



## Recovery of hazardous semiconductor-industry sludge as a useful resource

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### ABSTRACT

Sludge, a solid waste recovered from wastewater of semiconductor-industries composes of agglomerates of nano-particles like  $\text{SiO}_2$  and  $\text{CaF}_2$ . This sludge deflocculates in acidic and alkaline aqueous solutions into nano-particles smaller than 100 nm. Thus, this sludge is potentially hazardous to water resources when improperly dumped. It can cause considerable air-pollution when fed into rotary-kilns as a raw material for cement production. In this study, dried and pulverized sludge was used to replace 5–20 wt.% Portland cement in cement mortar. The compressive strength of the modified mortar was higher than that of plain cement mortar after curing for 3 days and more. In particular, the strength of mortar with 10 wt.% substitution improved by 25–35% after curing for 7–90 days. TCLP studies reveal no detectable release of heavy metals. Preliminary studies showed that nano-particles deflocculated from the sludge, when cured for up to 3 days retain in the modified mortar their nano-size, which become large-sized hydration compounds that contribute to the final mortar strength. Semiconductor sludge can thus be utilized as a useful resource to replace portion of cement in cement mortar, thereby avoiding their potential hazard on the environment.

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### 1. Introduction

Chemical mechanical polishing (CMP) is a conventionally adopted process in integrated-circuit (IC) factories during the process called “planarization” on silicon wafers. Because planarization consumes considerable amounts of water, large quantities of wastewater and sludge that are potentially dangerous are released into the environment. Numerous studies have attempted to develop treatment processes for this sludge and wastewater, specifically to recover water from wastewater. In 2006, the amount of such wastewater generated daily was 26,000 ton in Taiwan, a country known for its IC industries. In an IC factory, the etching process, which uses hydrofluoric acid, usually follows CMP and is used to remove silicon oxide and other unwanted debris from the wafer. The waste generated by CMP is then neutralized with sodium hydroxide (NaOH); water-soluble calcium chloride ( $\text{CaCl}_2$ ) is then added to precipitate fluorine ion into insoluble calcium fluoride ( $\text{CaF}_2$ ). Thus, CMP waste contains numerous chemicals. Such waste is called wet waste in the semiconductor-industry, and sometimes simply CMP waste. The solid waste recovered after water removal is called semiconductor sludge, or simply, sludge. Since the sludge

produced is approximately 2.53 kg/ton of wastewater, the recovered sludge per day is 65.8 ton, or corresponding to 24,000 ton/year which is a substantial amount.

There have been a lot of researches on the recovery of wastewater a few examples are briefly cited here. To improve treatment of semiconductor wastewater, Hu et al. added surfactants cetyltrimethylammonium bromide (CTAB) and sodium dodecyl-sulfate (SDS), which effectively reduced suspended  $\text{SiO}_2$  particles and removed all CTAB [1]. Lin and Yang treated CMP wastewater using chemical coagulation and reverse osmosis [2]. They removed 99% of suspended oxide particles and reduced chemical oxygen demand (COD) of the wastewater from 500 to  $\leq 100$  mg/L; thus, this treated wastewater was reusable. Lai et al. employed electro-coagulation to remove nano-particles in CMP wastewater [3,4]. They successfully removed nano-metallic oxides, such as copper oxide, and organic pollutants. Den and Huang treated CMP wastewater using an electro-coagulation process by continuously passing the wastewater through vertical-flow channels and removed 95% of suspended solids [5]. As Den and Huang did not use sedimentation additives such as poly-aluminum chloride, the amount of sludge generated was reduced.

However, disposal or reuse of semiconductor sludge after dewatering has not been investigated to the acknowledgement of current authors. The annually 24,000 ton of unused sludge in Taiwan, as calculated above, is said to be ‘safely dumped’ as an industrial garbage. As far as the authors acknowledge, quite a portion of the sludge is

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used as a raw material in cement production. In such a case, the sludge is fed into a high-temperature rotary kiln and co-fired with other raw materials.

Semiconductor sludge contains both organic and inorganic material. The organic material includes oxidizing agents, additives, and dispersing agents, mainly of proprietary compositions made of C, H, O, N, S and others. The inorganic material consists of nano-particles, principally  $\text{SiO}_2$ ,  $\text{CaF}_2$ , and others which are typically 20–300 nm in size, depending on the vendors.

Nano-particles can cause lung diseases when inhaled, and can penetrate the skin and eventually have adverse effects on human organs. Furthermore, the human body, which typically lacks immunity to new substances, is vulnerable to toxicity of nano-particle. Yacobi et al. conducted experiments using 20, 100, 120 nm nano-particles to test the barrier properties of rat alveolar epithelial cells [6]. Their experimental results indicated that exposure to different nano-particles causes various degrees of damage that depend on specific nano-particle compositions, shape and/or surface charge. According to Lin et al., *in-vitro* experiments revealed that exposure to  $\text{SiO}_2$  nano-particles (sized 15 and 46 nm) resulted in a dose-dependent cytotoxicity in cultural human bronchoalveolar carcinoma-derived cells that is closely correlated to increased oxidative stress [7]. Experiments by Chen and Mikecz showed that uptake of silica ( $\text{SiO}_2$ ) nano-particles (40–70 nm) by cell nuclei induces aberrant protein aggregates that inhibit replication, transcription and cell proliferation while not significantly altering cell viability [8]. Moore showed that nano-materials released in an aquatic environment can harm cells and tissues of aquatic animals via uptake through cell endocytotic routes, and further damage human health, and cause ecological and possible food chain risks for humans [9]. Moore concluded that caution is required when individually evaluating the effects of new nano-materials on health and the environment. Improper disposal of huge amounts of nano-particles such as 24,000 ton of sludge can be disastrous. When dumping sites are close to reservoirs or underground water sources, these nano-particles can pollute drinking water and cause lung and other diseases [6–9]. Even worse, if this sludge is utilized as raw material in rotary kilns for cement production, the nano-particles may be released into air due to the strong forced convection of burning hot gases. They will remain in the atmosphere for a very long time, counting by years, due to their fineness.

