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Characterization of Cenospheres from Malaysian Coal Generated Power Plants: Jimah, Kapar and Manjung

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ABSTRACT

Cenosphere is a component of fly ash (FA) and has been used as part of sustainable material in wastewater treatment, automotive, ceramic, and construction industries due to its properties. This research presents the first study on characterization of cenospheres from Malaysian power plants namely Jimah, Kapar and Manjung. The characterization was conducted via X-ray fluorescence (XRF), particle size analyzer (PSA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The XRF analysis consisted of oxides elements ranged from 14.70 to 22.63% (aluminum oxide, Al_2O_3), 3.78 to 13.44% (calcium oxide, CaO), 34.73 to 57.67% (silicon dioxide, SiO_2), 0.42 to 1.07% (sulphur trioxide, SO_3), 9.09 to 24.92% (iron oxide, Fe_2O_3), 3.62 to 3.67% (potassium oxide, K_2O), 1.76 to 4.24% (titanium oxide, TiO_2) and 0.16 to 0.93% (magnesium oxide, MgO). The classifications of cementitious materials by American Standard of Testing Materials were Class F (Jimah, Kapar) and Class C (Manjung). The classification represents the quality and capability of cementitious materials as cement replacement material, additive, and filler in concrete mix. The sizes of cenospheres were Kapar > Jimah > Manjung. The sizes of cenosphere were found to be larger than FA (Jimah: 2.720-49.21 µm, Kapar: 5.069-98.29 µm, Manjung: 1.084-3.986 µm). Cenospheres contained quarts (Jimah, Kapar, Manjung: 26°) and silicates (Kapar, Manjung: 45°). Ferrospheres, cenospheres, aluminosilicate-spheres, plerospheres and carbon fragments were observed. The cenosphere from Manjung showed high quality as cement replacement material, additive, and filler with 13.44% of CaO.

Keywords: Physicochemical properties; Cenospheres; XRF; PSA; XRD; SEM; Malaysian power plants

INTRODUCTION

Approximately 750 million tonnes of coal combustion by-products (CCPs) (FA and bottom ash, BA) are produced annually around the globe. These hazardous biomasses are rich in heavy metals (Beddu et al. 2020). The CCPs production is constantly growing, transformed lands into landfills making CCPs waste management as a significant global environmental concern (Ćwik et al. 2018)y. In Malaysia, 36 million tonnes of FA has been produced since 2008 from coal generated power plants (Beddu et al. 2018). The coal supply mainly comes from Australia (60%), China (20%), Indonesia (15%), and South Africa (5%). Coal based power plant is cheaper in comparison to natural gas (Blissett, 2015). Malaysian power plants namely Jimah, Kapar and Manjung operated since 2008, 1988 and 2003 (Table 1) (Oh, 2010). The capacities of the power plants are 1400 MW for Jimah, 600 (2nd phase) to 1000 MW (3rd phase) for Kapar, and 2100 MW for Manjung. The annual coal consumptions equal to 3.5 million tonnes (Jimah), 1.50 to 2.50 million tonnes for Kapar and 6.0 million tonnes for Manjung. The bottom ash production equals to 0.56 million tonnes (Jimah), 0.24 to 0.40 million tonnes (Kapar) and 0.96 million tonnes (Manjung) (Oh, 2010).

Cenosphere is a sub-component of FA. It constitutes 17% of FA initial weight (Hirajima et al. 2010; Wrona et al. 2020). It can be extracted from FA via wet and dry methods (Ramme et al. 2013). The wet method is a hydraulic extraction technique using water and separated by gravitational base. The lightweight cenosphere will float and the FA will be suspended at the bottom of the coal ash pond. This method requires a lot of water with possibilities of toxic materials leaching into the ground. The dry method is based on centrifugal air classifier that separates particles ranging from 100 to 200 microns (Abd Manan et al. 2021; Beddu et al. 2020). Cenosphere has been used as part of sustainable industrial technology in wastewater treatment (Markandeya et al. 2017), automotive (Wang et al. 2021), ceramic (Jiang et al. 2018) and construction (Brooks et al. 2020; Xi et al. 2020). Markandeya et al. (2017) applied cenospheres nanosyntactic foam for dye removal from wastewater. Wang et al. (2012) prepared thin-walled tube made of cenosphere-aluminum syntactic foam with high energy absorption capacity particularly axial and oblique loading for automotive application. Jiang et al. (2018) proposed a formation mechanism for porous ceramics under low sintering temperature in densification process. He observed that the microstructure of cenosphere produced a relatively high mechanical strength of porous ceramics. Brooks et al. (2020) developed a thermal insulation brick from inorganic synthetic foam contained of recycled fly-ash cenospheres. Xi et al. (2020) produced a green lightweight high performance cementitious composite containing cenosphere. Current off takers are India, Russia, USA, and China.

