าลอยลิกไนต์เพื่อทดแทนปูนซีเมนต์ในกระบวนการหล่อแข็งเพื่อกำจัดหลอดฟลูออเรสเซนต์ที่ผ่านการใช้งานแล้ว

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Abstract

The main objective of this research is aimed at the usage of lignite fly ash (power plant) and lime as cement replacement in hazardous - waste solidification process of spent fluorescent lamp. The study found that the increasing of waste ratio in solidification process has the trend to increase density and mercury leaching concentration. Different binder ratios and waste ratios produced different strength effects on the solidified sample. Mercury leaching concentration decreased with increasing curing times, whereas the density and the strength trend to decrease after 14 days. In consideration the properties of solidified sample and cost of solidifying material, a ratio of cement to lime to fly ash of 0:30:70 was found to be the most optimum ratio for solidifying spent fluorescent lamps (at a ratio of spent fluorescent lamp to binder of 2:1), with curing time more than 7-days. Accordingly, it is reasonable to assume lime and lignite fly ash are considerably better for use as a cement replacement alternative for spent fluorescent lamp solidification.

Key words: solidification / spent fluorescent lamp / cement replacement / fly ash / lime

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อในนำเถ้าลอยลิกไนต์และปูนขาวมาใช้ทดแทนปูนซีเมนต์ ในกระบวนการหล่อแข็งขยะอันตราย (หลอดฟลูออเรสเซนต์) ผลการศึกษาพบว่า เมื่ออัตราส่วนของขยะอันตรายเพิ่มขึ้นค่าความหนาแน่นและการชะละลายของปรอทจากก้อนหล่อแข็งฯ มีแนวโน้มเพิ่มขึ้น การศึกษาพบว่าค่าการชะละลายของปรอทจากก้อนหล่อแข็งฯ ลดลงเมื่อระยะเวลาบ่มเพิ่มขึ้น ในขณะที่ค่าความหนาแน่นและความแข็งแรงมีแนวโน้มลดลงหลังจากการบ่ม 14 วัน เมื่อพิจารณาคุณสมบัติของก้อนหล่อแข็งและต้นทุนวัตถุดิบในการหล่อแข็ง การศึกษาพบว่าที่อัตราส่วน ปูนซีเมนต์ต่อปูนขาวและเถ้าลอยเท่ากับ 0:30:70 จะมีเหมาะสมในการหล่อแข็งที่สัดส่วนของขยะหลอดฟลูออเรสเซนต์ต่อวัตถุประสานในอัตราส่วน 2:1 ที่ระยะเวลาบ่มอย่างน้อย 7 วันจึงอาจ

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สรุปว่าปูนขาวและเถ้าลอยลิกไนต์เป็นทางเลือกหนึ่งเพื่อใช้ทดแทนปูนซีเมนต์ในการหล่อแข็งหลอดฟลูออเรสเซนต์ที่ผ่านการใช้งานแล้ว

คำสำคัญ : การหล่อแข็ง / หลอดฟลูออเรสเซนต์ใช้แล้ว / การทดแทนซีเมนต์ / เถ้าลอยลิกไนต์ / ปูนขาว

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1. Introduction

Fluorescent lamp was widely and usefully used in the daily life of households. As well, the hazardous content of mercury as high as 10 to 23 milligrams in each fluorescent lamp (Daly, 2000), was consequently the main source of mercury contamination in environment at the end-life uses. The amount of 20,400 tons of spent fluorescent lamp (Tunyasathien et al., 2001) was estimated to be discarded into domestic landfill each year. This amount of mercury will disperse to environment as far as bioaccumulation, if there is no such well protected methods. However, there are several methods for mercury contamination protection, but the most appropriate method for Thailand at present, look like to be Stabilization/Solidification process (S/S). This process can be fixed and stabilized mercury within its‘ own hazardous waste mass (NEMA, 2004). The principle of this method involve mixing the hazardous waste with binder materials to formulate a solid mass which can immobilize mercury contaminants. Actually, the binder materials is the mixture of costly Portland cement with hazardous waste and water at various ratio. As well, the increasing of hazardous waste means the increasing of cement consumption, which presently becomes more costly. Hence, the low-cost binding materials to solidify waste instead of cement have been investigated. Lignite fly ash, the waste from Mae Moh thermal power plants, had been proven to be a cement substitute in mercury-waste solidification process (Punpanchai, 1996, Phadungkeitvongse, 1997, Ngamlertprsaert, 1998, Kinimarn, 1994). This is due to the high reactivity surface and it contents of high silica (SiO_2) and alumina (Al_2O_3) fly ash (Jang and Kim, 2000) can chemically react with $Ca(OH)_2$ from cement hydration reaction to form more CSH, and hence improve the properties of the solidified sample such as strength, workability, buffering capacity (capacity to resist pH change) and heavy metal leachability (Hang, 1990). However, the amount of fly ash as cement replacement was just a small portion due to the low amount of $Ca(OH)_2$ from cement hydration reaction (Punpanchai, 1996, Phadungkeitvongse, 1997, Ngamlertprsaert, 1998, Kinimarn, 1994). The increasing of fly ash as cement replacement in S/S required more $Ca(OH)_2$, and, thus, investigation on $Ca(OH)_2$ addition on S/S was necessary. Lime, which contains high calcium hydroxide (Tuinted, 1999) was an attractive material to react with fly ash as cement replacement. The pozzolanic materials in fly ash together with calcium rich in lime are expected to produce cementitious products upon hydration, which greatly reduced the leach ability of mercury (Taweesub, 1999).

