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Investigation of Metal and Trace Elements of Cenospheres from Lignite High-Calcium Fly Ash (Thailand)

Sorachon Yoriya * and **Phattarathicha Tepsri**

National Metal and Materials Technology Center, 114 Thailand Science Park, Pahonyothin Road, Khlong Nueang, Khlong Luang, Pathum Thani 12120, Thailand; phattarathicha.tep@mtec.or.th
* Correspondence: sorachy@mtec.or.th

Abstract: High-calcium fly ashes contain a large content of small particles including cenospheres of chemical constituents known to be similar to fly ash and the parent coal. Coal fly ash contains metal and trace elements that may leach out during disposal or utilization. This work aimed to understand an overview of cenosphere characteristics relating to fly ash and leaching study. To our knowledge, this is the first report on metal and trace element leaching of cenospheres separated from high-calcium (28.9 wt.%) class C fly ash produced from the Mae Moh coal-fired thermal power plant in Thailand. In this study, the cenospheres were separated from fly ash by a wet separation process (sink-float method) using water as medium. Physical properties, morphology, chemical composition, the mineral phases of cenospheres and fly ash have been characterized. Extraction was carried out by acid digestion; the selected metal and trace elements in this study are Mg, Al, Zn, Pb, Cd, Cr, and Cu; the obtained environmentally available concentrations of cenospheres were analyzed in comparison to those of fly ash. The concentrations of Cu, Cr, Pb, and Cd elements of interest in the leachates obtained from the toxicity characteristic leaching procedure (TCLP) showed the tendency to decrease in that order. All the elements were found below the permissible limit values regarding Thailand soil quality standards. Association of the heavy metal trace elements in cenospheres and fly ash was discussed in in terms of physico-chemical-geochemistry correlating with the leaching concentrations.

Keywords: cenospheres; fly ash; high calcium; water medium; heavy metals; extraction; leaching

1. Introduction

Coal contains significant quantities of minerals and a high concentration of trace elements. Coal ashes from different types of combustion processes produced toxicity [1]. Bouska and Pesak determined statistical characteristics of all the elements in thousands of coal samples and found that arithmetic mean values for Hg, Cd, Pb, As, Cu, and Cr are 0.13, 5.6, 11.1, 33.4, 35.3, and 54.5 mg/kg, respectively [2]. Lignite coal normally showed the trace elements in higher concentrations, e.g., 72 mg/kg of As, 95 mg/kg of Cr, and 254 mg/kg of Cr [3,4]. Various trace elements are emitted associated with surface formation of fly ash particles during coal combustion [5–7]. Concentrations of the trace elements were found in fly ash approximately 4–10 times higher than those in the parent coal [5].

One pathway of heavy metal release is the leaching of fly ash by favorable interactions in water when they are ponded or landfilled [7–9]. A number of trace elements could include Ce, Cl, Cd, Co, Cr, Cu, F, Mn, Ni, Sb, Pb, Sr, Ti, As, and Zn; many more cationic elements possibly found were reported in the literature [10,11]. These trace elements have been considered as being potentially toxic to the biological system. Some metal elements (e.g., V, Mo, and W) presenting in anionic form in solution exhibited a higher mobility that can lead to environmental pollution and significant human health issues [9]. Additionally, fly ash is considered a hazardous material for living organisms because of the presence of toxic elements such as As, Cr, B, V, and Sb [12]. Fly ash contains toxic elements, which is the main harmful aspect of fly ash disposal or utilization because of its negative effects on

water, soil, and air [13]. Therefore, special design for landfills is required to ensure disposal in a safe manner. Mobility and toxicity of heavy metals and trace elements present in ponds, landfills, or dumpsites depends on the chemical form of the elements. Knowledge of heavy metal contents and species, and leachability under various environmental conditions is a prerequisite for the assessment of waste management.

Studying the leaching of metal and trace elements is important in order to know the concentration of leachates of trace elements and to predict the environmental impacts in terms of disposal of fly ash into ponds or landfills. Some leaching tests are widely used to determine metals present in the solid sample and to quantify the amount of element species due to mobilization. The extraction methods are tools used to assess the release potential of constituents from the materials, providing data of the extractable analytes that are generally lower than the total concentration of the solid inputs. When ash particles, including fly ash and cenospheres, come into contact or interact with water, dissolution of primary solids and precipitation of secondary solids proceed, thereby affecting the leaching processes. The concentrations and the rates of released trace elements depend on the total concentration of those elements in the solid phases [14]. Dissolution characteristics of fly ash can be evaluated through the analysis of the leaching solutions or the extracts, which usually contain measurable concentrations of target elements. Estimation of concentrations of many trace elements can be done by measuring dissolved major constituents of the ashes.

Fly ash is pozzolanic in nature and can hardens when reacted with calcium hydroxide and water. The high-calcium fly ash normally produced from the low-rank lignite coal is both pozzolanic and cementitious, which can self-harden when reacted with water [10]. Fly ash is mostly rich in major and minor components and contains spheres with mainly amorphous aluminosilicate glass comparable to soil particles [15]. The alkaline fly ash with Ca-rich was found to be useful for acidic soil amendment [16]. Cenospheres are micro-spherical components mixing with fly ash. The fraction of cenospheres in fly ash varies over a wide range from 0.01 to 4.8 wt.% [17]. The major chemical components of cenospheres are Si, Al, and Fe, with their content significantly varying depending upon fly ash sources. Cenosphere constituents are multiphase systems consisting of the aluminosilicate glass phase and crystalline phases of mullite and quartz [18]. There are a number of studies that reported extensively on the characterization of physical structures, chemical composition, geochemistry and mineralogy of cenospheres [17,19–23]. Nonetheless, the study of leaching in combination with assessment of physical properties, morphologies, chemical components, and mineral phase compositions has been rarely reported [24]. It is important to keep in mind the toxicity and environmental impact of cenospheres for their effective utilization management and disposal, as they one of the components in fly ash. In such a case that the rate of production of fly ash is greater than consumption, normally the unused fly ash was subject to disposal at the ponds or landfills, depending on the location of each power plant and the environmental management criteria. The unused fly ash, with the incorporation of cenospheres and bottom ash, are one of the major problems of the coal combustion power plant because the disposal of these materials leads to negative impacts on the environment, such as air pollution and groundwater quality.