Cenosphere has the potential to be used as energy efficient material in the construction industries due to its properties (Beddu et al. 2021). Malaysian power plants are yet to produce cenosphere. The study on physicochemical properties of cenospheres from Malaysian power plants namely Jimah, Kapar and Manjung are presented in this research.

TABLE 1. Investigation on car-driver interaction

Malaysian Power Plants	Capacity (MW)	Operation Year	Annual consumption (Mil.ton)	Bottom ash production (Mil.ton)
Jimah	1400	2008	3.5	0.56
Kapar	1000	2001	2.50	0.40
Manjung	2100	2003	6.0	0.96

METHODOLOGY

SAMPLING LOCATIONS

The FA samples were collected from Jimah, Kapar and Manjung power plants in Malaysia (Figure 1). The Jimah Power Plant is in Port Dickson, Negeri Sembilan Darul Khusus, Malaysia (2◦35′40.0″N 101◦43′24.5″ E). Next, the Kapar Power Plant is in Kampung Tok Muda of Kapar district, Selangor Darul Ehsan (3° 7’ 2.193”N 101° 19’ 21.2802”E). Last but not least, the Manjung Power Plant is in the Manjung district of Perak Tengah, Perak Darul Ridzuan (4° 9’ 34.812”N 100° 38’ 29.7234”E).

FIGURE 1. The sampling stations of cenosphere; (a) Jimah, (b) Kapar and, (c) Manjung power plants

SAMPLE PREPARATION

The sample preparation of cenospheres was conducted using aqueous or wet separation technique (Noor-Ul-Amin, 2014; Yoriya et al. 2019) from FA producing maximum 2% from total FA weight. The percentage of cenospheres recoveries can be referred in Eq. 1 (Yoriya et al. 2019). The samples were oven dried for 24 hours to remove moisture and prepared in the pellet form using pressed pellet technique (Abd Manan et al. 2021). The FA and extracted cenospheres from Jimah, Kapar and Manjung power plants are shown in Figure 2.

$$\frac{Weight\ of\ floating\ cenospheres}{Weight\ of\ FA} \times 100\% \qquad (1)$$

PHYSICOCHEMICAL PROPERTIES

The characterization of physicochemical properties of cenospheres include identification of oxides, measurement on the particle sizes, determination of crystallinity and observation on the microstructure via XRF (RaynyEDX-700/800, Shimadzu Corporation, Tokyo, Japan), PSA (Shimadzu, SALD-2300), XRD (PANalytical and X'Pert PRO MPD PW 3040/60, BS EN 13925 – 3:2005), and SEM (ZEISS GeminiSEM 500, Oberkochen, Germany) accordingly.