Since human health is vulnerable to nano-particles in sludge, the disposal of the potentially hazardous sludge by immobilizing them as a useful resource warrants careful research. This is the purpose of this study.

## 2. Materials, methods and procedures

### 2.1. Materials

#### 2.1.1. Semiconductor sludge

Sludge cake from wet waste was obtained from an IC factory located at a science-based technology park in Taichung, central Taiwan. After drying at 100 °C for 24 h until complete dry (constant weight), the sludge was ground into a fine powder and passed through a No. 200 sieve. This ‘sludge powder’ is ivory white in color, has an apparent density  $2.4 \pm 0.1 \text{ g/cm}^3$ , and a specific area  $1.06 \text{ m}^2/\text{g}$ .

#### 2.1.2. Cement

The cement used was ordinary Type I Portland cement (OPC) obtained from the Taiwan Cement Company. The OPC has an apparent density  $3.11 \text{ g/cm}^3$ , and a specific area  $0.352 \text{ m}^2/\text{g}$ .

#### 2.1.3. Sand

Ottawa-type sand, meeting the ASTM C778 specification, with an apparent density  $2.63 \text{ g/cm}^3$ , was used.

### 2.2. Methods

#### 2.2.1. Chemical analysis of sludge powder

The chemical composition of sludge powder was analyzed with an inductively coupled plasma (ICP) spectroscopy (Jobin Yvon, Ultima 2000, France).

#### 2.2.2. Deflocculating tests of sludge powder

Sludge powder (1.0 g) was mixed and dispersed in 100 cc distilled water. A strong acidic HCl or alkaline NaOH aqueous solution was added drop-wise to adjust pH values, which were 1–14. The solution was stirred with a magnetic stirrer for 30 min, and then fed into a dynamic laser scattering particle-size analyzer (Protein Solutions Dynapro, Dynamics V6, USA) to determine particle size.

#### 2.2.3. SEM/EDS analyses

Sludge cake and sludge-substituted cement mortar samples were vacuum-dried at 80 °C. After being coated with platinum, these mortar samples were analyzed using a field-emission scanning electron microscope (FE-SEM) (JEOL, JSM-6700F, Japan). Elemental analysis was conducted using an energy dispersive X-ray spectrometer (EDS) (INCA<sub>X</sub>-sight) attached to the FE-SEM.

#### 2.2.4. X-ray diffraction (XRD)

Phases of sludge powder samples were analyzed with X-ray diffractometry (Rigaku, D/Max-2200, Japan) using  $\text{Cu K}\alpha_1$ ,  $2\theta$ : 10–80°, at a scanning speed of  $0.05^\circ/\text{s}$ .

#### 2.2.5. Toxicity characteristics leaching procedure (TCLP) analysis

Toxicity tests of CMP sludge powder and cured cement mortar were conducted on pulverized samples using TCLP leaching tests according to the specification SW 846-1311 “Heavy metal leachability (TCLP)”. The extraction procedure requires a preliminary evaluation of pH characteristic of the sample to determine the proper extraction fluid necessary for the experiment. After testing, extraction fluid at  $\text{pH } 2.88 \pm 0.05$  was selected for the TCLP analysis. This fluid was prepared by adding 5.7 mL of acid to 500 mL of double distilled water, diluted to a volume of 1 L. A 25 g sample was placed in a 1 L Erlenmeyer flask, and 500 mL of extraction fluid was added to each Erlenmeyer flask. The samples were then agitated for 18 h with an electric vibrator. The slurry was filtered using 6–8  $\mu\text{m}$  pore-sized Millipore filter paper. The leachates were preserved in 2%  $\text{HNO}_3$  [10]. Then it was subjected to analysis using inductively-coupled-plasma atomic-emission-spectroscopy (ICP-AES) to determine the concentration of heavy metals under concerns. Governmental regulation on the tolerable upper limit of heavy metals was used as a reference.

#### 2.2.6. Setting time tests

The setting time test was according to ASTM C187 to obtain the required water quantity for the cement. Then the Vicat needle method was used for the cement paste setting time test according to ASTM C191 to obtain the initial and final setting time of the ordinary Portland cement paste and CMP cement paste.

#### 2.2.7. Compressive strength tests of cured cement mortar

Compressive strength tests of cured cement mortar were done according to the ASTM C109 standard.

**Table 1**

Constituent weights of nine cement mortar test-pieces, including the ordinary Portland cement (OPC), and those with 5–20 wt.% cement substituted by sludge powder, named CMP (*I*) wherein *I* is the wt.% of substituting sludge powder.