The objective of this work is to investigate the characteristics of cenospheres separated from high-calcium fly ash in relation to the concentrations of metal and trace elements. Acid digestion and TCLP methods have been applied to evaluate potential leachability of the toxic substances from the fly ash and cenosphere samples. The leaching results of cenospheres were compared to those of their parent fly ash. Discussion focused on how the physical properties, chemical composition, and mineral phases influenced the leachability and concentrations of those metal and trace elements. The data obtained in this study are expected to serve as a reference for assessing the toxicity of cenospheres disposal and utilization.

2. Materials and Methods

2.1. Fly Ash and Cenospheres Separation

Fly ash samples was collected from Unit 5 of the Mae Moh thermal power plant, Mae Moh district, Lampang province, Thailand. The location coordinates are 18,296 latitude, 99,752 longitude. The Mae Moh power plant uses lignite coal in electricity production. Mae Moh fly ash has a high content of calcium and iron oxides and is enriched in aluminosilicates, being classified as class C fly ash according to American Society for Testing and Materials (ASTM) standard C618 [25].

In this study, cenospheres were separated from fly ash by the traditional wet separation-sink-float method. The cenosphere separation process was conducted in a water medium, as the fly ash-to-medium ratio was kept at 1:10 (g/mL) and the soaking time was fixed at 2 h to obtain cenospheres with good quality with no calcium carbonate crystals covering the particle surface [21]. After mixing fly ash and water, mechanical stirring was normally applied following the procedure described in our previous reports [21,26]. After leaving for 2 h of sedimentation, the floating part (low density cenospheres) was decanted, then filtered by vacuum filtration. The collected cenospheres were dried in an oven for at 105 °C for 48 h prior to characterization and leaching study. Thte pH of the water solutions of fly ash and cenospheres was measured.

2.2. Determination of Metal Elements in Fly Ash and Cenospheres by Acid Digestion

To determine the metal elements and their concentration contained in fly ash and cenospheres, this study adopted the use of a microwave-assisted procedure and acid digestion for the determination of heavy metals in fly ash and the collected cenospheres. Referring to United States Environmental Protection Agency (U.S. EPA) Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods [27], fly ash and cenosphere samples were prepared to be analyzed for the metal elements. The method was a rapid multi-element acid extraction prior to analysis. The acid solution for digestion was prepared by mixing 7.0 mL nitric acid (HNO_3), 1.0 mL hydrochloric acid (HCl) and 1.5 mL tetrafluoroboric acid (HBF_4). Then the reagent combination was adjusted the volume to 25 mL with nanopure water (>18 MΩ doubly deionized water) [28]. Reagent-grade chemicals were used in this study. Two hundred g of solid samples were mixed with acid solution for digestion. The mixture was heated by microwave to a temperature of 200 °C ± 5; followed by two steps of heating for 10 min and 20 min. The use of a microwave was to assist with the extraction in acid or dissolution of fly ash and cenospheres under an elevated temperature. This procedure was applied for determining the selected elements, including cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), magnesium (Mg), and aluminium (Al) by inductively coupled plasma-optical emission spectrometry (ICP-OES; HORIBA Ultima Expert ICP-OES spectrometer, Longjumeau, France). The environmentally available element concentrations in fly ash and cenospheres (parent or before leaching) are presented in mg/kg; herein Mg, Al, Zn, Pb, Cd, Cr and were investigated. The measurement results were obtained from the average of three readings. The resulting concentration of these elements of fly ash and cenospheres was analyzed in comparison.

2.3. Leaching Study of Cenospheres by TCLP Method

The leaching of metals was carried out using the toxicity characteristic leaching procedure (TCLP) [24,29–31]. This method requires the use of extraction fluid for the test. First, the extraction fluid-acetate buffer was prepared by mixing 5.7 mL glacial acetic acid (CH_3COOH) with 500 mL distilled water, then adjusting the volume to 1 L by adding 64.3 mL of 1 N sodium hydroxide (NaOH), following by pH adjusting to 4.93 ± 0.05 with 1 N sodium hydroxide (NaOH). The leaching test started with mixing fly ash with the prepared extraction fluid in a flash, with the solid-to-liquid ratio of 1:20 (w/v). The mixture was subject to shaking in a shaker incubator (NB205, N-BIOTEK, Gyeonggi-do, Korea) at 30 rpm for 18 h at 22 °C. The supernatant was decanted and filtered through a glass

fiber Whatman 42 filter membrane by vacuum filtration. The collected supernatant was acid digested solubilized following the standard method 3051A [27] prior to metal element analysis by inductively coupled plasma-optical emission spectrometer (ICP-OES; HORIBA Ultima Expert ICP-OES spectrometer, Longjumeau, France); the results were expressed also with the average, standard deviation (SD) and percent relative standard deviation (%RSD) values for the precision. The sediment portion was dried in an oven at $100 \pm 5\ °C$ for 24 h, stored in a polyethylene bottle and kept in a desiccator for further characterization. The extraction experiment was performed in triplicate.

The leachability of an element from cenospheres was calculated for the data sets from the microwave assisted digestion method and the TCLP method [28] by Equation (1).

$$\% \ Leached = C_c/C_e \times 100 \tag{1}$$

where C_c is the leached concentration of an element (mg/kg) from TCLP and C_e is the environmentally available concentration of an element from microwave assisted digestion (mg/kg) [27,28].