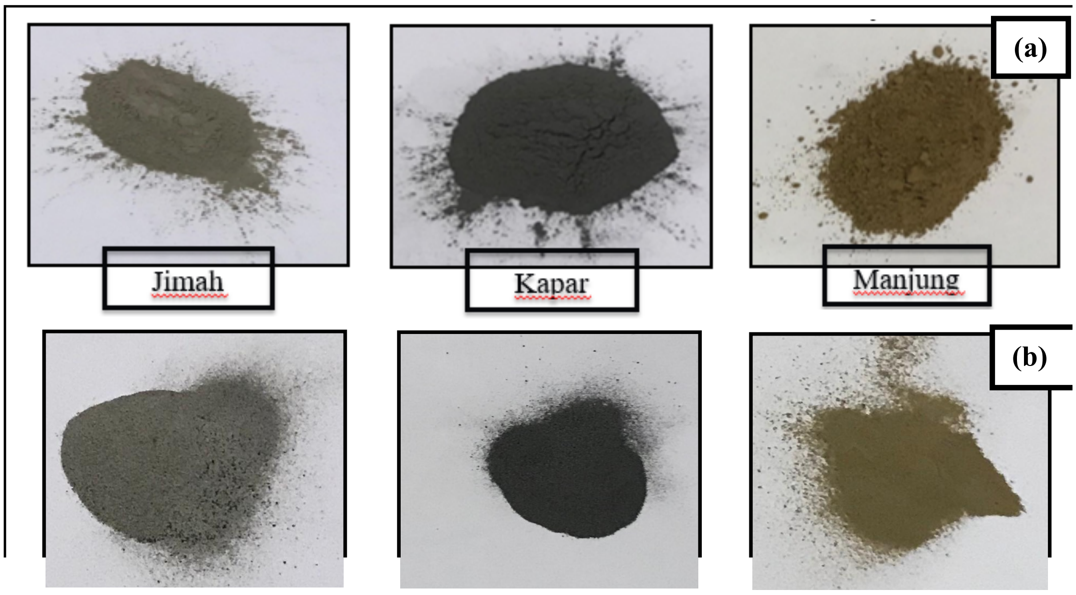

FIGURE 2. The (a) FA and (b) extracted cenosphere from Jimah, Kapar and Manjung

THE XRF ANALYSIS

The XRF analysis of cenospheres collected from the power plants in comparison with other literatures is shown in Table 2. The XRF analysis of cenospheres from Jimah, Kapar and Manjung consisted of oxides elements namely aluminium oxide (Al_2O_3), calcium oxide (CaO), silicon dioxide (SiO_2), sulphur trioxide (SO_3), iron oxide (Fe_2O_3), potassium oxide (K_2O), natrium oxide (Na_2O), titanium oxide (TiO_2), manganese oxide (MnO), and magnesium oxide (MgO) (Figure 3).

The XRF analysis consisted of oxides elements ranged from 14.70 to 22.63% (Al_2O_3), 3.78 to 13.44% (CaO), 34.73 to 57.67% (SiO_2), 0.42 to 1.07% (SO_3), 9.09 to 24.92% (Fe_2O_3), 3.62 to 3.67% (K_2O), 1.76 to 4.24% (TiO_2) and 0.16 to 0.93% (MgO). The percentages of Al_2O_3 and SiO_2 of cenosphere were comparable to literatures (Hanif et al. 2016; Wang et al. 2012; Xu et al. 2016; Zyrkowski et al. 2016). However, the CaO, SO_3, Fe_2O_3, K_2O, Na_2O, TiO_2, MnO, and MgO contents were much higher than those reported in the literatures.

The coal ash classification by American Standard of Testing Material (ASTM) is based on the total percentages of $SiO_2 + Al_2O_3 + FeO_3$ (American Society for Testing and Materials, 1994). Overall, the total percentages of chemical composition of $\geq 70\%$ is equivalent to Class F of FA (with CaO <10%, originates from bituminous coal, high silica, less lime) while $\geq 50\%$ equals to class C of FA (with CaO >10%, originates from sub-bituminous coal, high silica, high lime). The Class F of FA is pozzolan but less cementitious. The Class C of FA is pozzolan and highly cementitious.

Another alternative for coal ash classification is based on the percentage of CaO content (CSA A3001 Cementitious Materials for Use in Concrete). The classifications are Class F (< 8% of CaO), Class C (8 to 20% of CaO) and Class CH (>20% of CaO) of FA (Canadian Standards Association, 2004). Since the first classification by ASTM is met up, the alternative classification based on CaO can be bypassed.

The coal ash classification is based on the total percentages of $SiO_2 + Al_2O_3 + FeO_3$ (American Society for Testing and Materials, 1994). The total percentages of $\geq 70\%$ is equivalent to Class F of FA (with CaO <10%, originates from bituminous coal, high silica, less lime) while $\geq 50\%$ equals to class C of FA (with CaO >10%, originates from sub-bituminous coal, high silica, high lime). The chemical compositions ($SiO_2 + Al_2O_3 + FeO_3$) of cenosphere from Jimah, Kapar and Manjung were 89.39%, 78.32% and 74.35%.