Sample designation	OPC	CMP (5%)	CMP (10%)	CMP (15%)	CMP (20%)
wt.% cement substituted	0%	5%	10%	15%	20%
Cement (g)	740	703	666	629	592
Sand (g)	2035	2035	2035	2035	2035
CMP sludge powder (g)	0	37	74	111	148
Water (g)	359	359	359	359	359

### 2.3. Preparation of test pieces of cement mortar and their curing processes

Test pieces of cement mortar were prepared according to Taiwan's Material Testing Standard CNS1010 – “Test method for compressive strength of hydraulic cement mortar.” The test pieces were 50 mm × 50 mm × 50 mm in size. The sand-to-cement ratio was 2.75, and the water-to-cement ratio was 0.485. The cement mortar without sludge powder was taken as a reference. Sludge powder was used to partially replace cement in the cement mortar at replacement weight ratios 5%, 10%, 15% and 20%, respectively. Table 1 shows the constituents of test pieces.

All test pieces were cast in the same sized molds and kept in an isothermal (23 °C), iso-humidity (95% relative humidity) chamber for 1 day. Test pieces were then taken out of the mold and cured in an isothermal water chamber with an alkaline solution containing saturated Ca(OH)<sub>2</sub> and maintained at 23.0 ± 1.7 °C for a predetermined time. The curing periods were 1, 3, 7, 14, 28, 60 and 90 days, respectively. Three test pieces were harvested after each curing period for compressive strength testing.

## 3. Results and discussion

### 3.1. Chemical analysis of the sludge from wet waste

The chemical composition of dried sludge powder was analyzed by ICP spectroscopy. The major elements detected were, in weight percent anion species, Si 50.64, Ca 44.66, Al 0.5, Na 0.34, K 0.23, Fe 0.23, Mg 0.17, W 0.17 and Sr 0.03.

### 3.2. Morphology and phases of sludge powder from wet waste

Sludge cake was ground into powder and passed through a No. 200 mesh and analyzed by FE-SEM. The EDS attached to the SEM was used to determine the particle components. Fig. 1(a) presents a typical SEM micrograph of sludge powder, and Table 2

**Table 2**

EDS analyzed composition (wt. %) on the area identified as 'Spectrum 1'.

	1st run	2nd run	3rd run
O	46.97%	45.97%	44.22%
F	16.75%	20.29%	15.12%
Al	2.88%	1.83%	2.64%
Si	22.73%	18.03%	23.86%
S	0.08%	1.06%	1.15%
Ca	10.59%	12.82%	13.01%

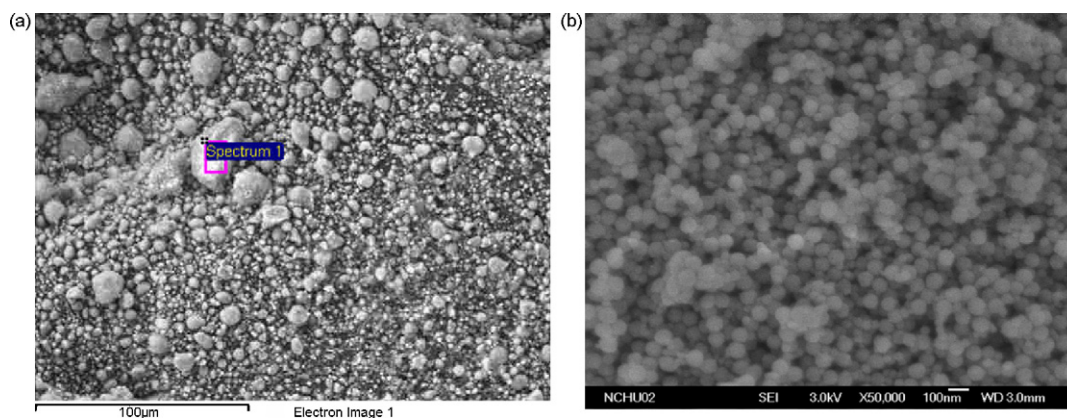
shows the corresponding EDS analysis results. Particle size was 1–50 μm (Fig. 1(a)). Most particles in powder samples were <10 μm. A close-up view of a central large particle (Fig. 1(a)) is composed of nano-particles 30–80 nm in size (Fig. 1(b)). The large 1–50 μm particles (Fig. 1(a)) are in fact agglomerates of nano-particles ('Spectrum 1' in Fig. 1(a)). The composition of the above nanoparticle-agglomerates shown in Table 2 correspond well the ICP analyzed one. Fig. 2 shows typical EDS spectra of nanoparticle-agglomerates.

Fig. 3 shows a typical X-ray diffraction pattern of the sludge powder. The identified peaks were all calcium fluorite, as indicated with arrows (Fig. 3). The lack of silica peaks, even though EDS results identified a large amount of Si in sludge powder, denotes that it is amorphous, which is in fact seen in the XRD pattern as a broadened scattering in the 2θ region 15–30°. Thus, the phases of the sludge are principally nano-crystalline calcium fluorite and amorphous silica nano-particles. Some alumina, alkaline-earth oxides may have been present, as seen from EDS results, however, their amounts were below the X-ray diffraction detection limit.

Particle size (*D*) of calcium fluorite was evaluated using the peak broadening method with the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray source used (1.5406 Å), β is the full-width at half maximum (FWHM), *k* is a constant of 0.94–1



**Fig. 1.** An SEM micrograph of sludge powder with the area of EDS analysis indicated (a), and the close-up view of a large particle in the middle portion of the left micrograph (b).