2.4. Material Characterization

The physical characterization of fly ash and cenospheres includes: true density determination, particle size analysis, pH determination of the water solutions of high-calcium fly ash and cenospheres. True density was examined by ultrapycnometer (Ultrapycnometer 1200e, Quantachrome Instruments, Boynton Beach, FL, USA). Particle size and distribution of the fly ash and cenosphere samples were determined by laser particle size analyzer (Masterizer 2000, Malvern Instrument, Malvern, UK). The determination of specific area of fly ash was done by gas adsorption via Burenauer-Emmett-Teller (BET) surface area analysis. The values of specific surface area, pore size, and pore volume of fly ash were examined by a BET surface analyzer (Micromeritics, Smart VacPrep, USA). The fly ash sample was kept in a dessiccator prior to measurement. The fly ash sample was prepared (pre-conditioning) by degassing under the temperature of 150 °C for 720 min, then the sample was cooled and analyzed under nitrogen adsorption to measure the volume of nitrogen gas adsorbed at specific pressures. For porous materials like the bulk cenospheres, the widely used mercury intrusion porosimetry (MIP) method was applied to determine the information about pore structure. In this study, total pore area, median pore diameter and percent porosity of cenospheres were investigated using a porosimeter (Micromeritics, AutoPore V, USA) The cenosphere sample was analyzed at a starting pressure of 0.5 psia and an ending pressure of 60,000 psia. Loss on ignition (LOI) was applied to the fly ash and cenosphere samples to estimate unburned carbon in the material. The LOI experiment was carried out by following the ASTM D7348-13 [32]. Note that ASTM C618 specifies maximum LOI of 6 wt.% for class C fly ash for being used in concrete [25]. Morphologies of fly ash and cenospheres were examined by scanning electron microscopy (SEM) (Phenom ProX, Eindhoven, Netherlands). The chemical compositions were characterized by energy dispersive X-ray fluorescence (EDXRF; EDAX Smart Insight, ORBIS PC, NJ, USA). The XRF was carried out for fly ash and cenospheres both before and after the TCLP leaching. The mineralogical composition of fly ash and cenospheres was determined by X-ray diffraction using PANalytical-X'Pert Pro diffractometer (PANalytical B.V., Almelo, The Netherlands).

3. Results

3.1. Physical, Chemical, Mineralogical Characterization of Fly Ash and Cenospheres

Important physical features of fly ash and cenospheres include particle size and distribution, surface area, pore diameter, and density. The physical characteristics of fly ash and the collected cenospheres are shown in Table 1.

The density of fly ash and cenospheres is 2.47 and 1.03 g/cm^3, respectively. Cenospheres are the lightweight material comparing to fly ash; the density of cenospheres separated from the Mae Moh lignite fly ash are usually about 1.0 g/cm^3 [19,33,34]. Fly ash and cenospheres have a wide variation in size, ranging from <1 μm to greater than 250 μm.

By means of volume mean diameter (D (4,3)), the average particle size of Mae Moh fly ash is 55.97 μm, while the average particle size of the collected cenospheres is 44.47 μm. The particle size characteristic (D (4,3)) for the cenosphere sample in this study is quite different than those observed in other reports [20–22] that found that the average particle size was smaller than that of fly ash. Typically, the average particle size (D (4,3)) of cenospheres observed in different sources (e.g., different power plants, coal type) was found significantly larger than their parent fly ash. In this study, the average particle size of cenospheres was not significantly different than fly ash. This was presumed to be a unique characteristic of cenospheres from lignite fly ash produced from the Mae Moh power plant, Unit 5.

Table 1. Density, average particle size and size distribution of fly ash and cenospheres.

Sample	Density (g/cm³)	Particle Size (μm)					Size Distribution (Wt.%)				
		D (4,3)	d_v10	d_v50	d_v90	<1 μm	1–10 μm	10–50 μm	50–100 μm	100–250 μm	250–500 μm
Fly ash	2.47	55.97	3.28	31.86	146.81	2.16	25.88	32.68	19.43	18.34	1.51
Cenospheres	1.03	44.47	8.30	37.42	84.92	2.20	9.58	54.52	27.87	5.41	0.42

As seen in Table 1, the volume weighted percentiles (d_v10, d_v50, and d_v90) of particles identified for the fly ash sample have shown a significant variation in particle size of fly ash comparing to cenospheres in different fractions of particles. The 10% fraction of particles has diameters smaller than 3.28 μm (d_v10), the 50% fraction of particles has diameters smaller than 31.86 μm (d_v50), and the 90% fraction of particles has diameters smaller than 146.81 μm (d_v90). The d_v10, d_v50, and d_v90 fractions of cenospheres are 8.30, 37.42, and 84.92 μm, respectively. Note that this is fairly typical for D (4,3) that is larger than the d_v50. The values of d_v10, d_v50, and d_v90 for cenospheres has shown the particle size in a relatively narrow range with respect to fly ash, with the larger sizes for the 10% and 50% fractions. This correlates to the distribution profile of particle size as shown in Figure 1. The distribution of fly ash sample seemed to be a bimodal distribution, presumably resulting from such wide variation in particle size above mentioned. The distribution of a cenosphere sample could be asymmetric unimodal or multimodal, as the slight humps observed at both ends of the profile. The distribution width in terms of calculated span of fly ash is 4.50 and that of the cenospheres is 2.05, suggesting that the collected cenospheres have a narrow size range compared to fly ash.
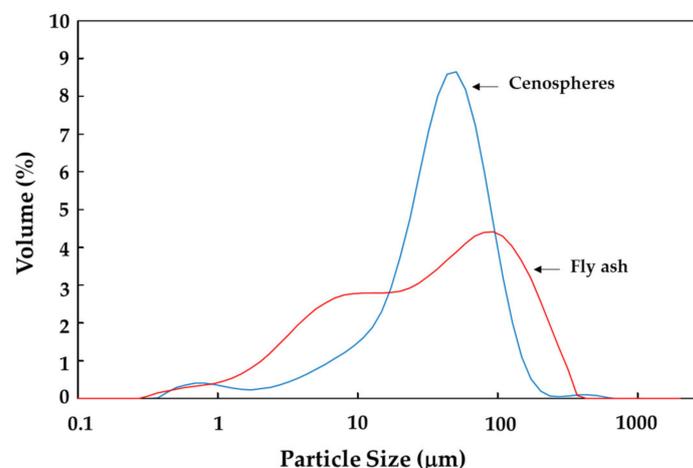
Figure 1. Particle size distribution profiles of fly ash and cenospheres collected by the sink-float method using 1:10 fly ash-to-medium ratio, 2 h soaking period.