FA with high calcium (Ca) can be classified into CaO, calcium sulphates (Ca_2SO_4), Ca−Al−Si compounds, and Ca−S−X (X: Fe, Al, Si, Mg, etc.) compounds (Zhao et al. 2010)the mineralogical, physical, and chemical properties of several high calcium fly ashes and their different density fractions (<1.0, 1.0-2.5, 2.5-2.89, and >2.89 g/cm3. Ptolemais FA has one of the world's highest CaO contents (35.27%) leading to interest in mineral carbonation (temperature: 160–290 °C, carbon dioxide (CO_2): 1–6 bars) for CO_2 sequestration up to 117.7 g CO_2/kg FA (Ćwik et al. 2018)but also for the valorization and new applications of industrial waste materials from coal-burning power plants. In this study, mineral carbonation of high–calcium fly ash is investigated under dry and moist conditions in a continuous flow reactor during up to 2 h, at temperatures ranging from 160 to 290 °C and CO2 pressures between 1 and 6 bar. A comprehensive characterization of treated and untreated samples was carried out before and after carbonation using X-ray diffraction, X-ray fluorescence spectroscopy, thermogravimetric analysis, infrared spectroscopy and scanning electron microscopy. The maximum sequestration capacity achieved was 117.7 g CO2/kg fly ash (48.14% carbonation efficiency. The CaO content of cenosphere from Jimah, Kapar and Manjung were low equivalent to 3.78, 7.57 and 13.44%.

Cenosphere from Jimah and Kapar are classified as Class F while Manjung is Class C. Concrete mixture for cenosphere from Jimah and Kapar will need extra support for lime (CaO) and can act as admixture. Concrete mixture that contains cenosphere from Manjung will have enough lime for a high calcium silicate hydrate (C-S-H) nucleation reaction and can act as cement replacement material. The C-S-H is a crystalline type of compound and will fill in pores in the concrete producing a denser concrete. Coal ash from Manjung is of high quality and the coal burning process in the plant is well controlled.

The classification depends on the type of oxides in the materials. If the classification does not meet the requirement by ASTM, the alternative classification using CaO content will be applied. Vice versa. Same purpose, different method.

TABLE 2. The XRF analysis for cenosphere from Jimah, Kapar and Manjung in comparison with literatures

Analysis	Parameters	Malaysian Coal Power Plants			(Zyrkowski et al. 2016)	(Wang et al. 2012)	(Xu et al. 2016)	(Hanif et al. 2016)
		Jimah	Kapar	Manjung				
XRF (%)	Al_2O_3	22.63	18.82	14.70	23.30-28.30	28.4	32.07	16.7
	CaO	3.78	7.57	13.44	0.00-14.81	0.8	0.71	1.06
	SiO_2	57.67	49.18	34.73	49.49-60.45	60.1	61.01	73.10
	SO_3	0.42	1.06	1.07	n.a.	0.03	n.a.	0.42
	Fe_2O_3	9.09	10.32	24.92	1.77-5.43	4.8	3.11	1.96
	K_2O	3.62	3.62	3.67	2.04-3.62	3.5	1.65	2.42
	Na_2O	n.a.	n.a.	n.a.	0.00-4.83	0.9	3.11	3.94
	TiO_2	1.76	4.24	3.18	n.a.	n.a.	1.31	0.35
	MnO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.05
	MgO	0.16	0.33	0.93	1.61-7.83	28.4	32.07	16.7