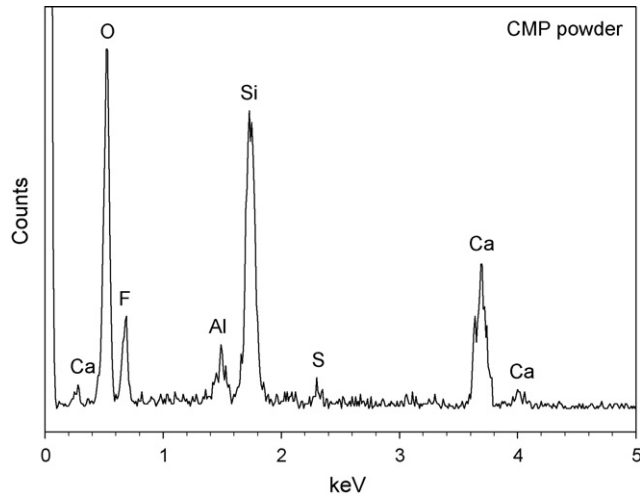


Fig. 2. Typical EDS spectra of sludge powder.

depending on particle residual stress, and  $\theta$  is the diffraction angle. Here,  $k=1$  as most particles are generally stress-free because they were precipitated from an aqueous solution. With the diffraction peak (1 1 1), calculated particle size is 15 nm, which is even smaller than that observed by SEM, namely 30–80 nm. This experimental result indicates that even the nano-particles observable in SEM are in fact aggregates of very small nano-particles, roughly 15 nm in size on average.

### 3.3. Deflocculating tests of sludge powder

Fig. 4 presents deflocculation test results. Both strong acidic and alkaline solutions can deflocculate the agglomerated particles, which were seen to be 1–50  $\mu\text{m}$  as in Fig. 1. The detected particle size after deflocculation is smaller than 100 nm when pH was <3 and >13.5.

Nano-particles in the sludge once deflocculated and then highly diluted with water – such that no further agglomeration occurs – can contaminate water resources when dumped irresponsibly near water reservoirs or underground water. If sludge powder is fed into a rotary kiln as a raw material for cement, nano-particles can be released into the atmosphere due to the very strong

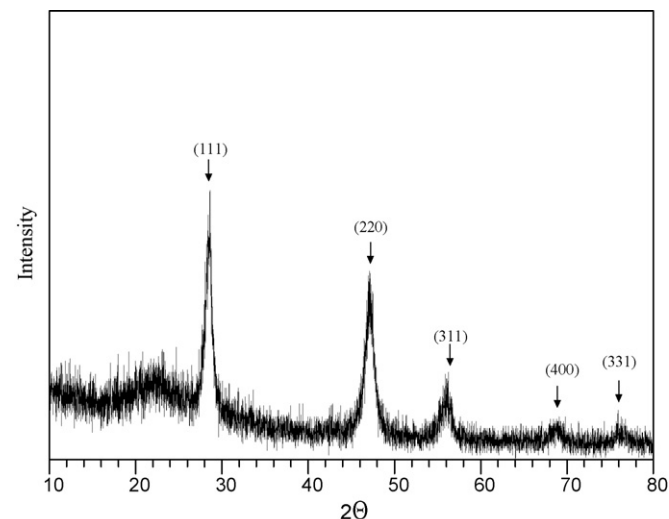


Fig. 3. A typical X-ray diffraction pattern of sludge powder.

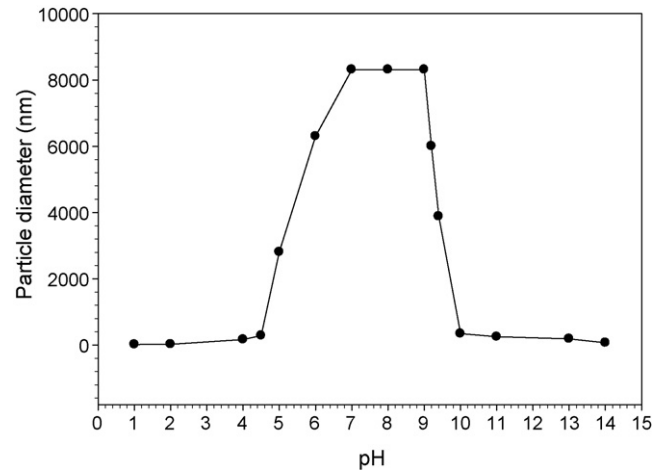


Fig. 4. Deflocculating test results showing the particles are deflocculated both in acidic and alkaline solutions

forced convective burning gas-stream, resulting in atmospheric pollution.

In both cases, the nano-particles are extremely hazardous to human health as being delineated in the Introduction [6–9].

### 3.4. Hydraulicity and setting time

Hydraulicity of the sludge powder was tested by feeding into steel molds, 5 cm  $\times$  5 cm  $\times$  5 cm in size, the watered cement and sludge powder, respectively, and cured in water for 7 days. After de-molding the test pieces, cement blocks showed high strength while the sludge blocks broken into small pieces which became loose powder upon pressing. This depicts that the sludge powder itself is not hydraulic and will not hydrate with water.