Particle size combined with the distribution is an informative characteristic, which is commonly related to the specific surface area. Obtained from the BET method, the fly

ash has the specific surface area of 0.9634 m^2/g. For the cenospheres, the pore distribution parameter information obtained from the MIP method has shown that the average pore diameter is 0.29 μm; the median pore diameter is 15.05 μm (volume) and 47.20 nm (area); and total pore area is 294,030 m^2/g, thus making them have a high porosity of 79.43%. Inferred by the MIP, the dispersive median pore diameters of cenospheres could be due to the heterogeneous characteristic of ash particles resulting from burning coals [35]. In addition, the unburned carbon particles could possibly be found and affect the particle size value by tending to be in the upper end of the size distribution, and hence influence the relative surface area [36]. In this study, the carbon contents of the fly ash and cenosphere samples determined by LOI are 3.79% and 3.67%, respectively.

A dissolution experiment was performed to investigate the reactivity of fly ash and cenospheres. The measured pH values of water solutions of fly ash and cenospheres are 12–13 and ~7, respectively. The water solution of fly ash resulted in the effluent to a basic solution of high pH. The alkaline pH and high calcium content indicates the presence of amorphous lime (CaO) in fly ash [28]. The earth alkalis (CaO, MgO), alkalis (Na_2O, K_2O) and iron oxide react with water producing hydroxyl ion (OH^-) species in pH > 12 [37]. The alkalinity of fly ash is generally due to dissolution of the free calcium, carbonates, soluble metal salts and oxides, and hydroxides [14]. The fly ash surface is more chemically reactive than the interior of the particles [38], as the surface reactivity could be determined by the difference of the initial pH and the final pH measured at the time of equilibrium [28]. Morphological features of fly ash and cenospheres are demonstrated in Figure 2. Typical fly ash taken from the electrostatic precipitator of a thermal power plant consists of spherical particles, as their morphology is controlled by the combustion conditions such as temperature and cooling rate [33]. Cenospheres are hollow and have rough surface structures and irregular shapes with the coverage of multi-particle agglomerates (Figure 2b), which may be due to inter-particle contact or rapid cooling. Cenospheres contain individual particles with irregular shapes and agglomerates (Figure 2c) of particles as a result of the fusion of small fragments and the incomplete melting in the combustion process. The particle morphologies are helpful for understanding the leaching behavior of fly ash and cenospheres. The morphologies of ashes were reported to affect the mobility of trace elements. The particles with a dense, smooth, nonporous outer surface could restrict leaching of heavy metals from the ashes [14,39] in terms of mobility.

The chemical compositions of fly ash and cenospheres investigated by XRF are shown in Table 2. SiO_2, Al_2O_3, Fe_2O_3, and CaO dominate the chemical compositions of fly ash, whereas SO_3, K_2O, TiO_2 and MnO have a lower content. CaO in the form of total and free CaO mostly originated from calcite in coal that was generated through thermal disruption of calcite [4]. The sum of SiO_2, Al_2O_3, and Fe_2O_3 in fly ash was 59.23%.

Table 2. Chemical compositions characterized by XRF of fly ash, cenospheres collected by the sink-float method using 1:10 fly ash-to-medium ratio, 2 h soaking period, and cenospheres after being leached by TCLP method.

Item	Composition (Wt.%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	TiO_2	MnO
Fly ash								
	30.52 ± 0.10	13.04 ± 0.10	15.67 ± 0.23	28.90 ± 0.39	9.02 ± 0.06	2.21 ± 0.02	0.50 ± 0.00	0.14 ± 0.00
Cenospheres (initial)								
	48.68 ± 0.33	23.24 ± 0.06	9.49 ± 0.06	9.52 ± 0.06	3.62 ± 0.82	4.68 ± 0.00	0.70 ± 0.00	0.60 ± 0.74
Cenospheres after being leached by TCLP method								
	53.12 ± 0.25	25.14 ± 0.13	8.73 ± 0.20	7.08 ± 0.10	0.34 ± 0.04	4.73 ± 0.04	0.80 ± 0.01	0.06 ± 0.00
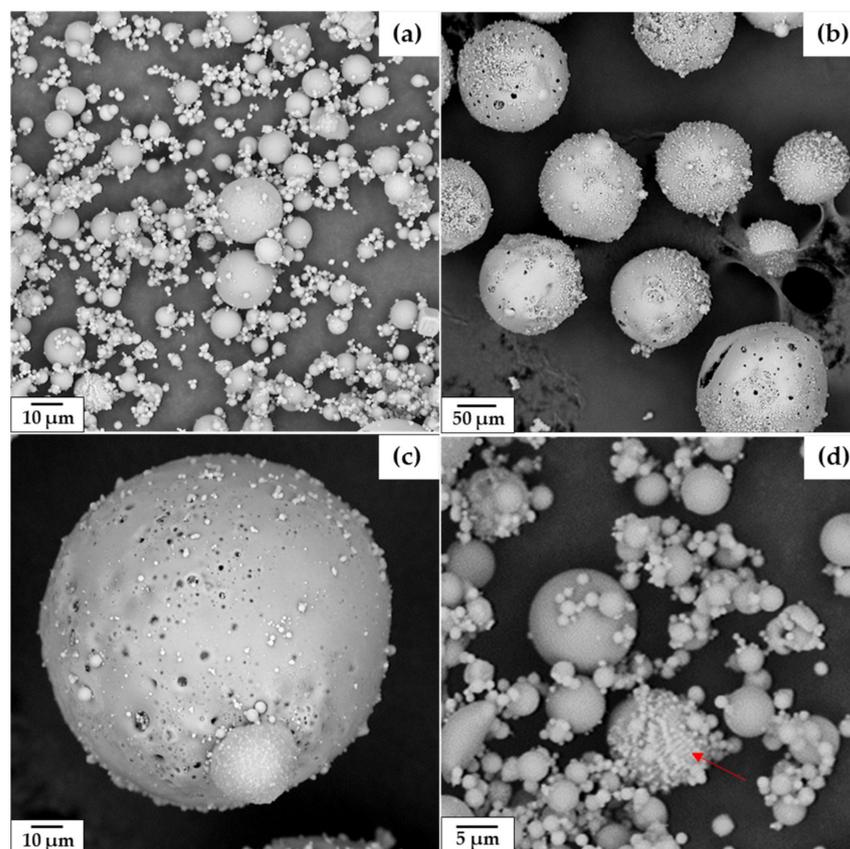
Figure 2. SEM image of (**a**) fly ash and (**b**) cenospheres collected by the sink-float method using 1:10 fly ash-to-medium ratio, 2 h soaking period. (**c**) The zoomed-in image of a cenosphere particle. (**d**) The appearance of iron surface condensation on the ash particle.