2. Materials and Methods

Due to the attempts of this study to find out the feasibility of the spent fluorescent lamp treatment by stabilization / Solidification process, in which lignite fly ash from the coal power plant and lime were use instead of Portland cement. The experimental design was conducted through the flow chart in Figure 1 as followed:

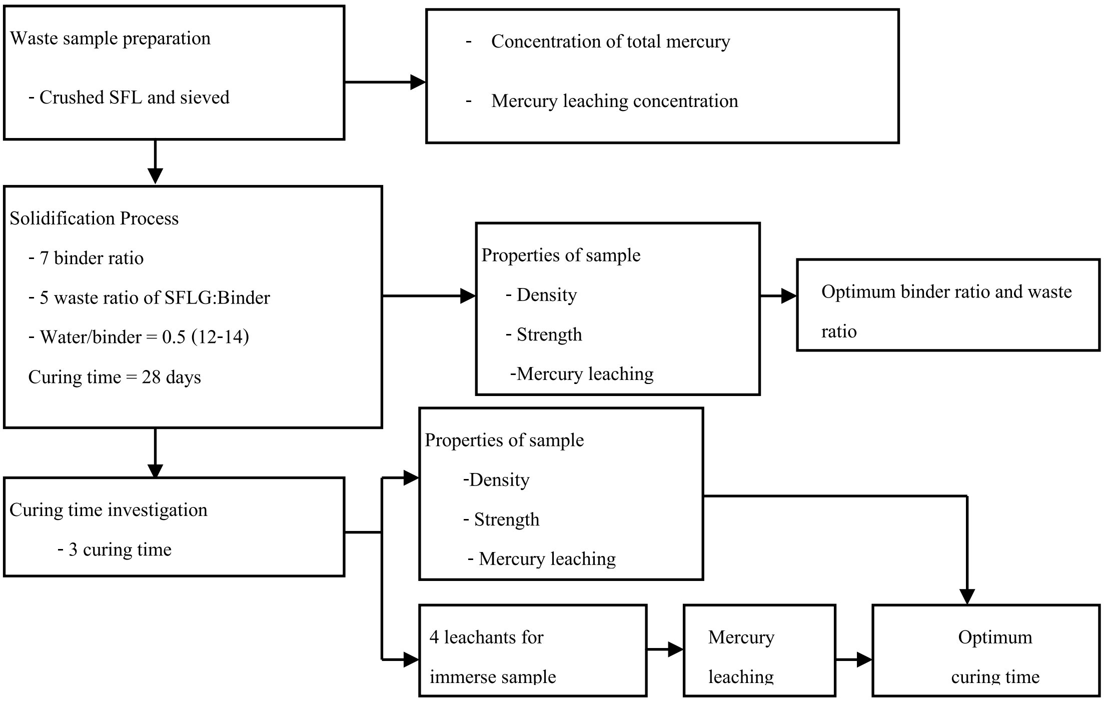

Figure 1 Flow diagram of the experimental procedure

2.1 Waste Sample preparation

The spent fluorescent lamps were initially washed in tap water to remove dust and undesirable contaminants. All lamps were broken under water to avoid the mercury releasing and then the glass pieces was separated from water followed by grounding and sieving to less than 9.5 mm. SFLG (spent fluorescent lamp ground waste) was further analyzed by the procedure prescribed in US.EPA. method 3051A (US.EPA., 2003) and the residue mercury-leaching concentration by the Ministry of Industry notification vol. 6 (1997). The concentration of mercury contained in wastewater was analyzed by the standard method for the examination of water and wastewater 19th ed. (APHA, AWWA, WEF., 1998).