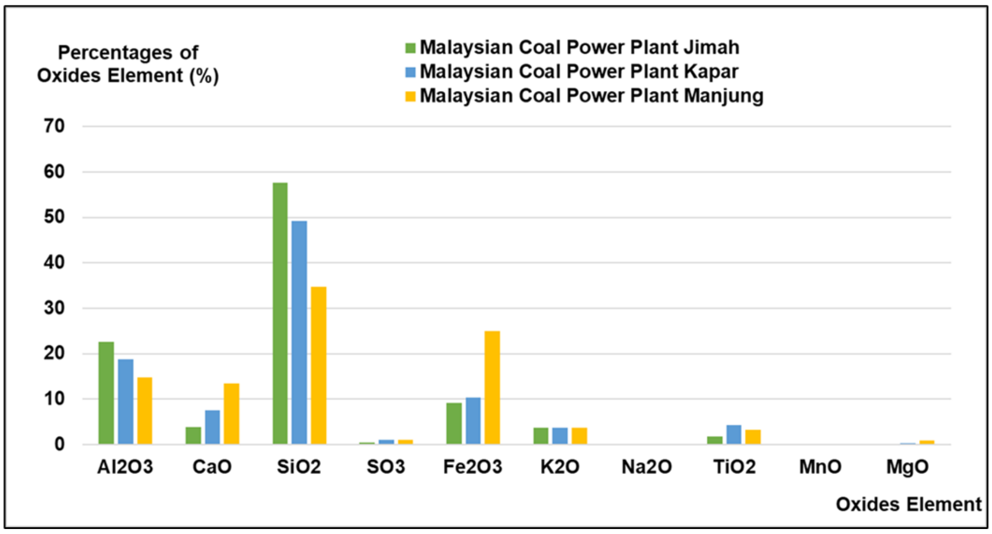

FIGURE 3. The XRF analysis for cenosphere from Jimah, Kapar and Manjung

THE PARTICLE SIZE ANALYSIS

The particles size analysis of cenospheres and FA from Jimah, Kapar and Manjung is shown in Table 3. The diagrams of PSA of cenospheres and FA are shown in Figure 4 and 5. The particles sizes of cenosphere from PSA analysis were ranged from 6.91 to 149.6µm (Jimah), 13.5 to 129.50 µm (Kapar) and 2.249 to 99.90 µm (Manjung). The particles sizes were in sequence of Kapar > Jimah> Manjung. The particle sizes of cenosphere were found to be larger than FA (Jimah: 2.720-49.21 µm, Kapar: 5.069-98.29 µm, Manjung: 1.084-3.986 µm) (Figure 4).

Mandal et al. (2017) reported that the particles size of FA and red mud are similar to clay showing potential to be used as part of raw material for brick production. Cenosphere particles size were larger than FA giving a large surface area practical as modified catalyst (Markandeya et al. 2017) and great thermal insulation behavior for composite material (Mandal et al. 2017).

TABLE 3. The PSA analysis for cenosphere from Jimah, Kapar and Manjung

	Power Plant	Cenosphere	FA
PSA (μm)	Jimah	6.91-149.6	2.720-49.21
	Kapar	13.50-129.50	5.069-98.29
	Manjung	2.249-99.90	1.084-3.986

THE XRD ANALYSIS

The XRD chromatograms of cenospheres from Malaysian power plants are shown in Figure 6. The 2θ scale is an angle between diffracted x-ray with incident x-ray beam. The XRD chromatogram peak or intensity is expressed in arbitrary unit (a.u.). A peak represents number of atoms and electrons in the unit cell of the material. The diffraction pattern of peaks describes atomic arrangement of a material. A smooth gradual scatter indicates the fully amorphous material, while a flat and sharp peak of the graph scatters indicates a fully crystalline material (Sadon et al. 2017). Amorphous content is vital in concrete technology because it increases the material reactivation towards hydration (e.g. water retaining structure), gives positive effect on the strength and durability of concrete. If it is not reactive, it will act as a filler (Mohamad et al. 2017; Mohd Kamal et al. 2021; Yahya et al. 2017). The cenosphere samples contained of both amorphous and crystalline compounds.

Sen (2014) reported that types of crystalline elements that can be detected in cenosphere are quartz (SiO_2), rutile (TiO_2), alumina (Al_2O_3), hematite (Fe_2O_3), dipotassium oxide (K_2O), calcium oxide (CaO), sodium oxide (Na_2O), magnesium oxide (MgO), sillimanite or aluminosilicate (Al_2SiO_5) and mullite or porcelainite ($3Al_2O_32SiO_2$ or $2Al_2O_3SiO_2$). The CaO peak can be detected at 15°. The mullite can be detected at 15°, 25°, 33° and 60°. The SiO_2 can be detected at 22°, 25° and 42°. The TiO_2 can be detected at 25°. The Al_2SiO_5 can be detected 32°, 33°, 60° and 75°. The Al_2O_3 can be detected at 33° and 35°. The K_2O can be detected at 39° and 41°. The CaO is marked at 39°. The Na_2O peak is at 58°. The CaO peak is at 60°. The MgO peak at 75° (Sen, 2014).