Fly ash used in this study are categorized as class C (sum in the range of 50–70% of SiO_2 + Al_2O_3 + Fe_2O_3 with high CaO content), according to the American Society for Testing and Materials (ASTM) standard C618 [25]. Classifications of fly ash could be based on its potential pozzolanic activity and cementitious properties; i.e., reactive water-soluble and amorphous phases, alkali aggregate reactivity, and sulphate resistance for industrial applications [40]. The chemical compositions of minerals found in cenospheres are similar to those of fly ash. The concentrations of SiO_2, Al_2O_3, K_2O, TiO_2 and MnO are higher, while the concentrations of Fe_2O_3, CaO, and SO_3 are lower.

The mineral composition and phase of fly ash and the cenospheres characterized by XRD are demonstrated in Figure 3. Both fly ash and cenospheres consist of amorphous and crystalline phases. The broad hump seen (2θ between 17–35 °C) for fly and cenospheres indicates the characteristic glass phase, typically found for the lignite ash spheres. The position of the hump was observed being centered at a lower angle for cenospheres. This observation was assumed to reflect the glass structure in the relatively low calcium content in the ash spheres [41]. The chemical composition results obtained in this study (Table 2) agreed well with such observation; the CaO content of cenospheres (9.52 wt.%) is lower than that of fly ash (28.90 wt.%).

The crystalline mineral phases of fly ash found in this study include magnetite (Fe_3O_4), anhydrite ($CaSO_4$), quartz (SiO_2), calcite ($CaCO_3$), calcium silicate (Ca_2SiO_4), merwinite ($Ca_3Mg(SiO_4)_2$), srebrodolskite $Ca_2((Fe_{1.559}Al_{0.441})O_5)$, mullite ($3Al_2O_3 \cdot 2SiO_2$), and portlandite ($Ca(OH)_2$). The commonly found mineral phases in fly ash were reported to include glass, mullite, quartz, magnetic phases of hematite-magnetite, anhydrite-gypsum, lime-portlandite, clay, cristobalite, and calcite [10]. For cenospheres, the phase composition was shown in Figure 3b, including calcite ($CaCO_3$), mullite ($3Al_2O_3 \cdot 2SiO_2$), quartz (SiO_2), anhydrite ($CaSO_4$), magnetite (Fe_3O_4), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$). Ad-

ditionally, cenospheres were found to contain small amounts of cristobalite, hematite, potassium feldspar, and hydromical depending on fly ash sources [17,42,43].
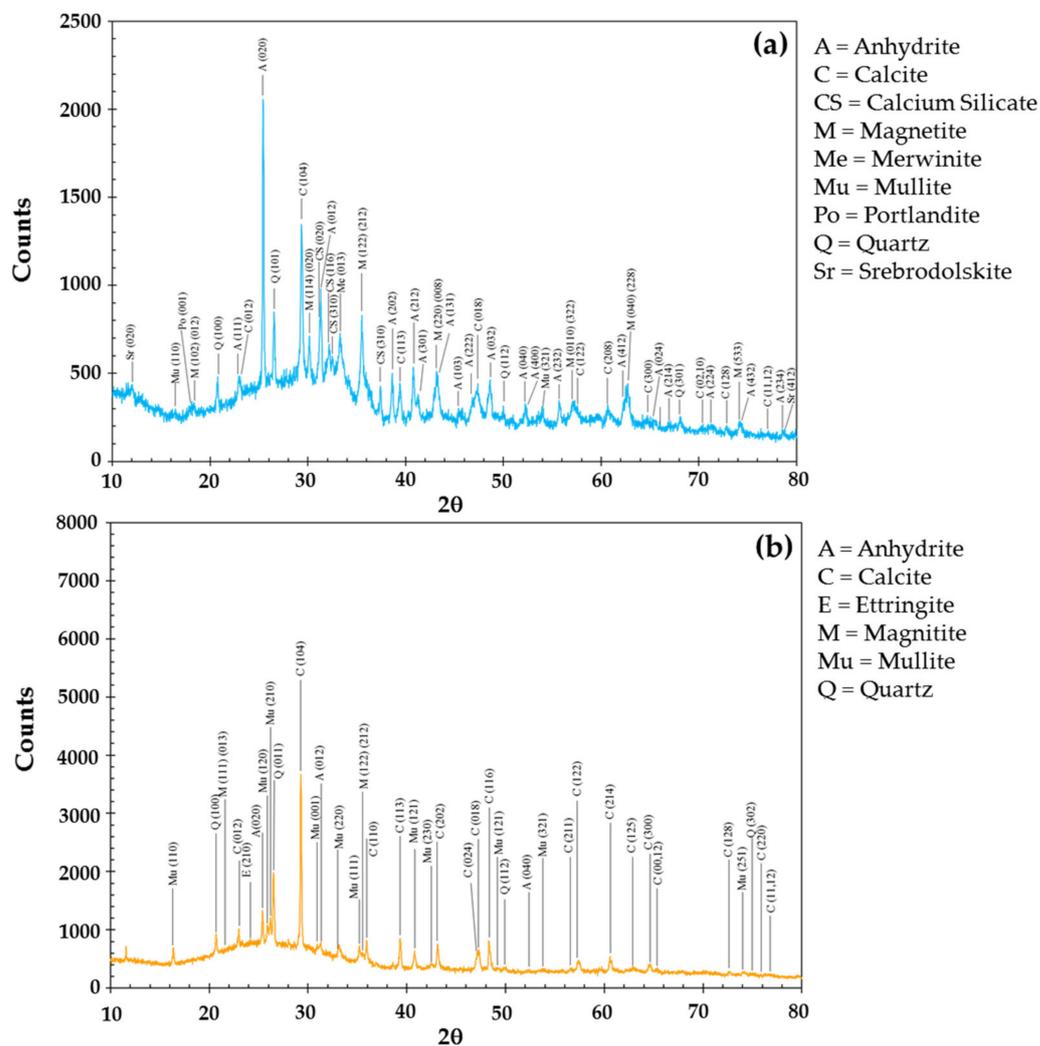
Figure 3. X-ray diffraction patterns of (**a**) fly ash and (**b**) cenospheres collected by the sink-float method using 1:10 fly ash-to-medium ratio, 2 h soaking period.