2.2 Solidification of spent fluorescent lamps

SFLG sample preparation was pretreated by adding sodium sulfide (Na_2S) 1.75 times of mercury contained in original waste sample (Phadungkeitvongse, 1997, Ngamlertprsaert, 1998). Then, both SFLG and wastewater were precipitated and turn into mercury sulfide. During the experimental study, solidified sample was performed in the same process by adding SFLG into binder material (as cement to lime to fly ash or C:L:F) with desired binder ratios and mixing ratios[1] , followed by addition of wastewater contained mercury that used in the stimulated samples instead of tap water, at water to binder ratio of 0.5 (Phadungkeitvongse, 1997, Ngamlertprsaert, 1998, Kinimarn, 1994). Then, mixture was poured in cylindrical molds (14.2 cm.-height and 7.1 cm.-diameter length).The formulate solidified sample was left at ambient condition for 28 days. In this section, density, unconfined compressive strength, and mercury leaching concentration of solidified sample were investigated, in order to find an optimum condition according to the notification of Ministry of Industry vol. 6 (1997) to solidify SFL which would be used in further studies.

2.3 Curing time and solidified sample properties

Solidified samples, at curing time period of 7, 14 and 28 days was then have the density; unconfined compressive strength and leaching determination. The optimum curing time was determined under the notification of Ministry of Industry vol. 6 (1997). Then, the property of leaching resistance of solidified samples is further investigated through the most dangerous mercury leaching, by means of the virtual circumstance[2] of leaching resistance potential in such leachants as acetic acid[3], seawater[4], -SO_4[5], and HCO_3[6] (Machutakul, 1996, Cheng et al., 1992, Shively et al., 1986, Cassell and Walker, 1970, Asavapisit, 2003).

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[1] Experimental procedure were conducted at 5 difference mixing ratios of SFLG to binder (waste ratio) were varied from 1:3, 0.5:1, 1:1, 2:1 and 3:1 and 7 various binder ratios (C:L:F) as 50:00:50, 40:10:50, 40:20:40, 30:10:60, 30:20:50, 30:30:40 and 00:30:70.

[2] The solidified sample (uncrushed sample) were immersed in 2.5 L of such leachants without agitation for 7 days. Then, the leahates of such leachants were filtered through 0.6-0.8 µm filters to determine the mercury concentration.

[3] The acetic acid solution was chosen to simulate the condition of sanitary landfill environment during the acid stage of decomposition of municipal solid waste. It was prepared from 0.1 M acetic acid diluted with distilled water to a pH equal to 5.

[4] Seawater was used to observe mercury leaching from the solidified sample which immersed near coastal area. Seawater was used in this study was the synthetic seawater, which was prepared by dissolving 2000 g of seawater granular in distilled water and then diluted to 60 liters.

[5] 60 ppm of SO_4^{2-}, It should be in a reproducible form, which was allowed to predict the sulfates in ground and rainwater of solidified sample. It was prepared by dissolving 8.88 g of Na_2SO_4 in distilled water and diluted to 10 liters.

[6] 400 ppm of HCO_3 was chosen to simulate the condition of salts or alkalis to solidified sample. It was prepared by dissolving 8.88 g of $NaHCO_3$ in distilled water and diluted to 10 liters (Wichai, 1995).

3. Results and Discussions

3.1 Characteristics of the waste samples

The study found that the total mercury concentration was 31.9 μg/g. This value was close to Jang et al. (2005) study, showing that 10-70 μg/g mercury remained onto broken glasses.

a) Spent fluorescent ground waste (SFLG)

b) Hg-wastewater

Figure 2 Two types of waste from the preparation process

Through the concentration of mercury leachate, it was found that 23.7 μg/l of mercury leached out from SFLG. This value was lower than the notification of the Ministry of Industry vol. 6 (1997) (200 μg/l) and values presented by Punpanchai, Phadungkeitvongse and Ngamlertprsaert (Punpanchai, 1996, Phadungkeitvongse, 1997, Ngamlertprsaert, 1998) studies. In which were 770 μg/l, 2,279 μg/l, and 307 μg/l, respectively. This might be the relation with the sources of waste sampling that was confirmed with Jang et.al. (2005), who indicated mercury existed on the lamp glasses at different sources of waste had the different mercury concentration. As well, Punpanchai (1996) and Phadungkeitvongse (1997), waste was collected from broken fluorescent lamp at the Samare-dum industrial waste treatment center. As Ngamlertprsaert (1998) used sludge discard out of control treatment of fluorescent lamp factory, total mercury consequently as high as, 240 μg/l was mentioned. This result was similar to the concentration of total mercury that reported by Jang et.al. (2005), 400 – 2,000 μg/l. It noted that this value was higher than Industrial Effluent Standard for factories of Thailand (5 μg/l) (1996) and surface water standard (2 μg/l) (1994).

