SHORT REPORT
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# Characterization of Ash Derived from Combustion of Paper Mill Waste Sludge: Comparison with Municipal Solid Waste Incinerator Ash

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**ABSTRACT:** Fly ash derived from incineration of Malaysian paper mill waste sludge (PMWS) was physically and chemically characterized in order to determine its potential toxicity as well as its application as cement replacement material. The results were compared with results obtained from similar characterization on Malaysian municipal solid waste incineration (MSWI) bottom ash. Principal analyses conducted include particle size distribution, elemental analysis, toxicity characteristic leaching procedure (TCLP) as well as thermogravimetric, x-ray diffractometry and FTIR analyses. TCLP result indicated that both the PMWS and MSWI ashes should not be classified as hazardous wastes in terms of heavy metal leachability, since leachable copper, cadmium, lead and nickel concentrations were detected below the stipulated leachability limits. Both ashes could be reused as cement replacement materials since both contained $SiO_2$ which is one of the main building components in cement and concrete utilizations. Nonetheless, PMWS ash could be more suitable as a cement replacement material as compared to MSWI ash, as the former had significantly smaller particle size distribution and lower organic content.

**KEYWORDS:** Municipal solid waste ash, paper mill waste sludge ash, characterization.

## INTRODUCTION

Incineration of dewatered organic-based waste sludge from activated sludge treatment systems as well as solid wastes has been one of the conventional methods of waste management in which its primary aim is to reduce the volume of the wastes prior to disposal. Fly ash as well as incinerator bottom ash are often the final products of high temperature incineration process. These ashes are often the subject of environmental concerns due to its potential toxicity as well as its disposal dilemma. The large quantity coupled with the potential leachability of high metal concentrations in these ashes has necessitated the study of its chemical, mineralogical and leaching properties[1]. A few studies were conducted to elucidate the compositions and/or potential toxicity of municipal solid waste incinerator (MSWI) bottom ash[1,2], coal combustion fly ash[3-5] and sewage sludge ash[6,7]. A recent study conducted by Saikia et al[7] indicated that all the aforestated sludges showed high amounts of metals such as lead, chromium and cadmium which could leach out into the environment in the presence of an acidic leachant such as acid rain and/or organic acids present in landfills. Instead of disposing the ash into a secure landfill, researchers are looking into reusing the ash as potential cement replacement for production of concrete[4] or as chemical binder for treatment (solidification/stabilization) of industrial waste sludge[2].

Paper mill waste sludge (PMWS) is a by-product of dewatered sludge generated from wastewater treatment plant. In order to reduce its volume prior to proper disposal, PMWS is often co-fired with other high-calorific materials in fluidized bed incinerators[8,9]. The paper mill from where the fly ash was obtained for this study was subjected to scrutiny and remonstration by environmentalists over the potential hazard that the ash may pose to the environment and the public in general. Currently, there is a lack of understanding of the constituents and characteristics of PMWS fly ash as evident by the little, if not non-existent, literatures which delve into this matter. In addition, the authors feel that the PMWS fly ash can be put into useful applications rather than disposed off in a waste lagoon or landfill. As such, there is an urgent need to characterize the ash to provide an initial platform for researchers to evaluate its toxicity and perhaps, look into the possibility of reusing the ash as cement replacement materials for production of concrete or as chemical binder to solidify/stabilize industrial sludge.

The primary objective of this study was to physically and chemically characterise PMWS ash and compare the results with MSWI ash (which has been established as potentially toxic albeit proven useful as cement replacement material)[1,10]. As such, the relative toxicity of the PMWS ash in terms of leachable heavy metals as well as its potential application as cement replacement material were discussed.

## Materials and Methods

### Ash Samples

PMWS fly ash was collected from a 110-ton-per-day fluidized bed incinerator (sand as media) in an industrial brown grade paper mill located at Kuala Langat, Selangor, Malaysia. The ash appeared to be bluish-grey in color and very fine in size. The precursor of the ash was dewatered waste sludge from the paper mill's wastewater treatment plant used as a co-fired material to generate heat energy. It should be noted that large and observable chunks of metals as well as non-combustible materials were manually removed from the PMWS prior to incineration at an approximate temperature of 850 °C.

MSWI ash was collected from a pilot-scale 1-ton-per-hour rotary kiln incinerator located within Universiti Teknologi MARA campus at Shah Alam, Selangor, Malaysia. The municipal solid wastes which consisted of food waste (25% w/w), organic yard (18% w/w), solid paper wastes (18% w/w), film plastics (13% w/w), metals (4% w/w) and other household waste materials were incinerated at an optimum temperature of 800 °C[11]. In contrast to the PMWS ash, the MSWI ash appeared to be dark in color and larger in size. It should be noted that incineration of organic wastes such as MSW actually produces unintentional persistent organic pollutants (POPs) such as dioxin. Detected level of dioxin from this pilot plant was approximately 1.2 ng which was low considering the plant had not been equipped with proper air pollution control equipment. The pilot plant will be properly equipped with air pollution control system in its next phase of development.