Phases with the same chemical composition can have drastically different patterns. The diffraction pattern of a mixture represents a combination of scattering of each phase. The curved line at the first 30° at 2θ position represents glass (SiO_2). Crystobalite (SiO_2) at 22° and quartz (SiO_2) at 26° (Banerjee et al. 2008). The calcium silicate (Ca_2O_4Si) (Hoy et al. 2018)which was evaluated by an unconfined compressive strength (UCS, akermanite ($Ca_2Mg(Si_2O_7)$) (Dimitrova et al. 2012; Thunuguntla and Gunneswara Rao, 2018), gehlenite ($Ca_2Al(AlSi)O_7$) (Dimitrova et al. 2012), melilite ($Ca_2(Al,Mg,Fe)((Al,Si,B)SiO_7)$) (Dimitrova et al. 2012), and quartz (SiO_2) (Łach et al. 2018)especially in construction industry. The paper presents the results of research of geopolymer composites based on geopolymer binders made of metakaolin and fly ash with the addition of titanium oxide and aluminum-calcium cements (including mainly calcium monoglinate can be detected at 45°. These elements are silicates.

The diffraction peaks identification from XRD analysis of cenospheres from Jimah, Kapar and Manjung is shown in Figure 7. The diffraction peaks observed from Jimah were at 15°, 21°, 22°, 25°, 30°, 31°, 33°, 35°, 37°, 39°, 40°, 42°, 50°, 54°, 58°, 61°, and 65°. The possible crystalline compounds observed were mullite (15°), quartz (22°, 25° and 42°), crystobalite (22°), TiO_2 (25°), Al_2SiO_5 (33°), Al_2O_3 (33° and 35°), K_2O (39°), CaO (39°), and Na_2O (58°). The observed diffraction peaks from Kapar were at 21°, 26°, 31°, 33°, 35°, 37°, 38°, 39°, 41°, 43°, 45°, 54°, 58°, 60°, 64° and 65°. The possible crystalline compounds observed were quartz (SiO_2) (26°), mullite (33°), Al_2SiO_5 (33° and 60°), Al_2O_3 (33° and 35°), K_2O (39° and 41°), CaO (39°), silicates (45°), and Na_2O (58°). The diffraction peaks observed from Manjung were at 26°, 38° and 45°. The crystalline compounds observed were quartz (SiO_2) (26°) and silicates (45°).

Cenospheres from Jimah contained quarts while Kapar and Manjung contained high silicates content based on the highest sharp peak at 45° indicating possible crystalline compounds such as Ca_2O_4Si, $Ca_2Mg(Si_2O_7)$, $Ca_2Al(AlSi)O_7$, $Ca_2(Al,Mg,Fe)((Al,Si,B)SiO_7)$, and quartz ($SiO_2$). According to Mandal (Mandal et al. 2017), mineralogical phases such as free silica (SiO_2), kyanite (Al_2SiO_5), Fe_2O_3 and Al_2O_3 exist in FA and red mud (RM) will facilitate fusion of particles and harder phases formation such as crystalline materials (iron and aluminium silicates) upon thermal treatment (1100°C) producing bricks (FA:RM of 60:40, 7.5 wt% saw dust) of higher strength and better bulk density.

THE SEM ANALYSIS

The SEM images of cenospheres from Jimah, Kapar and Manjung are shown in Figure 8. The micromorphology observation of cenosphere from Jimah showed that it has cenosphere and components of irregular-shaped of char particles scattered. The SEM image of cenosphere from Kapar has cenospheres, aluminosilicate spheres attached to cenospheres, dense amount of plerospheres around cenospheres, and subangular of coaly fragments dispersed. The SEM image of cenosphere samples from Manjung showed that the sample has cenospheres, aluminosilicate spheres clump on the surface of cenospheres, and components of irregular-shaped of carbon particles.

