Solidification of heavy metal sludge using cement, fly ash and silica fume

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In this paper, the properties of solidified waste using ordinary Portland cement (OPC) containing silica fume (SF) and fly ash (FA) as a binder are reported. Silica fume and fly ash are used to partially replace ordinary Portland cement by 10% and 30% by weight, respectively. Plating sludge is used of 40, 50 and 60% by weight of the binder. A water to binder (w/b) ratio of 0.40 is used for all of the mixtures. The compressive strength of the solidified wastes is investigated. The leachability of heavy metals is determined by TCLP and XRD, and XRF is used to study the chemical properties, while the fractured surfaces are studied by SEM, and the pore size distribution is studied by MIP. The test results show that the setting time of the blended cement increased as the amount of plating sludge in the mix increased. In addition, the compressive strength of the blended cement increased with increasing curing duration time but at a decreasing rate. The compressive strengths at 28 days of the SF solidified waste mixes are 12.4, 2.7, 1.34 MPa and those of FA solidified waste mixes are 1.1, 1.0, 0.5 MPa at the plating sludge of 40, 50 and 60% by weight of the binder, respectively. The quality of the solidified waste containing SF and FA is better than that with OPC alone in terms of the effectiveness in reducing the leachability. The concentrations of heavy metals in the leachates are within the limits specified by the US EPA.

Keywords: Leaching, Heavy metals, Solidified wastes, Fly ash, Silica fume

Hazardous waste, such as waste water from factories, is released from industrial facilities. Although treatment processes using sediment dry residue can reduce the concentration of toxic waste before removal to a final disposal site, treating waste sediment in this manner is not safe for storage and transport. Certain heavy metals in the environment are not stable and can cause environmental problems, so such hazardous toxic waste requires a process of reduction or storing that is not hazardous and will not easily spread toxicity to the environment[1,2]. Solidification is a process used to treat hazardous waste from industrial plants, particularly hazardous substances or inorganic substances contaminated by heavy metals. The hazardous substances are stored in the structure by chemical bonding which neutralizes them and reduces the chance of spreading. The placeholder used in this process is normally Portland cement blended with pozzolanic materials such as fly ash, rice husk ash and silica fume. Solidification eases the safe transport of the solid cast mass and allows disposal in a landfill[3,4].

Fly ash is a pozzolanic material and a by-product of the combustion of pulverized coal in electric power plants. The characteristics of fly ash vary with the type of coal and the combustion conditions. In Thailand, it is estimated that more than 3.5 million tons of fly ash have been produced since 2001. However, only half of this fly ash has been utilized. The utilization of fly ash is still limited due to a lack of understanding of the characteristics of fly ash itself and of the properties of concrete using fly ash. Although fly ash has been successfully used as a mineral admixture in concrete and brick production, there is still a large amount of superfluous fly ash in some countries that causes environmental and disposal problems. The utilization of fly ash as an adsorbent for dye removal from industrial wastewater could be beneficial to both the environment and the economy. Thus, in recent years much effort has been made to use fly ash as a cheap adsorbent for dye removal[5,6].

Silica fume is a by-product of silicon metal or silicon metal alloy factories. Although silica fume is an industrial waste, it has become the most valuable by-product among the pozzolanic materials due to its...
very active and high pozzolanic property. Currently, it is widely used as an admixture in concrete or cement. Silica fume reduces the workability of fresh concrete or mortar due to its very high specific surface area, but it improves many of the properties of hardened concrete or mortar.  

Sludge produced by the metal plating industry is generally considered to be "hazardous waste" because of its toxic heavy metal content. Solidification techniques that are applied prior to deposition of this waste in landfills provide good results allowing the safe disposal of inorganic sludge, particularly into landfills. The characteristics discussed above lead to the study of the possibility of using fly ash and silica fume to store or filter heavy metals from industrial waste. The use of materials such as fly ash and silica fume with its pozzolanic property and the ability to bind metal ions generally gives a good performance. The solidification can store a large amount of sludge and help protecting the environment. This study, therefore, aims to investigate an effective solidification technique for sludge from a metal plating factory fly ash and silica fume in corporation with Portland cement.

Experimental Procedure

Materials
The materials used were ordinary Portland cement (OPC) per ASTM C150, fly ash (FA) from a power plant in Lumpang province (Mae Moh fly ash), Silica fume (SF), sludge (S) from the treatment of wastewater from a nickel plating plant and tap water. The S contained 35% water and 65% solid. It was dried and then sieved through a no. 100 sieve.