Fly ash and cenospheres contain the intermixing of Fe and Al-Si mineral phases and the Ca non-silicate minerals. The major (except Ca) and minor elements were found typically associated with silicates [44]. In terms of elemental composition, Si, Al, Fe, and Ca are the major elements presenting in compounds in the order of decreasing amounts, whereas the minor elements are Mg, Ti, and K, with trace amounts of silicates, sulphates and borates, and lesser amounts of phosphates and carbonates [45]. The Fe-Al-Si glass amorphous phase and unburned carbon were found to present in the ashes in significant portions [36,46]. It should be noted that the magnetic matrix in the ash spheres was found to have great reactivity and potential for carrying and releasing the toxic elements [15]. Mineralogical information of the ashes including cenospheres could be used as a tool to predict the ash behavior in leaching.

3.2. Acid Digestion of Fly Ash and Cenospheres

The metal contents in fly ash and cenospheres obtained from the EPA Method 3051A acid digestion are shown in Table 3. It should be noted here that the acid digestion procedure following this method does not dissolve the silicate phase; the data of metal content obtained herein is defined as the environmentally available concentration, not the

total content in the material [27]. The procedure for determination of total metal content is available in the EPA 3052 digestion.

Table 3. Environmentally available concentrations of metal elements extracted from fly ash and cenospheres by acid digestion.

Sample		Concentration (mg/kg)						
		Mg	**Al**	**Zn**	**Pb**	**Cd**	**Cr**	**Cu**
Fly ash	Average	11,163.66	18,255.81	217.11	33.37	4.83	65.05	40.15
	SD	376.91	455.01	1.64	0.58	0.05	2.18	0.86
	%RSD	3.3800	2.4900	0.760	1.8	1	3.35	2.1
Cenospheres	Average	4341.47	20,818.32	68.67	30.48	2.69	38.11	27.41
	SD	64.65	334.06	0.92	0.73	0.04	0.87	0.42
	%RSD	1.490	1.6000	1.4	2.4	1	2.3	1.5
LOQ		0.00300	0.003	0.003	0.003	0.028	0.005	0.003

LOQ—Limit of Quantitation.

For both fly ash and cenospheres, the acid digestion method showed the result of metal extraction in three groups of concentrations: high, medium, and low. A large amount of Mg and Al was extracted to the high level of concentrations. As can be seen, fly ash contained relatively high concentrations of Mg and Al, whereas cenospheres contained lower concentrations of Mg and Al. Mg and Al are the major elements presenting in fly ash, with such high concentrations indicating a good solubility in acid solution. The acid solution solubilized Zn and allowed it to be removed from fly ash and cenospheres at a medium level. Zn was extracted in a high concentration from fly ash (217.1 mg/ kg), about three times larger than that of cenospheres (68.7 mg/ kg). The concentrations of Pb, Cd, Cr, and Cu ranked relatively low, indicating lower solubility. The concentrations of Pb, Cr, and Cu were similar, and lower than Zn. The extracted concentration of Cd was found to be the lowest one for both fly ash and cenospheres, confirming the least solubility of cadmium in the acid medium. The similar observation for the trend of Mg extracted to the large level, Zn to the medium level, and Pb, Cu, and Cd to the lower level, was also found for the heavy metal analysis of India fly ash from the Bhusawal thermal power plant being disposed in the ash pond [30]. Comparing in terms of fly ash classification, the environmentally available concentrations of Zn (217.1 mg/kg), Pb (33.4 mg/kg), Cr (65.0 mg/kg) and Cu (40.2 mg/kg) found for class C fly ash obtained in this study are lower than those reported for class F fly ash; 657.5, 147.7, 62.2, and 93.2 mg/kg, respectively [47].