Ferrospheres are ferric hollow spheres covered with coarse dendritic block surface and the diameter size is in microns up to 300 μm (Ćwik et al. 2018; Sokol et al. 2002)but also for the valorization and new applications of industrial waste materials from coal-burning power plants. In this study, mineral carbonation of high–calcium fly ash is investigated under dry and moist conditions in a continuous flow reactor during up to 2 h, at temperatures ranging from 160 to 290 °C and CO2 pressures between 1 and 6 bar. A comprehensive characterization of treated and untreated samples was carried out before and after carbonation using X-ray diffraction, X-ray fluorescence spectroscopy, thermogravimetric analysis, infrared spectroscopy and scanning electron microscopy. The maximum sequestration capacity achieved was 117.7 g CO2/kg fly ash (48.14% carbonation efficiency. It is used as catalyst for high-temperature oxidative conversion of methane (Sokol et al. 2002). Ferrospheres originates from brown coals (Sokol et al. 2002). The significant brown color of FA and cenosphere was observed from Manjung (Fe_2O_3: 24.92%) (Figure 2).

The cenosphere is mesoporous of smooth surface, rich in aluminum (Al) and silicon (Si) content (Goodarzi and Sanei, 2009; Guo et al. 2021; Xi et al. 2020). The microstructure itself beneficial as fillers and the minerals will assist fusion of particles and harder phases formation required for nucleation reaction, pozzolanic activity and accelerate pozzolanic activity (Mandal et al. 2017; Xi et al. 2020). Markandeya et al. (2017) synthesized chitosan cenospheres (10:3) nanocomposite using a crosslinking agent namely glutaraldehyde, precipitated in alkaline solution to adsorb dyes in wastewater (disperse orange 25 and disperse blue 79:1). Hanif et al. (2016) also reported that cenosphere from FA provide excellent structural lightweight ferrocement composites (fibrous mortar).

Aluminosilicate spheres (whitish color) are metal silicate spheres of functional permeable shell, with large inner space and lighter density (Kosari et al. 2020; Li et al. 2011). It can be fused with copper via a one-pot hydrothermal process and used as heterogeneous catalyst for advanced oxidation processes to remove olefin in refinery wastewater (Kosari et al. 2020). Plerospheres are thin walled silicate spheres encapsulated tiny spheres of FA particles inside with diameter less than 10 µm (Goodarzi and Sanei, 2009; Raask, 1985). Carbon content in FA ranged from 2.3 to 25.3 wt% (Shibaoka, 1986). Carbon or char particles are directly proportional to the carbon content of FA. The more carbon in the coal, the more irregular-shaped of char particles will be observed in the FA or cenosphere samples (Hanif et al. 2017, 2016; Markandeya et al. 2017; Shibaoka 1986).

FA contains of many spherical and other variant structures such as ferrospheres, cenospheres, aluminosilicate spheres, plerospheres, sub-angular minerals (quartz/feldspars) (Goodarzi and Sanei, 2009) and irregular-shaped char particles (Yadav, 2021; Yadav et al. 2020; Yadav and Fulekar, 2020). Since cenosphere is a part of components in FA, the morphological components will be relatively the same (Ćwik et al. 2018; Guo et al. 2021).

CONCLUSION

The current research conveys the first study on cenosphere from Malaysian power plants (Jimah, Kapar and Manjung) based on the physicochemical properties that are beneficial for various applications in industrial technology. Cenosphere has large particle size, large surface area, and unique chemical property. The percentages of CaO content detected in cenosphere samples were low and MgO was not detected at all indicating carbonation for sequestering CO_2 production is possible but not practical and cost sufficient. Therefore, reapplication of this sustainable material is highly recommended. At high temperature, other oxides elements will facilitate fusion of particles and harder phases formation (e.g. crystalline materials) especially for brick production. At normal temperature, these minerals will form nucleation and speed up pozzolanic reaction during hydration process of composite material containing cement. The particles sizes of cenosphere were larger than FA. It is a good indication as catalyst for wastewater treatment, promoting insulation behaviour and high strength to composite material. The sequence of cenosphere size is Kapar > Jimah> Manjung. Components of microstructure observed were ferrospheres, cenosphere, aluminosilicate spheres, plerospheres and sub-angular carbon fragments. Ferrospheres are useful as catalyst for methane production. Cenosphere can be used as a filler and also promoting high strength in concrete as cement replacement material whilst reducing greenhouse gas emission via cement usage cut down in concrete. It is also functioning as catalyst for dye removal in wastewater treatment. Aluminosilicate spheres can be used as catalyst for advanced oxidation process in removing olefin from plant wastewater. This research is significant because it promotes a sustainable material for the industrial technology such as engineering and manufacturing fields. Cenosphere will not only contribute towards energy conservation, reducing the greenhouse gas emission but also will boost economic growth in Malaysia.