Setting time of the OPC cement and the modified pastes (without sand) were studied as shown in Table 3. It is clear that setting time becomes shorter with increasing replacement amount of sludge, specifically the initial setting. The CMP (10%), CMP (15%) and CMP (20%) show an initial setting time 94%, 88% and 76%, respectively, that of OPC paste. While the maximum replacement amount of sludge was 20 wt.%, the final setting time is slightly decreased to 91% that of OPC paste.

The reason why the initial setting time is decreasing with the replacement amount of sludge is simply because that the more the replaced sludge, the larger is the amount of nano-particles after deflocculation in the highly alkaline mortar environment during hydration occurred. The nano-particles have much higher surface area which tends to absorb much more water at beginning. Thus, the initial setting time is decreased. While as hydration goes on nano-particles start to participate in the hydration reaction of cement by giving up the absorbed water, so that the final setting time is less affected.

Table 3  
The setting time of OPC paste and CMP paste.

Samples	Setting time (h:min)			
	Initial time		Final time	
OPC	2:50	(100%)	3:55	(100%)
CMP (5%)	2:50	(100%)	3:50	(98%)
CMP (10%)	2:40	(94%)	3:50	(98%)
CMP (15%)	2:30	(88%)	3:45	(96%)
CMP (20%)	2:10	(76%)	3:35	(91%)

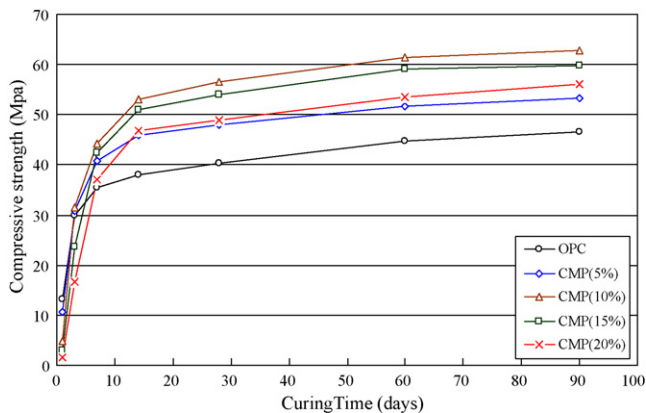


Fig. 5. Compressive strength versus curing time (in days) of the cement mortars.

### 3.5. Compressive strength tests

Fig. 5 and Table 4 present compressive strength test results. Data shown were the average for three test pieces. The sludge-substituted mortar had a 3 day strength of 55–105% of that of the reference OPC mortar (100%); as the amount of semiconductor sludge used increased, strength decreased. However, the strength after curing for  $\geq 7$  days was higher than that of the reference mortar. To quantitatively describe the strengthening effect, the strength of the mortar cured for 7, 28, 60 and 90 days was 104–125%, 119–140%, 116–137%, 114–135%, respectively, that of the reference mortar. These findings are significant; the maximum increase in compressive strength was 25–35% for 10 wt.% semiconductor sludge replacing cement in mortar cured for 7–90 days.

The increase in compressive strength is similar to that measured by Li et al., who studied the effect of mixing cement with nano-SiO<sub>2</sub> particles (diameter  $15 \pm 5$  nm, at a replacement weight percentage of 3–10%) [11,12]. They demonstrated that the compressive strength of modified cement mortar was 5.7–26% higher than that of OPC mortar after curing [11,12]. Jo et al. investigated the characteristics of cement mortar modified with SiO<sub>2</sub> nano-particles [13]. Their experimental results indicated that the compressive strength of modified mortar was higher than that of the control cement mortars. Based on these experimental results, nano-SiO<sub>2</sub> behaves as filler and an activator that promotes hydration and thereby improves the microstructure of cured mortar [11–13]. The nano-SiO<sub>2</sub> particles can absorb hydrated Ca(OH)<sub>2</sub> crystals, reducing their size and amount, thus increasing the density of binding in the paste matrix [14]. Furthermore, Pozzolanic reaction between silica fume and Ca(OH)<sub>2</sub> crystals was found to occur after a hydra-

tion period of 3-day [15–17]. This experimental finding agrees well with our experimental results. However, the reasons for the increase in strength in sludge-modified cement mortar remain unclear as sludge compositions differ significantly from silica fume. The strength of sludge-modified cement mortar after curing for 1 day was significantly lower than that of the reference mortar. The reasons for this difference are unclear. Extensive studies have analyzed these phenomena to develop remedy strategies.

It is interesting to note that the 10 wt.% sludge replaced mortar has the highest 14 days strength. The reason is attributed to the fact that CMP sludge itself is not hydraulic (see Section 3.4). The addition of sludge into mortar will intrinsically weaken the mortar in this sense. While however the nano-particles inside triggers Pozzolanic reaction at the early curing stage which helps to increase the strength, as analogous to the study of nano-SiO<sub>2</sub> modified cement and mortars as being depicted in earlier literature [11–17]. The final strength is a tradeoff between the two effects. The optimal addition amount occurs at 10% sludge by this experiment. However, the difference is small (the 14 days strength-increment for the CMP (10%), CMP (15%) and CMP (20%) is 139%, 134% and 123%, respectively). The 'deteriorating effect' of a substantial amount of non-hydraulic sludge plays more and more important role as the replacement of cement becomes more and more amount.

