

Study on the influence of additives in an industrial calcium fluoride and waterworks sludge co-melting system

Jeng-Shiow Hsiung^a, Yi-Chin Huang^b, Kung-Cheh Li^{b,*}, Shinhao Yang^c

^aProcess Engineering, Taiwan Semiconductor Manufacturing Company, Ltd., Hsinchu 300, Taiwan, ROC

^bGraduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei, Taiwan 106, ROC

^cDepartment of Leisure and Recreation Management, Toko University, Chia Yi County, Taiwan, ROC

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Abstract

This work explores the effect of additives on the pouring temperature in a waterworks and industrial calcium fluoride sludge co-melting system. Two kinds of sludge were mixed in various ratios to find a mixing ratio at which the operating temperature for subsequent additive tests was relatively low. Various proportions of either sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) reagent were added to the mixed-sludge samples to elucidate the consequent changes in pouring temperature.

The experimental results revealed that the pouring temperature was lowest when calcium fluoride was mixed with waterworks sludge in a ratio of 4:6 (w/w). Adding sodium carbonate or potassium carbonate reagent to the mixed-sludge samples further reduced the pouring temperature. Increasing the amount of sodium carbonate did not significantly reduce the pouring temperature beyond that observed when 2% was added, suggesting that 2% was the optimal additional percentage of sodium carbonate. In contrast, the pouring temperature was increased when over 2% potassium carbonate was added to the mixed-sludge samples, revealing that the optimal additional percentage of potassium carbonate was also 2%. These findings indicate that both sodium carbonate and potassium carbonate can be used as additives to increase the energy efficiency of the melting process, but sodium carbonate is more operationally convenient.

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1. Introduction

The water-supply system, which provides clean water to the people of Taiwan, generates very large quantities of waterworks sludge. In Taiwan, the semiconductor industry also generates a great amount of calcium fluoride sludge. Presently, at least 6000 m³ of waterworks sludge cake is produced by water treatment plants and 66 tons of calcium fluoride sludge is generated from semiconductor manufacturing plants monthly. The main approach for treating these two forms of sludge is currently disposal in landfills, but public resistance and the unavailability of landfill sites have made the disposal of sludge a major issue in Taiwan. The best approach is to reduce the quantity of sludge produced during the treatment process or to recover the

sludge, which should be a top priority of any subsequent sludge-management systems.

Of all approaches for reducing the quantity of sludge, sludge melting has attracted substantial attention since the 1990s, for use in recovering sewage sludge (Oku et al., 1990; Ohshima and Masuta, 1991). The benefits of using melting to dispose of sludge are the reduction of waste and the fixation of heavy metals. The basicity index (the weight ratio of CaO/SiO_2) of sewage sludge must be adjusted to one in either sintering or melting, to yield a relatively low pouring temperature (Murakami et al., 1991; Huang et al., 2005a, b). During this process, the operational temperature is estimated by the pouring temperature of sludge and maintained at around 1350–1500 °C in order to decompose the organic matter and melt the inorganic matter. At such high temperatures, over 60% of the cadmium, lead, zinc and copper present in the slag, and 60% of the nickel, chromium and arsenic are associated with fly ash in the

*Corresponding author. Tel.: +886 2 23698112; fax: +886 2 23638173.
E-mail address: kcli@ntu.edu.tw (K.-C. Li).

melting furnace, so air pollution-control equipment must be applied after melting (Takaoka et al., 1997). The melted material is cooled in either water or air, and eventually forms slag. This sludge-derived slag can be used in construction materials, including aggregate and paving. Following post-melting or sintering, the slag can also be formed into blocks and other crystal materials (Bijen, 1996; Endo et al., 1997; Okuno and Takahashi, 1997; Wiebusch and Seyfried, 1997).

Sewage sludge co-melting with industrial waste has been suggested to reduce the problem of industrial waste-related pollution. Sakai et al. (1990) reported that co-melting with sewage sludge made asbestos less hazardous, and Wang et al. (1997) applied the melting process to the treatment of municipal incinerator fly ash.