3.2 Solidification properties

Binder ratios (Cement:Lime:Fly ash) were varied from 50:00:50, 40:10:50, 40:20:40, 30:10:60, 30:20:50, 30:30:40 and 00:30:70, and added to solidify SFLG at the mixing ratio of SFLG to binder (waste ratio) of 0.33:1, 0.5:1, 1:1 and 2:1. The waste ratio exceeded 3:1, was not recommend (the mixture became so dry and did not retain their physical integrity after molding period). The water to binder ratio was fixed to be 0.5. Due to samples contained fly ash had the lower specific surface to adsorb water (Leangon, 1993), the over ratio of water performed the much water leaked out of mold. This solidified samples are left on ambient condition for 28 days.

3.3 Density of solidified samples of various waste and binder ratios

The density of solidified samples increased upwards as the waste ratio increased from 0.33:1 to 2:1 in all binder ratios. At 2:1 waste ratio, highest density was detected. This result was similar to Ngamlertprsaert (1998) and Narumit (1994). Moreover, Thepsittra (1999) indicated that density was increased with the increasing of waste amount, due to the higher specific gravity of waste than binder. Therefore, no significantly difference ($p\text{-value} < 0.05$) at different waste ratios was shown. As well, the density of solidified samples at 50:00:50 binder ratio was highest as the sample at ratio 00:30:70 binder ratio was lowest (see table 1). Thepsittra (1999) and Poon et al. (2001) explained this appearances that the replacement of cement by lime and fly ash gave adversely affected on density, because lime and fly ash had lower specific surface area than cement as mentioned above (Leangon, 1993). However, density of all solidified samples gave the higher density than the requirement[1] (1.15 ton/m^3) for secured landfill and no statistically significantly difference ($p\text{-value} < 0.05$) was shown in different binder ratios (at same waste ratio). So the study would like to conclude that the density of solidified samples directly increased with the increasing of waste ratio, and decreased with the increasing of lime and fly ash in binder ratio.

3.4 Binder and waste ratios on unconfined compressive strength of solidified samples

All of these solidified samples in various binder ratios and waste ratios gave the higher compressive strength than the requirement[2], which required for landfill solidified waste (3.5 kg/cm^2).

The highest strength was 133 kg/cm^2 at 1:1 waste ratio with 50:00:50 binder ratio and the lowest was 14.48 kg/cm^2 at 2:1 waste ratio with 00:30:70 binder ratio. It was noted that, there were the statistically significant differences among binder ratios (at same waste ratio). However the added up of waste than 2:1 ratios had eliminated the formation of compressive strength at all binder ratios, as shown in table 2. In which there were two different trends of unconfined compress strength.

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[1] Notification of the Ministry of Industry No.6 (1997) is not less than 1.15 ton/m

[2] notification of the Ministry of Industry volume.6 (1997)

Table 1 The results of density of solidified samples in various binder ratios and waste ratios

Binder ratios (Cement:Lime:Fly ash)	Density (ton/m^3)* in various waste ratios			
	0.33:1	0.5:1	1:1	2:1
50:00:50	$1.8668^{ab,a}$	$1.9569^{a,a}$	$1.8989^{d,a}$	$1.9970^{d,a}$
40:10:50	$1.7648^{a,a}$	$1.8612^{ab,ab}$	$1.8695^{cd,b}$	$1.9262^{c,b}$
40:20:40	$1.7011^{a,a}$	$1.8252^{ab,b}$	$1.8562^{cd,b}$	$1.8535^{b,b}$
30:10:60	$1.7057^{ab,a}$	$1.7801^{ab,b}$	$1.8311^{bc,b}$	$1.9256^{c,c}$
30:20:50	$1.6567^{ab,a}$	$1.7375^{b,b}$	$1.8155^{bc,c}$	$1.8590^{b,d}$
30:30:40	$1.6346^{ab,a}$	$1.7165^{b,b}$	$1.7969^{b,c}$	$1.8489^{b,d}$
00:30:70	$1.4246^{b,a}$	$1.5817^{ab,ab}$	$1.6592^{a,b}$	$1.7281^{a,b}$