### 3.6. SEM microstructure of cured cement mortars

The cement mortar with 20 wt.% semiconductor sludge was examined by FE-SEM after being cured for different periods. Fig. 6(a)–(d) present typical micrographs of sludge-modified cement mortar. Nano-particles appear clearly in the sample cured for 1 day (Fig. 6(a)). In Fig. 6(b), cotton-shaped hydration compounds are visible. Since wet cement mortar is highly alkaline with a pH >13, sludge powder will be deflocculated into very small nano-particles when preparing the mortar mixes. In the sample cured for 3 days, the hydration compounds are needle- and cotton-shaped; the nano-particles are barely noticeable and difficult to find (Fig. 6(b)). After curing for 7 days, no nano-particles are observable. Rather, hydration compounds became regular and needle-shaped with some branched whiskers (Fig. 6(c)). After curing for 90 days, the structure is typical of hardened cement mortar with a network of hydration compounds (Fig. 6(d)).

Fig. 7 shows SEM micrographs of mortars after curing for 90 days, (a) CMP (0%), (b) CMP (5%), (c) CMP (10%), and (d) CMP (15%). The surface structure depicting the interconnecting hydration products becomes finer with increasing sludge amount while the porosity becomes smaller and smaller. This corresponds very well the increase in compressive strengths. By comparing Fig. 6(d)

Table 4

Compressive strengths of the cement-mortar test specimens cured for the periods shown.

Notation of specimens	Compressive strength (MPa)						
	1 day	3 days	7 days	14 days	28 days	60 days	90 days
OPC	13.2 (100%)	30.0 (100%)	35.5 (100%)	38.1 (100%)	40.4 (100%)	44.8 (100%)	46.6 (100%)
CMP (5%)	10.7 (81%) <sup>a</sup>	30.9 (103%)	40.9 (115%)	45.9 (120%)	48.0 (119%)	51.8 (116%)	53.2 (114%)
CMP (10%)	4.92 (37%)	31.5 (105%)	44.2 (125%)	53.1 (139%)	56.5 (140%)	61.5 (137%)	62.8 (135%)
CMP (15%)	3.09 (23%)	23.6 (79%)	42.4 (119%)	51.1 (134%)	54.0 (134%)	59.1 (132%)	59.7 (128%)
CMP (20%)	1.64 (12%)	16.6 (55%)	37.0 (104%)	46.9 (123%)	49.0 (121%)	53.5 (119%)	56.2 (121%)

<sup>a</sup> The number in bracket denotes percentage versus the value of OPC mortar (100%) as reference.

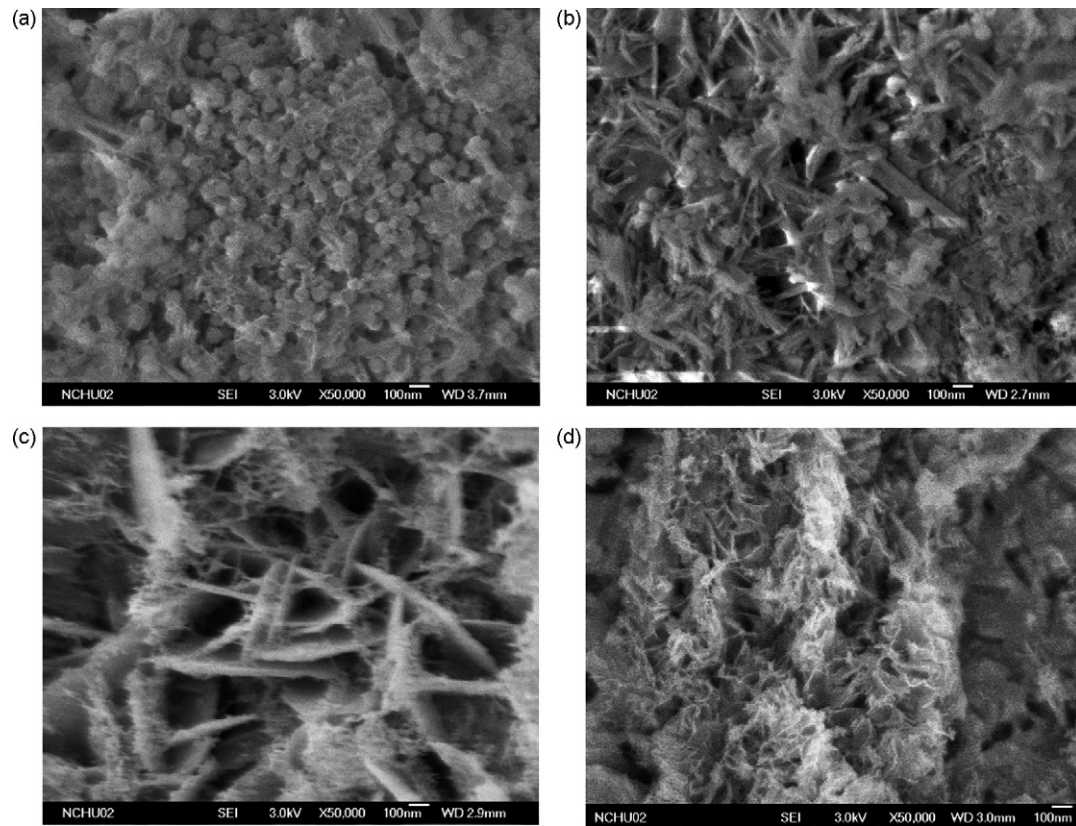


Fig. 6. SEM micrograph of cement mortar with 20 wt.% cement substituted by sludge powder cured for (a) 1 day, (b) 3 days, (c) 7 days and (d) 90 days.