### Characterization

The particle size distribution of the as-received ashes was determined via sieving with mechanical shaker with stainless steel mesh screens with aperture sizes of 500, 400, 300, 212 and 125 µm.

Elemental analysis was performed using Flash EA 1112 ThermoFinnigan elemental analyzer. The ashes were weighed on tin foil before inserted into the instrument. The system was purged with helium gas at 140 mL/min prior to flash combustion process. This analysis was conducted in triplicates to provide an average reading. Determination of weight percent organic contents in the ashes was conducted via loss-on-ignition method[12]. The calorific values of the ashes were determined via IKA D79010 calorimeter bomb. Toxicity characteristic leaching procedure (TCLP) Method 1311 from the United States Environmental Protection Agency[13] was conducted in order to determine the potential toxicity of the ashes. The leachant used in the TCLP test was acetic acid at pH 2.88. All pH measurements in this study were determined via SevenMulti Mettler-Toledo pH meter. Heavy metal concentrations in the leachate were measured by Perkin Elmer 3110 Atomic Absorption Spectrometer (AAS).

Thermogravimetric (TG) analysis was conducted via Mettler-Toledo TGA/SDTA851 Thermogravimetric Analyzer. The instrument was set to increase temperature at a rate of 10 °C/min under nitrogen atmosphere with a flow rate of 100 ml/min.

X-ray diffractometry analysis to determine crystalline phases of the ashes was conducted using the Rigaku D/Max 2000 diffractometer operated at 40 kV and 30 mA for the reflection angle ($2\theta$) in the range 3° to 90°.

Fourier-transform infrared (FTIR) analysis was conducted on a Perkin-Elmer SpectrumOne FTIR. The ashes were mixed and ground with KBr at a ratio of 20:80. FTIR spectra were recorded within a range of 500 – 4000 $cm^{-1}$. The equipment was run prior to each measurement to record a background spectrum which was automatically subtracted from the spectrum of each sample.

**Table 1**. Physicochemical characteristics of ash samples.

| | PMWS | MSWI |
|---|---|---|
| **Particle size distribution** | | |
| > 500 µm (%) | 0.08 | 50.82 |
| 400 - 500 µm (%) | 0.21 | 5.68 |
| 300 - 400 µm (%) | 1.57 | 8.96 |
| 212 - 300 µm (%) | 2.38 | 12.48 |
| 125 – 212 µm (%) | 10.71 | 22.05 |
| < 125 µm (%) | 85.05 | 0.01 |
| **Elemental analysis** | | |
| Carbon (% w/w) | 2.08 | 13.85 |
| Hydrogen (% w/w) | 0.47 | 0.89 |
| Nitrogen (% w/w) | Not detected | 0.41 |
| Other (% w/w) | 97.45 | 84.85 |
| **Loss-on-ignition analysis** | | |
| Organic content (% w/w) | 1.83 | 11.24 |
| Calorific value (J/g) | Not detected | 4621 |
| **TCLP analysis** | | |
| Copper (mg/L) | 0.04 | 0.06 |
| Cadmium (mg/L) | Not detected | Not detected |
| Lead (mg/L) | 0.18 | 0.06 |
| Nickel (mg/L) | 0.11 | 0.01 |
| Leachate pH | 10.10 | 6.64 |

## Results and Discussion

### Physicochemical Characteristics

Table 1 shows the physicochemical characteristics of the ash samples. Generally, MSWI ash particles are significantly larger than PMWS ash particles, in which more than 50% of MSWI ash particles are larger than 500 µm while the bulk of PMWS ash particles (> 85%) are smaller than 125 µm. This result is expected due to the nature of fly ash generated from combustion of relatively homogeneous PMWS as well as due to the fact that the incineration of municipal solid wastes to fine ash is rendered a more complex proposition as the wastes contained an amalgamation of materials with different chemical compositions. In view of this, it can be suggested that the PMWS ash is more suitable to be reused as cement replacement since the available surface areas of smaller ash particles are appreciably higher as compared to that of larger ash particles[14]. Higher surface area is favorable for reaction of cementitious materials. Nonetheless, it should be noted that in a study conducted by Chimenos et al[15], it was reported that for bottom ash from an incinerator, heavy metals concentrated on the finest fractions of ash particle distribution which indicated increased toxicity for smaller ash particles. This is further discussed in tandem with the result of leaching test.