Mix ratio
Solidified wastes using silica fume, fly ash and ordinary Portland cement as binders were mixed. SF and FA were used to partially replace OPC in amounts of 10% and 30% by weight, respectively. And plating sludge was used in amounts of 40, 50 and 60% by weight of the binder. A constant water-to-binder ratio (w/b) of 0.40 was used to control the workability of the pastes (Table 1). The pastes were mixed in a mechanical mixer and the specimens were cast in 50 mm cube molds. The fresh samples were covered with plastic sheets to prevent water evaporation. After casting for 24 h, the samples were removed from the mold and cured in saturated lime water to the hydration and pozzolanic reaction is complete.

Test Programs
Specific gravity and particle size
The specific gravity of OPC, SF, FA and S was measured in accordance with ASTM C188, and their particle sizes were measured using laser particle size analysis.

Normal consistency
The normal consistency of the pastes was measured in accordance with ASTM C187 using Vicat apparatus.

Compressive strength
The compressive strength of the solidified waste was tested in accordance with ASTM C109 at ages of 7, 28, and 90 days. Five samples were tested for each age group.

Scanning electron microscopy (SEM)
A JEOL scanning electron microscope (model JSM6400) was used to examine the phase development and microstructure of the solidified plating waste. The paste cubes at the ages of 7 and 28 days were broken and the fractions in the middle part of the specimens were used for the analyses. The solid was placed on a brass stub sample holder with double stick carbon tape. Then, the sample was dried using infrared light for five minutes. Subsequently, the sample was coated with a layer of gold approximately 20-25 Å thick using a blazer sputtering coater. Micrographs were recorded at 12 kV and 500-10,000x magnifications.

X-ray diffractometer (XRD) and X-ray fluorescence (XRF) analyses
The XRD scans were performed for 2θ between 10°and 70°, with an increment of 0.03°/step and a scan speed of 0.5 s/step. XRD analysis using Bruker’s TOPAS software and using wavelength dispersive

<table>
<thead>
<tr>
<th>Table 1—Sample mix proportion (by weight)</th>
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<tbody>
<tr>
<td>Binder</td>
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</tr>
<tr>
<td>OPC</td>
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<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>90%</td>
</tr>
<tr>
<td></td>
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<td></td>
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<tr>
<td>70%</td>
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XRF (WDXRF). The positions of the diffraction peaks were identified by comparison to reference database compounds.

**Mercury intrusion porosimetry procedure (MIP)**

The pore diameter distribution in the hardened cement pastes was measured by mercury intrusion porosimetry (MIP, Autopore III 9400) at a pressure capacity of 228 MPa. After curing for 7, 28 and 90 days, the samples were split from the middle portion of the hardened, blended cement paste. To stop the hydration reaction, the samples were submerged directly into liquid nitrogen for 5 min and were then evacuated at a pressure of 0.5 Pa at -40ºC for 48 h. This method has previously been used to stop the hydration reaction of cement paste.

**Toxicity characteristic leaching procedure (TCLP)**

Metal leaching from the solidified plating waste cured for 7, 28 and 90 days was assessed using the TCLP as defined by the US EPA. The samples were crushed to reduce the particle size to less than 9.5 mm. The crushed sample was extracted using an acetic acid solution (pH 2.88) in a volume with a weight equal to 20 times the weight of the sample. The extraction vessels were rotated in an end-over-end manner at 30 rpm for 18 h. The leachate was filtered through a 0.45-µm membrane filter to remove suspended solids and was then divided into two portions. One portion was used for a pH measurement, and the other was used for the determination of the metals present in the leachate by ICP-AES. Each extraction was performed in triplicate, and the average value was reported to ensure the reproducibility of the data.

**Results and Discussion**

**Properties of materials**

**Physical results for OPC, SF, FA and S**

The specific gravity and median particle size \(d_{50}\) of OPC, SF, FA and S are shown in Table 2. The median particle size \(d_{50}\) of OPC was approximately 14.1 microns, and those of SF, FA and S were 0.15, 20.13 and 34.81 microns, respectively. The surface areas of OPC, SF, FA and S were 0.36, 14.48, 0.31 and 0.19 m²/g, respectively. The particle size distribution for OPC, SF, FA and S was measured with a Mastersizer and is graphically shown in Fig. 1. For OPC and S, the particle shapes were solid and angular, whereas the surfaces of SF and FA were smooth (Fig. 2).

**Chemical composition and material patterns**

Table 3 shows the chemical compositions of OPC, SF, FA and S, which were analyzed by XRF. SF and FA were found to consist primarily of SiO₂ and Al₂O₃. As can be seen, these two components comprised 95% of SF and 70% of FA. The main elements of S were NiO (40.88%), CaO (25.32%), CuO (13.08%) and ZnO (10.33%).