Although calcium fluoride sludge is a legal general industrial waste, two issues must be considered. First, water saturated with calcium fluoride has a fluoride concentration of 8.1 mg/L, which significantly exceeds the regulatory limit of 0.8 mg/L for the source water of the public water-supply system in Taiwan. Hence, the potential problem of fluoride-related toxicity is increased if source water is contaminated by calcium fluoride sludge. Second, heavy metals may leach and pollute the environment, including water resources and soil. However, the hazardous potential of heavy metals in calcium fluoride sludge is negligible because the amount of heavy metal that leaches from the slag is two or three orders of magnitude lower than that from the original ash (Nishino and Tahara, 1998). The toxicity characteristic leaching procedure (TCLP) results and the long-term concentrations of heavy metals leached from the slag are also far under the regulatory limits when it is used as a fine aggregate in cement mortar (Huang and Li, 2004). Additionally, calcium fluoride is regarded as a flux agent in metallurgy, so the SiO_4 tetrahedral network is depolymerized by replacing the oxide ion with a singly charged fluoride ion. This ion exchange reduces the eutectic temperature of the co-melting sludge and also reduces the hazardous potential of the calcium fluoride sludge.

Moreover, the feasibility of using the melting process to recover calcium fluoride and waterworks sludge for use in construction materials has been investigated. The water- and air-cooled slag obtained from this co-melting system can replace 20% and 40% of fine aggregate in the cement mortar, respectively (Lo et al., 2003; Huang et al., 2005a). Hence, the use of calcium fluoride as a metallurgical flux not only effectively reduces the potential dangers posed by the sludge to the environment and to human health, but also allows advantageous operational temperature reductions.

Various factors affect the operational temperature of the melting process, including the basicity of the sludge (Murakami et al., 1991), ambient gases in the furnace (Huang and Li, 2003) and additives in the sludge (Hsiau, 1992). The eutectic temperature of the sewage sludge and municipal incinerator fly ash co-melting system has been

suggested to be further reduced when borax (sodium borate), soda (sodium carbonate) and lime (calcium carbonate) are added to the system (Hsiau, 1992). These results also indicate that adding more additives can improve sludge-melting.

Alkali oxides are known to modify the tetrahedral structure of SiO_4 , increasing the relative proportion of nonbridging oxygens associated with the glass network, and reducing the melting point of sludge. This work elucidates the relationship between alkali additives and changes in pouring temperature during the melting process. The optimal quantity of additives in relation to the pouring temperature is also considered.

2. Materials and methods

2.1. Preparing sludge

Fig. 1 presents the experimental procedure implemented herein. The gathered calcium fluoride sludge was dried at 105 °C in an oven for 24 h, whereas the waterworks sludge from northern Taiwan was incinerated at 800 °C in a lab-scale incinerator for 8 h. After they had been ground and sieved using a 200 mesh, the two sludge samples were stored at 105 °C in an oven before the experiments were undertaken. The main components of the sludge were determined using an inductivity coupled plasma-atomic emission spectrometer (ICP-AES) with a sensitivity in the mg/L range following acid digestion.

2.2. TCLP test

A TCLP test was conducted to measure the concentration of heavy metals that leached from the sludge. The TCLP was based on the Taiwan Environmental Protection Administration's (EPA) standard method and the National Institute of Environmental Analysis (NIEA) R201.13C (ROC-EPA, 2003). The liquid-to-solid weight ratio was 20:1 and the extraction solution was acetic acid (pH = 2.9). An inductivity coupled plasma-mass spectrometer (ICP-MS) was used to analyze the metal with a sensitivity in the $\mu\text{g/L}$ range.

2.3. Triangular pyramid test

A triangular pyramid test was used to determine the melting and pouring temperatures of the sludge samples in a tube furnace (Carbolite Inc., England). The mixed-sludge samples were molded into the triangular pyramid pattern before they were placed in a furnace. A total of eight mixed-sludge samples on four sample tiles were employed for each test run. The highest temperature set was 1600 °C; the temperature increase was set to 5 °C/min and the ambient gas was air. A high-resolution video system with an infrared camera recorded the shapes of the samples as they were heated to measure the pouring temperatures; the increase in temperature was also recorded. Following

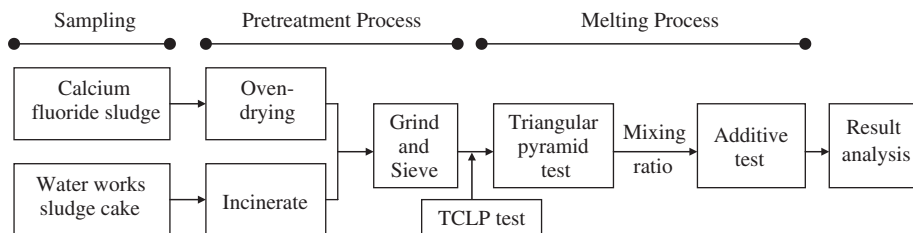


Fig. 1. The experimental procedure of this study.