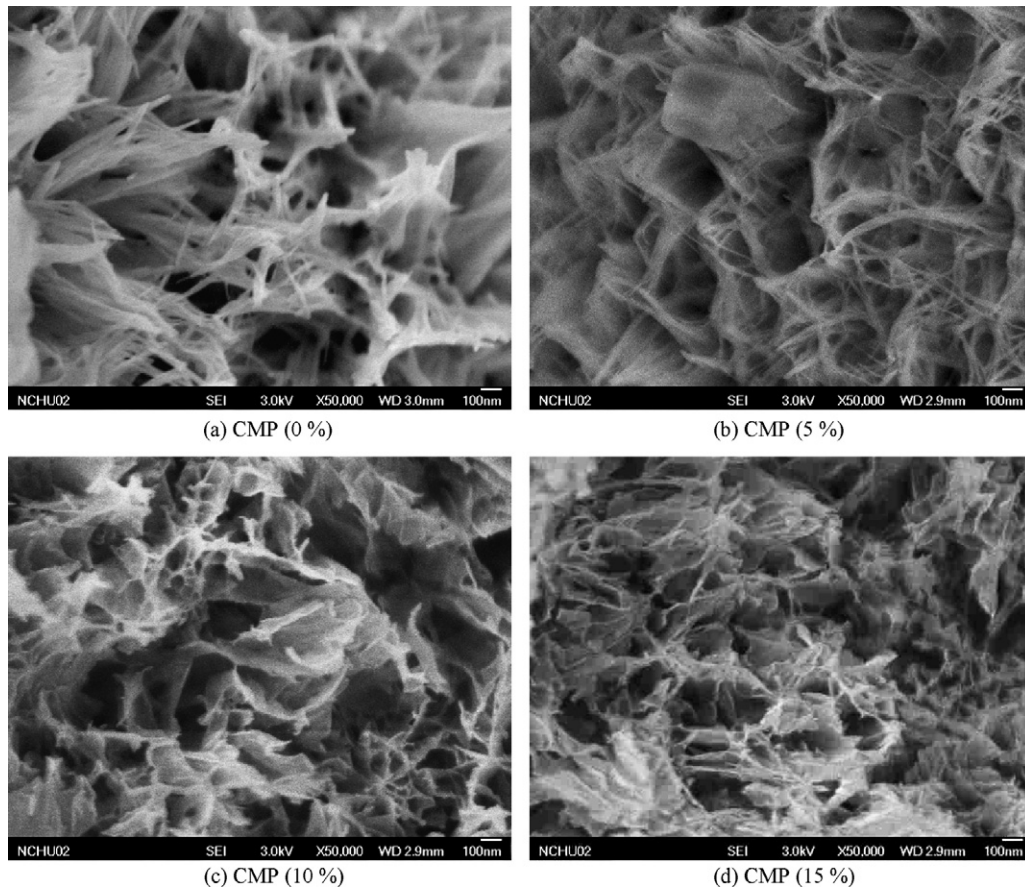


Fig. 7. SEM micrographs showing the structure of mortar after curing for 90 days, (a) CMP (0%), (b) CMP (5%), (c) CMP (10%), and (d) CMP (15%).

**Table 5**  
TCLP leaching results (concentration in mg/L) of CMP sludge and mortars.

Sample	Element symbol						
	Ba	Ni	Cd	Zn	Cu	Pb	Cr
CMP sludge	0.26	0.07	ND	0.98	4.12	0.18	0.09
OPC	0.97	ND	ND	ND	0.09	0.01	ND
CMP (5%)	0.46	ND	ND	ND	0.10	0.01	0.03
CMP (20%)	0.38	ND	ND	ND	0.10	0.01	0.02
Regulatory limits	100.00	–	1.00	–	15.00	5.00	1.00

with Fig. 7(c), the surface morphology is finer and denser (less porosity) in 20% sludge replaced mortar (Fig. 6(d)) than that of 10% sludge replaced one (Fig. 7 (c)), while the strength of the former is lower. This is due to the non-hydraulic nature the more sludge brings about, as explained above.

The disappearance of nano-particles as increasing curing period has two important implications. First, the originally hazardous nano-particles, through the hydration reaction, become part of the hydration products and cannot be released to pollute the environment. Second, the increase in strength occurs with the disappearance of nano-particles, implying that nano-particle-enriched hydration products are the primary cause of strength enhancement. The detailed mechanism remains unknown.

### 3.7. TCLP analysis

Table 5 shows the TCLP test results of sludge powder, OPC cement mortar, and sludge-substituted cement mortar. The leached toxins, particularly heavy metals, are far below regulatory limits, meaning that the use of sludge powder as a cement mortar strengthener is toxicity-free.

Thus, semiconductor sludge is a useful resource to partially replace cement in the mortar. The 10–20 wt.% sludge replaced mortars show compressive strengths 135%–120% that of sludge free ordinary Portland cement mortar when 90 days cured. Alternatively, the sludge can be solidified with cement and disposed of safely. In the latter case, mortar strength is not the major concern, and the amount of cement replacement can far exceed 20 wt.%. In both cases, they are non-toxic and pollution-free.