It is obvious that the PMWS ash is a product of near complete combustion of dewatered waste sludge whereas MSWI ash still contains relatively higher percentage of organic content. The physicochemical characterization clearly suggests that the PMWS ash is predominantly in mineralized form, as opposed to MSWI ash which has high organic content judging by the latter's absence of calorific value. This result was expected as the municipal solid wastes contained large amount of high organic wastes. High organic content in the MSWI ash suggests possible interference in cementitious reactions if it is reused as cement replacement material as many organic compounds are known to have retarding effect on cement hydration reactions and adversely affect the microstructural, mechanical and leaching properties of the cementitious materials[16]. In contrast, the appreciably lower organic content of the PMWS ash implies that inhibition due to presence of organics may be negligible.

Leaching tests were conducted on the ash to simulate typical leaching conditions caused by presence of organic acids on landfilled wastes. The leachability limits are extracted from the Waste Evaluation Guidelines stipulated by Kualiti Alam Sdn Bhd (the only integrated hazardous wastes treatment center in Malaysia). The leachability limits for cadmium, lead, copper and nickel listed in the guidelines are 1, 5, 100 and 100 mg/L respectively[17]. The result of TCLP test obviously indicates that both PMWS and MSWI ashes are non-toxic in terms of leachable heavy metals as their concentrations are lower than 0.2 mg/L. It is surprising to note that the leached lead and nickel concentrations for MSWI ash are lower than for the PMWS ash since the municipal solid wastes contain relatively significant amounts of solid metals. This observation, however, can be correlated with the size of the ashes as indicated earlier. As the particle size distribution of PMWS ash is significantly smaller than that of MSWI ash, it is highly possible that the former has higher surface area which facilitated the acidic leaching process resulting in higher leached concentrations of lead and nickel. The higher leachate pH recorded for PMWS ash suggests that in its raw form, it is more basic than MSWI ash. This further implies that the advantage that the PMWS ash has over MSWI ash as a cement replacement material since cement itself is a highly basic material which generally yields a pH of more than 10 when dissolved in water.

### TG Analysis

Figure 1 shows the TG analysis profiles for PMWS and MSWI ashes under the flow of $N_2$ gas. Generally, the MSWI ash experiences higher weight loss percentage corresponding to increased temperature as compared to PMWS ash due to the presence of more combustible organic substances in the latter. This observation confirms the physicochemical results in the previous section in which it was postulated that the PMWS experienced near complete combustion of organic substances whereas the MSWI was otherwise. In general, the weight loss of PMWS ash is more gradual than MSWI ash with the exception of the latter's sudden decrease within a temperature range of 600 - 700 °C. The loss of weight from 400 to 650 °C for MSWI ash seems to indicate possible elimination of structural water formed from $OH^-$ ions[18] whereas this is less observable in the case of PMWS ash.