**Properties of pastes**

**Normal consistency of pastes**

The normal consistencies of OPC100, OPC10SF and OPC30FA were found to be 25.5, 34.1 and 35.3%, respectively. The results show that using a higher percent replacement of SF and FA resulted in a higher normal consistency. When the material had higher fineness and high porosity, the normal consistency was higher than that of the coarser pastes. This occurred because the classifying process reduced the particle size and shape while increasing the surface area of the particle, which is due to the SF and FA particles having high porosity and thus absorbing more water, resulting in higher water consumption.

**Setting time of blended cement pastes and pastes containing solidified plating waste**

The blended cement pastes containing SF and FA were characterized by a longer setting time than those
using only Portland cement paste. The setting times increased because the pastes mixed with SF and FA have higher water contents at the normal consistency than the Portland cement paste. Moreover, using SF and FA to replace Portland cement resulted in a smaller amount of $C_3S$ in the pastes and thus resulted in a longer setting time.

**Compressive strength of the blended cement pastes**

Table 4 shows the development of compressive strength in the cement pastes at 7, 28 and 90 days when 10% SF and 30% FA by weight were used to replace Portland cement. When SF was used, the compressive strength in the initial stage increased in comparison with that of the cement paste control, whereas when FA was used as a replacement the compressive strength was less than that of the mixture with SF. More silica dioxide is present in SF than in FA, which causes SF to react better than FA.

**Compressive strength of pastes containing solidified plating waste**

The experimental results showed that the rates of strength development in the solidified wastes using SF and FA as solidification binders were higher than the strength development rates for OPC. The rates were higher for a couple of reasons, including the fixation of metallic waste species in the cement paste following solubility reduction and precipitation, ionic substitution and incorporation in cement hydrates, and sorption onto the surface area of cement hydrates. The composition of OPC hydration product is dominated by calcium silicate hydrate (C-S-H) which typically comprises 70-80% of the product\textsuperscript{13}. The metals may

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>OPC</th>
<th>SF</th>
<th>FA</th>
<th>S</th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>19.85</td>
<td>94.88</td>
<td>43.87</td>
<td>5.53</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>4.49</td>
<td>0.73</td>
<td>26.33</td>
<td>3.78</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.56</td>
<td>1.34</td>
<td>10.81</td>
<td>-</td>
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<tr>
<td>CaO</td>
<td>66.96</td>
<td>0.99</td>
<td>12.69</td>
<td>25.32</td>
</tr>
<tr>
<td>MgO</td>
<td>1.36</td>
<td>-</td>
<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.34</td>
<td>1.42</td>
<td>1.10</td>
<td>-</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.46</td>
<td>-</td>
<td>2.74</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NiO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40.88</td>
</tr>
<tr>
<td>CuO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13.08</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.33</td>
</tr>
<tr>
<td>CrO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.64</td>
</tr>
<tr>
<td>LOI</td>
<td>0.98</td>
<td>0.64</td>
<td>1.23</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Fig. 2—SEM micrographs of (a) OPC at 4,000X magnification, (b) SF at 15,000 X magnification, (c) FA at 1,500 X magnification and (d) S at 1,500 X magnification
react with calcium hydroxide to produce insoluble compounds in the form of metal hydroxides; this mechanism inhibited hydration and decreased the strength of the wastes, especially when the concentration of metal in the solidified waste was more than 0.3% by weight. Additionally, the strength of the solidified waste decreased when the amount of waste increased. For example, the strengths of pastes OPC10SF40S, OPC10SF50S, and OPC10SF60S were 12.4, 2.8 and 1.3 MPa, respectively, at 28 days. The lower strength could also be due to the fact that the very fine particles of the plating sludge supplied a large amount of surface area per unit volume to be coated with cement. The results indicated that the plating sludge can be added in a proportion as high as 60 wt% of the cement blended with 10 wt% for SF and 30% for FA with a 28-day cure to achieve a compressive strength that meets the minimum requirement for disposal in a secure landfill (0.34 MPa).

Porosity and average pore diameter of blended cement pastes

The total porosity, capillary porosity and average pore diameter of the pastes at 7, 28 and 90 days are shown in Table 5. At all ages, the incorporation of SF and FA increased the total porosity of the blended cement pastes in comparison with the OPC paste. The total porosity increased with an increase in the percentages of SF and FA. The increase in total porosity as a result of the utilization of SF and FA was primarily due to the increase in capillary porosity. Note that the compressive strength decreased, whereas the porosity of the blended cement paste increased. The capillary porosity of the cement paste blended with SF decreased in comparison with FA at all replacement levels.