Remark: Alphabet above the experimental value had test the significant correlation into various waste ratio (row) and various binder ratio in column, supposed value $1.8668^{ab,a}$ ("ab" is the performance of correlation in row or various waste ratio and "a" is the performance of correlation in column or various binder ratios). Different letters (row, column) is significant differences at p-value < 0.05 Notification of the Ministry of Industry No.6 (1997) is not less than 1.15 ton/m^3

Table 2 Unconfined compressive strength of solidified samples in various binder ratios and waste ratios

Binder ratios (Cement:Lime:Fly ash)	Unconfined compressive strength (kg/cm^2)* in various waste ratios			
	0.33:1	0.5:1	1:1	2:1
50:00:50	$121.60^{d,a}$	$129.40^{d,b}$	$133.30^{d,b}$	$85.33^{cd,b}$
40:10:50	$122.68^{d,b}$	$115.13^{cd,b}$	$86.91^{d,a}$	$99.72^{e,ab}$
40:20:40	$96.72^{c,bc}$	$113.02^{cd,c}$	$87.21^{c,b}$	$69.17^{b,a}$
30:10:60	$76.99^{b,a}$	$104.50^{c,ab}$	$124.44^{c,b}$	$91.54^{de,a}$
30:20:50	$118.30^{d,b}$	$80.46^{b,a}$	$69.00^{bc,a}$	$77.16^{bc,a}$
30:30:40	$95.27^{c,b}$	$66.12^{ab,a}$	$57.16^{b,a}$	$70.73^{b,a}$
00:30:70	$19.45^{a,ab}$	$53.91^{a,c}$	$24.44^{a,b}$	$14.48^{a,a}$

Remark: Alphabet above the experimental value had test the significant correlation into various waste ratio (row) and various binder ratio (column), supposed value $1.8668^{ab,a}$ ("ab" is the performance of correlation in row or various waste ratio and "a" is the performance of correlation in column or various binder ratios). Different letters (row, column) is significant differences at p-value < 0.05. Notification of the Ministry of Industry No.6 (B.E.2540) is not less than 3.5 kg/cm^2

One, the unconfined compressive strength trended to increase with the addition of waste from 0.33:1 to 1:1 ratio, then strength of the samples was gradually decreased. It noted that at 50:00:50 and 30:10:60 binder ratios, the strength was reached maximum at 1:1 waste ratio, and at 40:20:40 and

00:30:70 binder ratios, the strength was reached maximum at 0.5:1 waste ratio. While the other binder ratios performed the trends of decreasing with the addition of waste from 0.33:1 to 2:1. This was consistent with Rijai (1990), who reported that the different ratios of cement, fly ash, and lime content in binder were produced different strength effects. It was also noted by Roy and Eaton (1992) that the increasing of fly ash as cement replacement decreased the strength, this is due to the less hydration reaction products, $Ca(OH_2)$, to react with silica oxide and alumina oxide in fly ash. The insufficient pozzolanic reaction was extended to allow the strength of the high amount of fly ash exceed that of the high amount of cement binder (Kinimarn, 1994, Taweesub, 1999, Poon et.al., 2001). Moreover, Lanas and Alvarez (2003) and Antiohos and Tsimas (2004) reported that the strength of sample was increased with the increasing of lime into such pozzolans material as fly ash. But in the other hand, the large amounts of lime caused the decreasing of strength in sample. Because it was accepted that lime did not have cementitious properties, when cement was substituted by more lime, the active silica was reduced. So, more lime remaining in the sample, caused lower active silica which led to the less strength of the sample. Additionally, Nawal (1988) indicated the less amount of waste ratio interfered the hardened properties of solidified samples, this due to the higher waste content ratio could cover on cement particles and retard ed the hydration reaction process. This means less $Ca(OH)_2$ and SiO_2 reaction, or the CSH formation to strengthen solidified sample could not formulate in normal. Several reports such as Punpanchai (1996), Phadungkeitvongse (1997), and Kinimarn (1994) also supported this assumptions. Therefore, waste ratio and the cement ratio to lime and fly ash have affected on the strength value. It was slightly decreased, as the waste, lime and fly ash ratios in binder was increased.