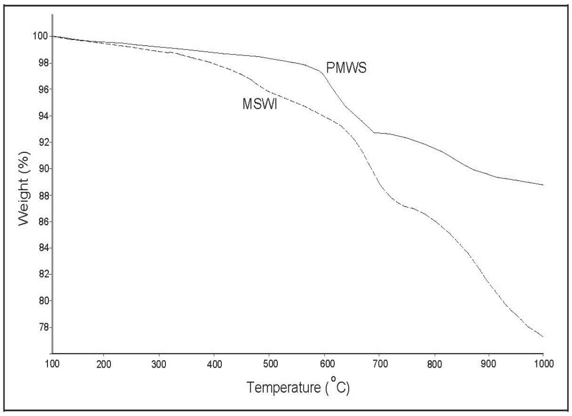


**Fig 1.** TGA profiles for PMWS and MSWI ashes.

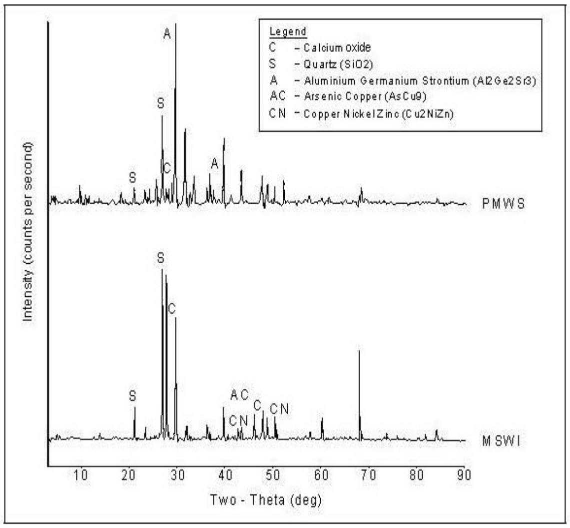


**Fig 2.** XRD patterns of PMWS and MSWI ashes.

## Mineralogy

Figure 2 shows the XRD patterns of PMWS and MSWI ashes, which reveal the qualitative presence of certain crystalline minerals. The diffraction intensities as reflected by corresponding counts per second were used as the indication of changes among the patterns of the ashes. A surprise observation is that metal-based substances of $AsCu_9$ and $Cu_2NiZn$ are detected in the MSWI ash but absent from PMWS ash. $Al_2Ge_2Sr_3$ is a substance detected only in PMWS ash. This observation is surprising as XRD usually detects crystalline compounds in oxidized forms. Nonetheless, it should be noted that the mineralogical compositions of the ashes are very complex in nature due to the complex formation processes such as vaporization, melting, crystallization, vitrification, condensation and precipitation which occur during combustion of wastes[7]. For the benefit of the readers, the authors would like to point out that these substances were detected via the Rigaku D/Max 2000 diffractometer library and they were probably formed during the incineration process and emerged in crystalline forms once the temperature was reduced to ambient temperature. Another possible explanation is that these metal-based substances probably exist in oxidized forms but the XRD only detected the metals as the oxidized substances are probably not listed in the XRD detection library. The detection of heavy metals in MSWI ash is most probably due to the initial presence of metals as well as household wastes such as batteries in the municipal solid wastes prior to incineration. It is interesting to note that even though crystalline phases of metal-based substances of $AsCu_9$ and $Cu_2NiZn$ are only detected in MSWI ash, the leached nickel concentration (TCLP test) at 0.01 mg/L for MSWI ash is lower than that of PMWS ash (0.11 mg/L). This reinforces the postulate that at high incineration temperature of 800 °C, nickel may have fused together with other metals to form a relatively stable crystalline form which is capable of resisting leaching. $SiO_2$ is detected at prominent peaks of 2¸ of 21.0° and 26.5° for both MSWI and PMWS ashes while calcium oxide is detected at peaks of 2¸ of 27.6° and 46.0° for MSWI ash and 27.6° for PMWS ash. The presence of $SiO_2$ and calcium oxide in both ashes is significant in this study as silicon and calcium are essential elements in cement reactions (calcium-silicate-hydrate, CSH is an important substance during the preliminary stages of cement hardening).

## FTIR Analysis

The FTIR transmission spectra of the PMWS and MSWI ashes are shown in Figure 3. The spectrum of the MSWI ash appears to be very similar to the FTIR spectrum of a calcium-rich Type C Turkish coal fly ash studied by Acemioglu[19] in terms of location of their peaks. Peaks observed at 3644 $cm^{-1}$ by both PMWS and MSWI ash are probably due to adsorption band of O-H in the crystal structure[19]. A prominent peak for MSWI ash observed at about 1100 $cm^{-1}$ is assigned to Si-O bonds[20]. This peak is less discernible in the case of PMWS ash perhaps due to the relative lesser amount of $SiO_2$ present in the ash. The small peaks detected at around 800 $cm^{-1}$ for both ashes are assigned to Al-O or Si-O-Al[21].

Detection of silicon-based materials for both ashes in the XRD and FTIR analyses indicates the presence of $SiO_2$ which is one of the main building components in cement and concrete utilizations. This further implies that both the PMWS and MSWI ashes has the potential to be used as cement replacement for production of concrete or as chemical binder for solidification/ stabilization of industrial waste sludge.

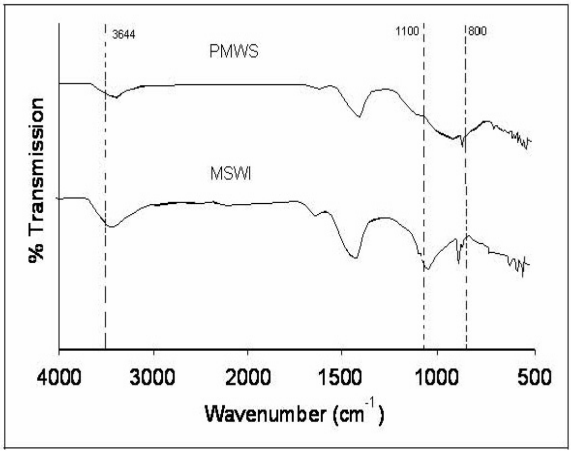


**Fig 3.** FTIR spectra for PMWS and MSWI ashes.

## CONCLUSIONS

The TCLP result clearly indicated that both the PMWS and MSWI ashes should not be classified as hazardous wastes in terms of heavy metal leachability. As such, pre-treatment for the ashes is not required prior to sanitary landfill disposal. It was possible that during the incineration process of municipal solid wastes, metals may have fused with one another to form a relatively stable crystalline form resulting in hybrid solid metal-based substances in the MSWI ash. In terms of application as cement replacement material, both ashes could be used with reasonable technical practicability, since both contained $SiO_2$ which is one of the main building components in cement and concrete utilizations. The study suggested that PMWS ash could be more suitable as a cement replacement material as compared to MSWI ash as the former had significantly smaller particle size distribution and lower organic content.

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