The low concentration (several tens of concentration level) of Zn extracted from cenospheres could probably be due to dissolution of the spherical mass during the cenosphere separation process. In the ash spheres, zinc was found primarily in non-silicate constituents, not only associated with the glass phase of the spherical ash but also the Fe-Mn oxide fractions [44]. In this study, soaking the ash in water for two hours while leaving the ash-water mixture to sedimentation and cenosphere separation could probably have some effect on Zn to be dissolved for a certain amount from the cenosphere surface into water; that is from the soluble glass and the Fe-Mn fractions, which are water soluble phases. As a consequence, the obtained environmentally available concentration of Zn in cenospheres was hence relatively lower than that of fly ash. Beside Zn, the glass phase is also an important location for Cu and Cr, and higher concentration of Cr in fly ash were found particularly in the magnetite phase [48]. Observed in this study in Table 3, the Cr concentration for fly ash is higher than Cu. This trend was observed to be similar to that of cenospheres. One may assume that the dissolution mechanism of Cr in fly ash and cenospheres in acid digestion is also likely similar, as dissolution of Cr from the magnetite phase in fly ash is more progressive than cenospheres. It should be noted that Cr was also extractable under reducing conditions from the potentially available phases of Fe-Mn oxides and organic

fractions [47], and it was deemed to be associated with the aluminosilicates found most primarily in glass phase [48,49]. It was reported that more than 21% of the environmentally available concentration of Cr was water soluble or exchangeable in high calcium fly ash [50], affecting its mobilization from the solid material. Further, as seen in Table 3 for fly ash, the concentration of Pb is comparatively close to that of Cu. The dissolution mechanism of Pb and Cu was presumed to be due to the prominent dissolution of labile carbonate and Fe-Mn oxide fractions from the ash spheres [47].

Arsenic and mercury volatilize during combustion and could be captured by fly ash. However, in this study arsenic and mercury were not detectable for both Mae Moh class C lignite fly ash and the collected cenospheres. The LOQ for As and Hg is 0.092 and 0.040 mg/kg. This is attributed to the low availability of As during extraction of fly ash and cenospheres, then probably delaying in detecting [51]. There have been many studies of As and Hg in coal and ashes in literature. Arsenic was primarily associated with pyrite in coals and found a dominant surface association in fly ash [9,49]. Total As of about 10–15% was found in some fly ashes produced from high-sulfur bituminous coal [52]. Arsenic was leached at a slow rate from the major phases of hematite and portlandite, and showed maximum solubility in the solution with pH ranging from 7–11, leading to the low affinity of arsenic to metal oxides during this pH range [49]. Mercury is a highly volatile and toxic element found in coals. Mercury in the particulate mercury (Hg^P) form is associated with the ash particles [49]. Sorption of mercury in fly ash depends on the presence of chlorine and sulfur, which are the main elements that play an important role in the sorption as Hg-Cl and Hg-S bond, respectively [53]. The concentration of mercury in fly ash is known to be extremely low [54]; as a consequence, the leachability of mercury was reported very low in fly ash and considered to be a negligible risk in terms of the environmental concern due to the ash leachate [55].

3.3. Leachability of Heavy Metal Elements from Cenospheres

In this study, particular attention was paid to the investigation of the selected heavy metal elements Pb, Cd, Cr, and Cu. The leached concentrations of these elements obtained from the TCLP test are demonstrated in Table 4. A comparison of data was made between the environmentally available concentrations obtained from the acid digestion and the leached concentrations obtained from the TCLP test. The leachability of the elements in cenospheres calculated using Equation (1) was analyzed by means of the percent leached.

Table 4. Concentrations of heavy metal elements leached out from cenospheres by TCLP method.

Analyte	Concentration (mg/kg)		%Leached	Soil Quality Criteria (mg/kg)	
	Acid Digestion	TCLP Test		Residential Area/Agriculture	Non-Residential Area/Agriculture
Pb	30.48	17	55.77	<400	<750
Cd	2.69	0.21	7.81	<37	<810
Cr	38.11	23.80	62.45	<300	<640
Cu	27.41	30.60	111.64	-	-

The Pb, Cd, Cr, and Cu elements were detectable in the cenosphere samples after being leached by the TCLP method. Among these elements, Cu shows solubility with the highest leached concentration and the highest percentage leached under the TCLP test. This implies the preferential dissolution of Cu-carbonate association in the TCLP condition compared to the acid digestion. It has been reported that majority of the labile Cu was associated with the carbonate labile fraction of the ash particle [47]. As seen in Table 4, the leached concentrations of Cu and Cr from the TCLP test are comparatively high. Dissolution of these two elements was presumed to be more effective in the weak acid medium, as they were located in the glass phase in the ash particles [48]. However, the concentrations of Cu and Cr possibly varied depending on specific fly ashes [2,14]. Pb has been leached in relatively smaller amounts with respect to Cu and Cr, while Cd was

leached out at the lowest concentration. Cd was found insoluble in acid solution using the TCLP test for India fly ash in the Bhusawal Thermal Power Plant [30]. A majority of Pb was found associated with the internal glassy matrix of the ash sphere [56]. Note that leachability varied with type of ashes, elements and leaching methods. For both acid and alkaline fly ash, it was found that Pb was highly insoluble regardless of pH and the leaching method [54]. Thus, in this study for the cenospheres from fly ash with high calcium content, the combination of the physico-chemical-mineral phases factor may affect the dissolution of Pb under the TCLP condition. The TCLP method employed in this study has shown a significant role in determining the leachability of the heavy metal elements from cenospheres.