The relationship between the pore diameter and the incremental pore volume of the blended cement paste at 28 days is shown in Fig. 3. The critical pores sizes of the OPC100, OPC10SF and OPC30FA pastes were 52.1 nm, 60.5 nm and 63.2 nm, respectively, and the
pores were distributed as large capillary pores. The values for the blended pastes were higher than the values for the OPC100 paste, which suggests that the greater fineness of OPC was more effective in reducing the pore diameter of the paste. Similar results have also been reported in other studies\textsuperscript{16-18}.

The relationship between the pore diameter and the incremental pore volume of the solidified wastes using OPC, SF and FA as binders at 28 days is shown in Fig. 4. The critical pore sizes of OPC10SF40S, OPC10SF50S and OPC10SF60S were 112.7, 123.4 and 142.2 nm, respectively. Additionally, the critical pore sizes of OPC30FA40S, OPC30FA50S and OPC30FA60S were 115.4, 128.6 and 147.1 nm, respectively, and these pores were distributed as large capillary pores. These results suggest that the higher the amount of plating used in the sludge, the greater the pore diameter of the paste increased.

Fracture surface analysis by scanning electron microscope (SEM)

Fig. 5 shows the fractured surfaces of the solidified plating wastes at 28 days, as determined by SEM. The paste with more plating sludge showed a lower density because the proportion of binder in the mixture decreased. Because heavy metals inhibit hydration, the cement reaction was not completed, and some heavy metals did not react\textsuperscript{19}. The replacement of Portland cement by SF and FA resulted in a higher density than for Portland cement alone. As a result, the solidified waste was more porous, and the compressive strength of the solidified waste decreased significantly in comparison with the waste without plating sludge in the mixture.

Leaching analysis

Table 6 shows the leachate pH values and the metal concentration in the TCLP leachates. The pH of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
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<tbody>
<tr>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>OPC100</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC40S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC50S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC60S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC10SF40S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC10SF50S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC10SF60S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC30FA40S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC30FA50S</td>
<td>2.88</td>
</tr>
<tr>
<td>OPC30FA60S</td>
<td>2.88</td>
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</table>
solution extracted from the solidified waste is increased from the initial pH. For example, for solidified waste at 28 days, the pH increased from an initial pH of 2.8 to 6.6, 7.5 and 9.5 for OPC40S, OPC10SF40S and OPC30FA40S, respectively. The pH values increased because calcium hydroxide in the pores dissolved into the acid. Fig. 6 shows the metal concentrations in TCLP leachates, the results showed that the concentration of Cr in the leachate for all solidified waste samples was lower than the limit.
specified by the standards of the US EPA (< 5.0 mg/L). There are no regulatory standards for Ni, Cu and Zn because these three metals are not classified as hazardous waste by the US EPA. The results showed that when the sample age increased, the effectiveness of the samples at reducing the leachability also increased. For example, OPC20NZ40S contained 46.63 mg/L of Ni at 7 days, which decreased to only 10.61 mg/L at 90 days. Using SF as a binder effectively reduced leaching more than using FA. For OPC10SF60S and OPC30FA60S, the reductions in Ni at 28 days were 77.2% and 74.4%, respectively. Additionally, the metal concentrations in the TCLP leachates that were extracted from the cement-based solidified plating wastes were...
much lower than in the leachates extracted from the plating sludge. At 28 days, the solidified wastes with SF and FA acting as binders were 80% effective at reducing leachability, whereas the plating sludge showed an effectiveness of less than 50%. SF and FA are more effective because they primarily consist of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$. Thus, SF and FA were more effective than OPC alone for reducing the leachability$^{20,21}$. These results indicated that during the ion-exchange process, the metal ions had to move through the pores of SF, FA and through channels of the lattice, and they had to replace exchangeable cations. The diffusion was fast through the pores, but was retarded when the ions moved through the smaller diameter channels. In this case, the metal ions uptake could mainly be attributed to the ion-exchange reactions in the microporous minerals of SF and FA$^{23}$.

**Conclusions**

Based on the results of this study, the following conclusions can be drawn:

The solidified waste with higher compressive strength to reduce the leaching of heavy metals resulted in a better outcome than the solidified waste with lower compressive strength.

The use of silica fume and fly ash to partially replace Portland cement as a solidification binder produced solidified waste with lower strength. However, it is more effectiveness in terms of leachability than the use of Portland cement alone.

The use of silica fume and fly ash to replace part of Portland cement to reduce the leaching of Ni and Cr was not significantly different.

The use of silica fume to replace part of Portland cement to reduce the leaching of Zn resulted in a better outcome than the use of fly ash with Portland cement.

The application of silica fume and fly ash as a binder with Portland cement to reduce the leaching of heavy metals resulted in a better outcome than using cement alone. The use of silica fume and fly ash with Portland cement as a binder to solidify waste sludge is appropriate as the leachability was reduced and the compressive strength complied with the US EPA standard.

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