3.5 Mercury leaching concentration at various binder and waste ratios

Table 3 showed the mercury leaching concentration at various binder and waste ratios. Waste ratio at 0.33:1 gave the lowest leaching of mercury in each binder ratios. Some waste ratio with various binder ratios such as 50:00:50, 40:10:50 was significantly increased with increasing the ratio of waste. In this study, binder ratios without cement as 00:30:70 gave the highest leaching of mercury.

At 50:00:50 binder ratio gave significantly the lowest mercury leaching, as the 00:30:70 binder ratio gave the highest. In particular, the amount of mercury leached out from all solidified samples were not excess the Notification of the Ministry of Industry (RTG) vol. 6 (1997) requirement for landfill (Notification of the Ministry of Industry No.6 (1997) is not more than 200 µg/l). As well, Rijai (1990) noted the mercury leaching concentration was increased with the increasing of waste ratio. This might be the occurrence of mechanism of waste particles to cover binder particle and retarded the hydration process more than the less waste ratio. As a result, less $Ca(OH)_2$ and also CSH, hydration reaction product, was produced for enmeshed and/or adsorbed mercury in solidified sample. Hence, the more SFLG contained in sample, the more mercury was leached out. This result was corresponded to Punpanchai (1996), Ngamlertprsaert (1998), Kinimarn (1994) and Taweesub (1999) studies.

Furthermore, Poon et al. (1985), all noted that binding of heavy metal and their consequent leaching was related to the binding mechanisms of mercury in the binder. The mercury that was in actual located or adsorbed on pore surface of solidified sample and would leach out under the alkalinity condition in leachate. The more, in cement replacement with fly ash increased the mercury leaching from sample. As well, lime in the binder was so porous and did not have cementitious properties. Thus, more lime content induced to increase the porosity of sample, lead, which was consequently lost the capacity of mercury binding (Lanas and Alvarez, 2003). So less mercury could be entrapped in the solidified sample, in particular the performance of higher mercury absorption in 50:00:50 binder ratio than 00:30:70 binder ratio. This was agreed with Punpanchai (1996), Ngamlertprsaert (1998) and Kinimarn (1994) studies.

Table 3 Mercury leaching concentration of solidified samples in various binder ratios and waste ratios

Binder ratios (Cement:Lime:Fly ash)	Mercury leaching concentration (μg/l)* in various waste ratios			
	0.33:1	0.5:1	1:1	2:1
50:00:50	$0.53^{ab,a}$	$0.80^{a,a}$	$0.83^{a,a}$	$1.40^{a,b}$
40:10:50	$0.77^{ab,a}$	$0.97^{a,a}$	$1.67^{b,b}$	$2.20^{b,c}$
40:20:40	$0.77^{a,a}$	$1.07^{a,a}$	$1.80^{bc,b}$	$2.27^{b,c}$
30:10:60	$0.83^{a,a}$	$1.10^{a,a}$	$2.10^{bcd,a}$	$2.53^{b,a}$
30:20:50	$1.07^{ab,a}$	$1.13^{a,a}$	$2.20^{cd,b}$	$3.50^{c,c}$
30:30:40	$1.10^{ab,a}$	$1.17^{a,a}$	$2.50^{de,b}$	$3.90^{cd,c}$
00:30:70	$1.27^{b,a}$	$2.27^{b,b}$	$2.83^{e,c}$	$4.03^{d,d}$

Remark: Alphabet above the experimental value had test the significant correlation into various waste ratio(row) and various binder ratio (column), supposed value $1.8668^{ab,a}$ ("ab" is the performance of correlation in row or various waste ratio and "a" is the performance of correlation in column or various binder ratios). Different letters (row, column) is significant differences at p-value < 0.05. , Different letters (row, column) is significant differences at p- value < 0.05. Notification of the Ministry of Industry No.6 (1997) is not more than 200 μg/l.