## 4. Conclusions

In summary, dried and pulverized sludge from wet waste produced by the semiconductor-industry was analyzed. The large apparent aggregates (1–50  $\mu\text{m}$ ) of sludge powder are composed of nano-particles of silica and calcium fluorite, 8–80 nm in size when examine by SEM. The particle size of calcium fluorite ( $\text{CaF}_2$ ) was calculated using the peak-broadening method in X-ray diffraction. There are some other minor oxides and proprietary organic additives. The large agglomerates will be deflocculated into nano-particles smaller than 100 nm in acid solution with a pH <3, as well as in alkaline solution with a pH >13.5. These nano-particles are hazardous to water resources when improperly dumped. Additionally, these nano-particles can become airborne pollutants when fed into rotary kilns as raw material during cement production. In this study, semiconductor sludge was used as a substitute for ordinary Portland cement in cement mortars. At 10 wt.% sludge, the compressive strength of the modified cement mortar becomes 125–135% that of mortar made of ordinary Portland cement after

curing for 7–90 days compared with. The TCLP test results indicate that the leaching of toxic elements is much lower than regulatory limits. The SEM micrographs reveal that nano-particles start disappearing into a hydration product when cured for 3 days. Thus, the hazard associated with nano-particles in the sludge inside cement mortar is minimal. The increase in strength combined with simultaneous disappearance of nano-particles implies possible strengthening mechanisms. This engenders an opportunity for using semiconductor sludge as a resource that strengthens cement mortar. Alternatively, semiconductor sludge can be safely solidified using cement to immobilize the nano-particles and be disposed of safely. In the later case, the amount of sludge substitution for cement can be significantly higher than 20 wt.% as compressive strength is not a concern. However, the inferior early strength is a problem for construction usage. The strengthening mechanisms and ways of overcoming early strength weakening warrant further studies.

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## References

- [1] C.Y. Hu, S.L. Lo, C.M. Li, W.H. Kuan, Treating chemical mechanical polishing (CMP) wastewater by electro-coagulation-flotation process with surfactant, *J. Hazard. Mater.* A120 (2005) 15–20.
- [2] S.H. Lin, C.R. Yang, Chemical and physical treatments of chemical mechanical polishing wastewater from semiconductor fabrication, *J. Hazard. Mater.* B108 (2004) 103–109.
- [3] C.L. Lai, K.S. Lin, Sludge conditioning characteristics of copper chemical mechanical polishing wastewaters treated by electrocoagulation, *J. Hazard. Mater.* B136 (2006) 183–187.
- [4] C.L. Lai, S.H. Lin, Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics, *Chemosphere* 54 (2004) 235–242.
- [5] W. Den, C. Huang, Electrocoagulation for removal of silica nano-particles from chemical-mechanical-planarization wastewater, *Colloid. Surf. A* 254 (2005) 81–89.
- [6] N.R. Yacobi, H.C. Phuleria, L. Demajo, C.H. Liang, C.A. Peng, C. Sioutas, Z. Borok, K.J. Kim, E.D. Crandall, Nanoparticle effects on rat alveolar epithelial cell monolayer barrier properties, *Toxicol. In Vitro* 21 (2007) 1373–1381.
- [7] W.S. Lin, Y.W. Hung, X.D. Zhou, Y.F. Ma, In vitro toxicity of silica nanoparticles in human lung cancer cells, *Toxicol. Appl. Pharmacol.* 217 (2006) 252–259.
- [8] M. Chen, A.V. Mikecz, Formation of nucleoplasmic protein aggregates impairs nuclear function in response to  $\text{SiO}_2$  nano-particles, *Exp. Cell. Res.* 305 (2005) 51–62.
- [9] M.N. Moore, Do nanoparticles present ecotoxicological risks for the health of the aquatic environment, *Environ. Int.* 32 (2006) 967–976.
- [10] K.L. Lin, C.T. Chang, Leaching characteristics of slag from the melting treatment of municipal solid waste incinerator ash, *J. Hazard. Mater.* B135 (2006) 296–302.
- [11] H. Li, H.G. Xiao, J. Yuan, J.P. Ou, Microstructure of cement mortar with nano-particles, *Composites Part B* 35 (2004) 185–189.
- [12] H. Li, H.G. Xiao, J.P. Ou, A study on mechanical and pressure-sensitive properties of cement mortar with nanophase materials, *Cem. Concr. Res.* 34 (2004) 435–438.
- [13] B.W. Jo, C.H. Kim, G.H. Tae, J.B. Park, Characteristics of cement mortar with nano- $\text{SiO}_2$  particles, *Constr. Build. Mater.* 21 (2007) 1351–1355.
- [14] T. Ji, Preliminary study on the water permeability and microstructure of concrete incorporating nano- $\text{SiO}_2$ , *Cem. Concr. Res.* 35 (2005) 1943–1947.
- [15] V.G. Papadakis, Experimental investigation and theoretical modeling of silica fume activity in concrete, *Cem. Concr. Res.* 29 (1999) 79–86.
- [16] J. Zelic, D. Rusic, D. Veza, R. Krstulovic, The role of silica fume in the kinetics and mechanisms during the early stage of cement hydration, *Cem. Concr. Res.* 30 (2000) 1655–1662.
- [17] Q. Ye, Z. Zhang, D. Kong, R. Chen, Influence of nano- $\text{SiO}_2$  addition on properties of hardened cement paste as compared with silica fume, *Constr. Build. Mater.* 21 (2007) 539–545.