Considering the XRF result in Table 2, the TCLP leaching test resulted in the decrease in the CaO and SO_3 compositions of cenospheres after being leached. Comparing to the compositions of cenospheres before leaching, such a significant decrease in the CaO and SO_3 contents could probably be attributed to the major dissolution fraction of calcium oxide and sulfur bearing species at the outer surface layer. The glass components of CaO, MgO, K_2O, N_2O, and Fe_2O_3 were found concentrated in the exterior hull [37]. Calcium was found to predominantly control the leachate composition and the leachability of the trace elements [57]. Sulfur in fly ash in the form of sulfate (SO_4^{2-}) is also a major soluble species having a strong relationship with calcium leaching. Ca and S are the main elements playing a key role in governing pH of ash leachate, accordingly promoting the precipitation of the metalloid-bearing ettringite phase [9]. In an aqueous environment, when the ashes are in contact with water, the pH of ash materials has a significant effect on mobility of trace elements [5]. Also, the solubility of trace elements depends on the pH of the solution [4]. The ash leachate was found to vary in a pH range from 4.5 to 12 [58]. The metal release from fly ash could be more pronounced at either low or high pH, with lower solubility seen at neutral pH. Furthermore a number of physical and chemical parameters can influence the leachability of constituents from fly ash in the leaching test. Particle size is an important factor influencing the reaction kinetics in leaching of ash spheres. The smaller particle size of the ashes with the relatively larger surface area was found to be more susceptible to hydrolysis [51]. An idea for further study might involve a better insight into the release behavior of cenospheres done by, for example, evaluating the metal release as a function of pH, and investigating the influence of particle size on mobilization of the heavy metals and the released contents.

Lignite fly ash is the active type fly ash that contains high contents of newly formed oxyhyroxides, sulphates, carbonates, and active silicates. This type of fly ash showed the maximum values of water-soluble, magnetic, and heavy fractions (e.g., Fe, Mg, S, Mn, LOI, Si/Al, hematite, corundum, calcite + ankerite, and gypsum + anhydrite), and the relatively high values of Ca, lime + portlandite, and feldspars [10]. The environmental concerns may result from the active phase minerals, the high content of Ca-bearing oxyhydroxides, sulphates, carbonates, and phosphates, and the trace elements (e.g., As, B, Cl, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr, V, and Zn) associated with them. The trace elements in fly ash such as Cd, Cu, V, Mo, Sb, As, Se, Mo and Zn [56] are remarkably enriched on the particle surface, while the Co, Cr, Mn, Ni, Ba, and Pb elements tends to distribute along the surface through the matrix [59]. The enrichment of the trace elements in the ash spheres was attributed to their adsorption on iron oxides and the silicate matrix [47].

Association of the trace elements with particular minerals or matrices plays an important role in determining their forms and quantities in the ash spheres. The leaching of coal fly ash markedly depends on surface chemistry that plays a key role determining mass transfer of leachable species [51]. The key mechanisms controlling metal mobility and release were attributed to the dissolution of primary solids [47]. Most of the trace elements in the ash spheres were enriched in the finer fractions, indicating surface associations. The surface are of the fly ash contained a significant amount of leachable heavy metals (e.g., Cr, Ca, and Mg) due to their condensation on the surface, while Si, Al, K, Pb and other trace elements distributed throughout the thickness of the particle [60]. The surface layer,

only a few microns in thickness, of fly ash particles contained a significant amount of leachable material deposited during the cooling process after combustion [61]. The primary phases, even though they were highly soluble in water due to being trapped in the glass and crystalline aluminosilicates, dissolved very slowly, as the ion transport between phases is in turn controlled by diffusion. The secondary hydrous aluminosilicate glass phase was found to be less stable in an aqueous environment than mullite and quartz [62].

The results of the leaching TCLP test in Table 4 were presented along with the limit values of acceptance criteria for the soil quality standard [63]. All heavy metal elements have lower leaching concentrations than the limit values for the soil quality standard for both residential area/agriculture and non-residential area/agriculture criteria. The release of all these heavy metal elements was lower than the allowed limits for soil imposed by the National Environment Board (2004), Pollution Control Department, Thailand. It could be assumed from the result that cenospheres from the high-calcium fly ash may not have significant concerns for the soil utilization or disposal for those area categories due to the low concentrations of trace elements. In view of cenospheres naturally mixing with fly ash, regarding the Resource Conservation and Recovery Act (RCRA) and the U.S. Environmental Protection Agency (EPA), fly ashes remain exempt from regulation in USA as a hazardous waste based on the contents of quartz, trace elements, leachable compounds, particle size distribution, radionuclides, phenols, dioxins, and polycyclic aromatic hydrocarbons. Fly ashes have been designated that are environmentally harmless material and can be used safely, and are considered to be a negligible risk to the environment [10,64]. Nonetheless, careful use and disposal is essential to prevent cumulative build-up and the possible releasing of toxic trace elements into neighboring environment surroundings such as surface, soil, and ground water.

4. Conclusions

This work presented the separation of cenospheres from lignite high-calcium fly ash via the sink-float method using water as the medium. Physical properties including density, particle size and distribution of fly ash and cenospheres were discussed in comparison. The morphology, chemical composition, and mineral phases confirmed the cenosphere characteristics from class C fly ash. Microwave-assisted acid digestion of fly ash and cenospheres showed the environmentally available metal elements of Mg, Al, Zn, Pb, Cd, Cr, and Cu, with the concentration levels classified into groups of high, medium, and low. The high-calcium fly ash was found richer in these metal elements than the obtained cenospheres, except for Al. A leachability study of the cenospheres by the TCLP test showed that Cu had the highest leached concentration, confirming the association of this element with the most labile carbonate fraction in the glass phase under the weakly acid solution. The degree of solubility of Cu, Cr, Pb, and Cd by means of the percent leached was determined, and it was found that the concentrations decreased in that order. Cd was found the least soluble concentration from cenospheres obtained from high-calcium fly ash. In addition, the concentrations of the heavy metal elements found in the leachates were invariably below the limit values for the Thai soil quality standard. The concentration limits of Pb, Cd, and Cr for the Thai soil quality criteria for the non-residential area/agriculture are <750, <810, <640 mg/kg, respectively. This is important to note, particularly for disposal of the ashes containing cenosphres in non-residential areas such as landfills. Dissolution of the trace elements was mainly attributed to their association with the surface of spheres and to some extent the incorporation within the glass matrix, thus controlling the mobility of the metal elements and reflecting the varied percentage leached.

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