3.6 Curing time

Due to such physical properties as density**,** unconfined compressive strength, mercury leaching of solidified sample met the requirement of all notification of the Ministry of Industry No.6 (1997), and the objective of the study was to investigate the capacity of lime and lignite fly ash as cement replacement. So the solidified sample of binder ratios of 00:30:70 (no cement) and 10:20:70 (small amount of cement and lime with fix amount of lignite fly ash) at the highest waste ratio of 2:1 was selected in study the curing time. The solidified samples were cured in ambient condition for 7, 14 and 28 days. The performances of these curing period on density, unconfined compressive strength and mercury concentration were conducted. Then leaching of mercury in the condition of immersed solidified samples in SO_4^{2-}, HCO_3^-, seawater and acetic acid for 7 days was also conducted. The study details was as followed,

3.6.1 Curing times and density

The density of both binder ratios 00:30:70 and 10:20:70 binder ratios have looked like slightly increased with the increasing of curing time to 14 days and then gradually decreased through 28 days. These performances were not in accordance with Punpanchai (1996) and Ngamlertprsaert (1998) studies, which reported that the density increased with the increasing of curing time. This might be the incompletion of the hydration reaction at the time of 14 days in curing, the high content of water ratio in mixture, and the alkaline condition of mixture (described later). However the statistic analysis had perform the nonsignificant differences of density (p-value <0.05) after curing time of 14 days in the binder ratio of 00:30:70, as well as the nonsignificant difference of density (p-value <0.05) after curing of 7 days in the binder ratio of 10:20:70, see table 4.

Table 4 The density of solidified samples at different curing times.

Binder Ratio (Cement:Lime:Fly ash)	Density (ton/m^3)* at different curing times		
	7 days	14 days	28 days
00:30:70	1.8080^a	1.8437^b	1.8395^b
10:20:70	1.8869^a	1.8977^a	1.8500^a
Paired T-test	NS	NS	NS

Remark: *Mean value, Different letters (row) is significant differences at p-value < 0.05
Notification of the Ministry of Industry No.6 (1997) is not less than 1.15 ton/m^3
The t-tests, NS is not significant differences at p-value < 0.05

3.6.2 Curing times and unconfined compressive strength

At 2:1 ratio (waste:binder) as shown in table 5, it performed that the strength of both binder ratios increased with the increasing of curing time from 7 to 14 days. Their strength slightly decreased when extended the curing time to 28 days. The maximum strength value was reached at 14 days. Most of the solidified samples with the 7 days of curing period had the strength values higher than the standard requirement for secure landfill (3.5 kg/cm^2). However at 00:30:70 binder ratios, the exaltedly curing period between 7- 14 days had to be further studied.

Again, the strength of solidified samples increased with the increasing of curing time as observed in Punpanchai (1996), Phadungkeitvongse (1997), Ngamlertprsaert (1998) and Kinimarn (1994) studies. The decreasing of strength after 14 days of curing time was probably as the mentioned of incompletetion of hydration reaction and the amount of water ratio in the mixture. As well, Lanas and Alvarez (2003) found that the strength determined at early age (between 3 and 28 day) are strongly influenced by the water content of the mixture. Most of the samples were still lost the water at 28 day as a result of limitation of the pozzolanic reaction and thereby reduce the strength of the solidified sample. Jawed and Skalny (1990) noted that the alkaline condition could act as catalysts in forming CSH at early age, and promoting early strength development but high content of lime in sample could result in a decreased of 28 day strength in solidified sample. Moreover, CSH gel, which produced from the reaction of fly ash, cement and lime was retarded the diffusion of water and thereby shown the process for strength development (Youn, 1990). As well as, Rijai (1990) suggested that the reaction of sulphate content in fly ash with free calcium hydroxide was led to the reduction of the pozzolanic reaction of fly ash, that caused the expansion of sample volume and deteriorated the compressive strength.

Table 5 The results of unconfined compressive strength of solidified samples at different curing times

Binder Ratio (Cement : Lime: Fly ash)	unconfined compressive strength (kgf/cm^2) at different curing times		
	7 days	14 days	28 days
00:30:70	1.88^a	14.88^b	11.91^c
10:20:70	7.18^a	39.88^b	30.76^c
Paired T-test	DS	DS	DS

Remark: *Mean value, Different letters (a,b,c in row) is significant differences at p-value < 0.05
Notification of the Ministry of Industry No.6 (1997) is not less than 3.5 kg/cm^2
The t-test, DS is significant differences at p-value < 0.05

3.6.3 Curing times and mercury leaching concentration

At 2:1 ratio (waste:binders at 00:30:70 and 10:20:70) as shown in table 6, performed that curing time was inversely proportional to the concentration of mercury leaching. This was the binding effect of the cementitious binder, when the proportion of waste increase, more hydration reaction occurrence and reduced the porosity and permeability over the curing time (Youn, 1990). As short as curing time had been, the hydration reaction was not quite complete, so the solidified sample was not completely formulate the CSH. It was still in the form of liquid gel which low capability of mercury binding. It allowed mercury to leach out at higher concentration than those of the solidified sample with longer curing. This was agreed with Punpanchai (1996), Phadungkeitvongse (1997) and Ngamlertprsaert (1998) studies which was obviously shown that the lower of the curing time gave the higher mercury leaching.