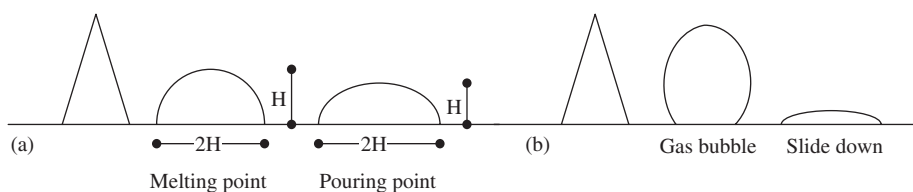


Fig. 2. The shape changes of the triangular pyramid sample at different states: (a) at normal state, the melting and pouring temperatures were estimated by the height to width ratio of the sample; and (b) the gas produced by combustible content was bound in the melted material, and the melting and pouring temperatures cannot be estimated at this state.

meltdown, molten samples were cooled in air in the furnace and the tape was then replayed to determine the deformation temperature.

Two alkali compounds were selected for use as additives in this work. The purity of both the sodium carbonate (Na_2CO_3) and the potassium carbonate (K_2CO_3) reagents employed in this test exceeded 99.5%. The additional percentages of either sodium carbonate or potassium carbonate were 1–3%, 5%, 9% and 17% (w/w).

3. Results and discussion

3.1. Characteristics of sludge

The water, ash and combustible contents, and the pH value of the two sludge samples were measured herein. Among these factors, the water content was utilized as a threshold index in the operations, as different melting furnaces require different water contents to avoid damage. For example, a coke bed furnace supports 46% water content whereas a plasma furnace only allows 5–20%. The heat-drying pretreatment process must be undertaken if the feed sludge has a water content that exceeds the threshold value. Similarly, in a lab-scale electric melting furnace, a high water content damages the furnace because the gas pressure is increased. A tube furnace will even crack if the gas pressure exceeds the load capacity of the tube.

Furthermore, the combustible content in the sludge affects the triangular pyramid test. The combustible content is heated in the furnace and decomposes into gas, some of which escapes, and some of which is bound, forming a bubble because of the surface tension and viscosity of the melted material (Fig. 2). The melted material does not slide down at its actual melting or pouring temperature. The melting or pouring temperatures are overestimated because the melted material does not

pour until the bubble is broken. Accordingly, either an oven or an incinerator should be used in the pretreatment process to reduce the combustible content of the sludge.

The results listed in Table 1 indicate that the calcium fluoride sludge had high water and low combustible contents, revealing that the incineration process can be replaced by oven-drying to save energy. Therefore, the two sludge samples required different pre-treatment processes (Fig. 1). Additionally, the calcium fluoride and waterworks sludge both were weak alkaline pH at which the heavy metals were stable.

The heavy metal leaching concentrations were measured to determine the environmental suitability of the sludge samples. Table 2 presents the TCLP results of the two sludge samples based on the NIEA R201.12C method (2003). The original heavy metal contents of the calcium fluoride and waterworks sludge were low. Accordingly, the TCLP data were far below the regulatory limits of the Taiwan-EPA.

Component analysis was conducted to estimate the basicity of the two sludge samples. The main constituents (such as CaO , SiO_2 , Al_2O_3 , P_2O_5 , Fe_2O_3 , MgO , Na_2O_3 and K_2O) of the sludge were analyzed using an ICP-AES. The basicities of the calcium fluoride and waterworks sludge were 25.44 and 0.02, respectively, suggesting the effectiveness of mixing the two sludge samples in changing the basicity. The pouring temperatures of the original calcium fluoride and waterworks sludge were 1378 and 1518 °C, respectively.