Table 6 Results of mercury leaching concentration of solidified samples at different curing times

Binder Ratio	Mercury leaching concentration (μg/l) at different curing times		
	7 days	14 days	28 days
00:30:70	6.75^{a}	4.23^{b}	2.17^{c}
10:20:70	3.47^{a}	0.49^{b}	0.16^{b}
Paired T-test	DS	DS	DS

Remark: *Mean value, Different letters (row) is significant differences at p-value < 0.05
Notification of the Ministry of Industry No.6 (1997) is not more than 200 (μg/l)
The t-test, DS is significant differences at p-value < 0.05

3.7 Mercury leaching concentration in various curing time and leachant types

As shown in table 7, the mercury concentration leached from both binder ratios, and various leachant types had slightly decreased when curing time increased from 7 to 28 days. The lower mercury concentration was observed in 10:20:70 than 0:30:70 binder ratios samples. Moreover, among the all leachants, acetic and sea water had the highest and higher significantly ($p<0.05$) on mercury leaching concentration than other leachants at 28 days of curing time. This result was similar to Machutakul (1996) study who reported that the highest leaching concentration of mercury by Acetic acid was due to the deterioration of cement matrix. In case of leached out by seawater, the study noted that the occurrence of reaction between $Ca(OH)_2$ and sulphate in seawater generated gypsum which had the property to reduce CSH capacity in mercury binding.

Table 7 Results of mercury leaching concentration of solidified samples at different curing times and leachant types

Binder Ratio	Leachant type	Mercury leaching concentration (μg/l)		
		7 days	14 days	28 days
00:30:70	Sea Water	$3.09^{a,a}$	$2.25^{b,b}$	$1.18^{b,c}$
	HCO_3^-	$3.07^{a,a}$	$2.16^{a,b}$	$0.52^{b,c}$
	SO^{2-}_4	$3.05^{a,a}$	$2.24^{b,b}$	$0.45^{b,c}$
	Acetic Acid	$3.10^{a,a}$	$2.25^{b,b}$	$0.31^{a,c}$
10:20:70	Sea Water	$2.18^{a,a}$	$1.25^{b,b}$	$0.67^{c,c}$
	HCO_3^-	$2.15^{b,a}$	$1.23^{a,b}$	$0.45^{b,c}$
	SO^{2-}_4	$2.16^{c,a}$	$1.24^{b,b}$	$0.37^{ab,c}$
	Acetic Acid	$2.21^{d,a}$	$1.26^{c,b}$	$0.35^{a,c}$

Remark: *Mean value, Different letters (row, column) is not significant differences at p-value < 0.05
Notification of the Ministry of Industry No.6 (1997) is not more than 200 (μg/l)

3.8 Binder and waste ratio in cement replacement

Three factors, density, unconfined compressive strength and mercury leaching, were considered in selecting the optimum curing time through the notification of the Ministry of Industry vol. 6 (1997) requirement for landfill solidified waste[1]. So, the less curing time with 3 factor values to meet the requirement for landfill disposal was considered whether lime and lignite fly ash could be cement replacement or not. Which was clearly determined that the ratio of waste at 2:1 (waste:binders) in both binder 00:30:70 and 10:20:70) had density highly enough for securing landfill disposal, while leaching of mercury from various leachant types were lower than notification value at all curing time. Nevertheless, the strength to meet the notification of the Ministry of Industry vol. 6 (1997) have noted to be cured more than 7 days, excepted binder ratio of 00:30:70 need the more curing time than 7-day (the exacted time between 7-14 days need more study).

4. Conclusion

In conclusion, the capability of lime and lignite fly ash in order to replace cement in spent fluorescent lamp solidification process, solidified sample of 2:1 waste ratio (waste:binder) with 10:20:70 binder ratio (cement : lime : fly ash) at 7 days of curing time was appropriate for this study, (meet the requirements of the notification of Ministry of Industry vol . 6 (1997)). However, the optimum binder and waste ratio had to further consideration the cost spending in such treatments. An economic study at various binder and waste ratios as mentioned had to be adopted in process practices, in particular the location of secure landfill disposal existing.

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[1] density less than 1.15 ton/m^3, unconfined compressive strength was not less than 3.5 kg/cm^2 and mercury leaching was not more than 200 µg/l.

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