Table 3 presents the changes in pouring temperature for various mixing ratios of calcium fluoride sludge co-melted with waterworks sludge. The experimental results demonstrate that when the basicity was close to one relatively low pouring temperature was observed. The lowest temperature obtained at any of the 11 mixing ratios was 1193 °C, and the weight ratio of the calcium fluoride to waterworks

Table 1
The characteristics of calcium fluoride sludge and the water works sludge

| | Water contents (%) | Ash contents (%) | Combustible contents (%) | pH |
|-------------------------|--------------------|------------------|--------------------------|------|
| Calcium fluoride sludge | 46.0 | 50.7 | 3.2 | 7.92 |
| Water works sludge | 4.2 | 87.1 | 8.7 | 7.29 |

Table 2
The heavy metals and TCLP leaching results of calcium fluoride sludge and the water works sludge

| Elements | Calcium fluoride sludge | | Water works sludge | | Taiwan's TCLP standards |
|----------|------------------------------|---------------------|------------------------------|---------------------|-------------------------|
| | Heavy metal contents (mg/kg) | TCLP results (mg/L) | Heavy metal contents (mg/kg) | TCLP results (mg/L) | |
| As | 5.89 | 0.005 | 15.11 | 0.003 | 5.0 |
| Cd | ND | ND | 0.13 | ND | 1.0 |
| Cr | 9.34 | 0.151 | 93.72 | ND | 5.0 |
| Cu | ND | ND | 29.44 | ND | 15.0 |
| Hg | 18.60 | ND | ND | 0.001 | 0.2 |
| Mn | 22.10 | 0.781 | 461.00 | 1.823 | — |
| Ni | 7.37 | 2.606 | 43.92 | 0.672 | — |
| Pb | ND | 0.341 | 36.88 | 0.729 | 5.0 |
| Sn | ND | 1.413 | 4.59 | 1.043 | — |
| Zn | 12.20 | 0.724 | 151.62 | 0.151 | — |

—, No regulation in Taiwan; ND = not detected.

Table 3
The pouring temperatures of the mixed-sludge samples in different mixing ratios

| Calcium fluoride sludge mixing ratio | Water works sludge mixing ratio | Basicity (CaO/SiO ₂) (w/w) | Pouring temperature (°C) |
|--------------------------------------|---------------------------------|--|--------------------------|
| 10 | 0 | 25.44 | 1378 |
| 9 | 1 | 7.79 | 1345 |
| 8 | 2 | 4.18 | 1296 |
| 7 | 3 | 2.62 | 1284 |
| 6 | 4 | 1.75 | 1268 |
| 5 | 5 | 1.20 | 1208 |
| 4 | 6 | 0.82 | 1193 |
| 3 | 7 | 0.54 | 1210 |
| 2 | 8 | 0.32 | 1307 |
| 1 | 9 | 0.15 | 1314 |
| 0 | 10 | 0.02 | 1518 |

sludge was 4:6. This eutectic pouring temperature was 185 and 325 °C lower than the values for the original calcium fluoride and the waterworks sludge, respectively. The reason for these results is that the SiO₄ tetrahedral networks were depolymerized by the replacement of the oxide ion with the singly charged fluoride ion (Kirk–Othmer Encyclopedia of Chemical Technology, 2003), which is similar in both size and electronegativity, causing the eutectic temperature to be reduced.

3.2. Effect of additives

The mixed-sludge sample used in the subsequent additive experiment was modified to a weight ratio of 4/6 (calcium

fluoride/waterworks sludge mixture). The original sodium carbonate and potassium carbonate contents in the mixed-sludge sample were 0.7% and 1.0%, respectively. The influence of the additives on the mixed-sludge samples was examined at additive percentages of 1–3%, 5%, 9% and 17% (w/w). Sodium carbonate and potassium carbonate were adopted in this experiment because alkali oxides can form 'alkali channels' in SiO₄ tetrahedra (Greaves, 1984), which are expected to influence the pouring temperature of the mixed-sludge samples.

3.2.1. Addition of sodium carbonate

Fig. 3 depicts the results of adding sodium carbonate. The pouring temperatures of the original mixed-sludge samples were reduced at all percentages of sodium carbonate added. Adding 2% sodium carbonate significantly reduced the pouring temperature from 1193 to 1105 °C. This trend was interrupted when the pouring temperature rose for 2–5% added sodium carbonate. However, the pouring temperature declined again as the amount of sodium carbonate added was increased beyond 5%. As the amount added rose to 17%, the pouring temperature dropped from 1193 to 1100 °C, which was 5 °C lower than that obtained when 2% was added. However, the decreases observed at 2% and 17% did not differ significantly and adding 2% sodium carbonate provided an advantage in terms of economical efficiency via decreasing the operating temperature. Although adding over 17% sodium carbonate might cause a larger decline in the pouring temperature, the cost-effectiveness of the process must also be considered. Therefore, this work shows that sodium carbonate can be used as an additive to increase the

energy efficiency (decreasing the operating temperature) of the melting process, and that 2% is the optimum level of sodium carbonate for a calcium fluoride and waterworks sludge co-melting system.

3.2.2. Addition of potassium carbonate

Fig. 3 also displays the results of adding approximately 1–17% (w/w) potassium carbonate. When 2% potassium carbonate was added to the mixed-sludge sample, the pouring temperature was reduced from 1193 to 1109 °C. However, when over 2% potassium carbonate was added, the pouring temperature began to rise. The pouring temperature was even higher than that of the original mixed-sludge sample when more than 5% potassium carbonate was added. Although increasing the concentration of the modifying oxide (R_2O) increased the relative fraction of the nonbridging oxygens in the SiO_4 tetrahedra, sludge that contains more potassium oxide is markedly more difficult to melt because it is more viscous. These facts indicate that potassium carbonate has a particular acceptable range of addition, in a calcium fluoride and waterworks sludge co-melting system and the optimal proportion is 2%.

Fig. 3 shows that both sodium carbonate and potassium carbonate have the advantage of reducing the pouring temperature of the mixed-sludge sample and increase the energy efficiency by decreasing the operating temperature in the melting process. From the perspective of operational convenience, sodium carbonate was favorable because the pouring temperature still decreased when an excess of 2% sodium carbonate was added to the sludge. Adding potassium carbonate also reduced the pouring temperature of the sludge, but adding more than 2% (2.98% in sludge) increased the pouring temperature. The constituents of the sludge vary with the season and source, so this work claims that both sodium carbonate and potassium carbonate can be used as additives in the melting process,

but sodium carbonate is preferred for reasons of operational convenience.

4. Conclusions

Both calcium fluoride and waterworks sludge are legal general industrial waste products that contain low concentrations of heavy metals and have TCLP values that are far below the allowed limits of the Taiwan-EPA.

The basicities of calcium fluoride and waterworks sludge were 25.44 and 0.02, respectively. At a weight ratio of calcium fluoride to waterworks sludge of 40–60 (a basicity of 0.8), a relatively low eutectic pouring temperature of around 1193 °C was obtained, which is significantly lower than that of either calcium fluoride sludge (1378 °C) or waterworks sludge (1518 °C).

Adding 2% sodium carbonate to the mixed-sludge sample significantly reduced the pouring temperature. The pouring temperature rose in response to the addition of 2–5%, but fell again when more sodium carbonate was added. For its cost-effectiveness and improved energy efficiency, 2% sodium carbonate was judged to be the optimal addition.

Adding 2% potassium carbonate to the mixed-sludge sample reduced the pouring temperature. However, the pouring temperature rose when more than 2% potassium carbonate was added. These results suggested that 2% potassium carbonate was the optimal additional percentage to improve the energy efficiency in a calcium fluoride and waterworks sludge co-melting system.

The eutectic pouring temperature was further reduced to 88 and 84 °C by adding 2% sodium carbonate or potassium carbonate, respectively, to the mixed-sludge samples. This work claims that both substances can be used as additives in the melting process, but sodium carbonate is preferred for reasons of operational convenience.

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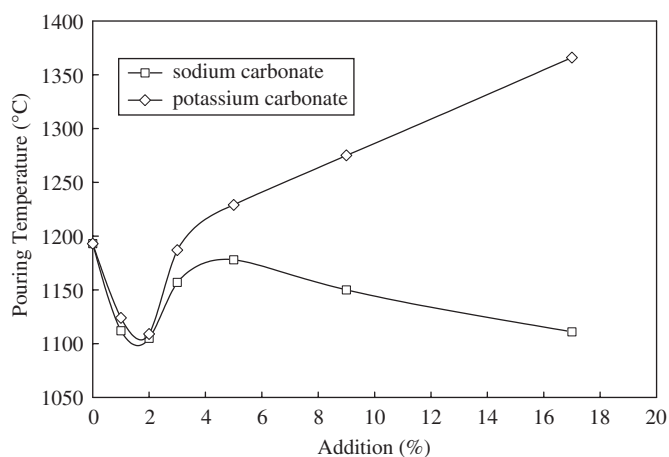


Fig. 3. Additional amounts of sodium carbonate and potassium carbonate versus pouring temperature.

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