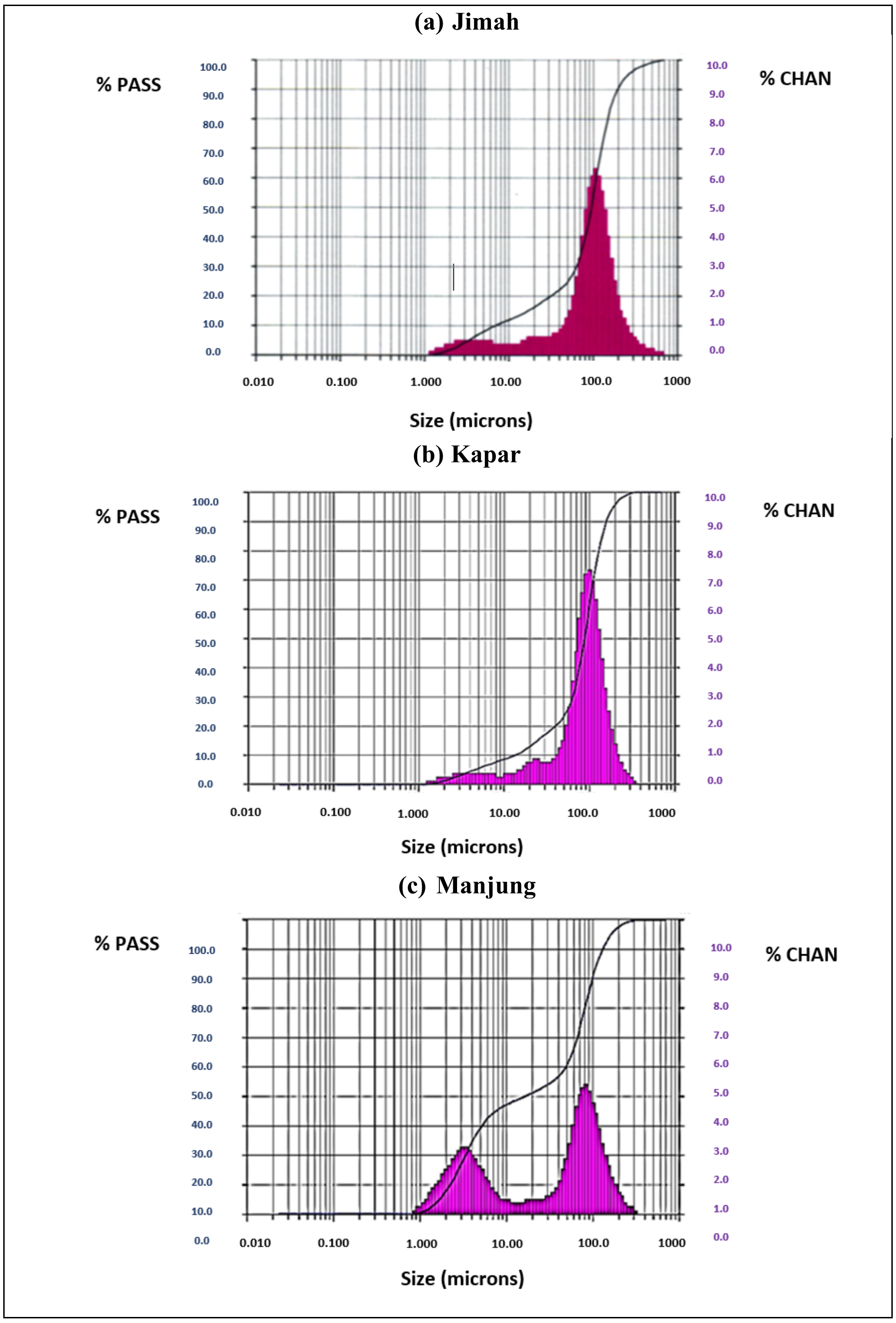

FIGURE 4. PSA images for cenospheres from Jimah, Kapar and Manjung

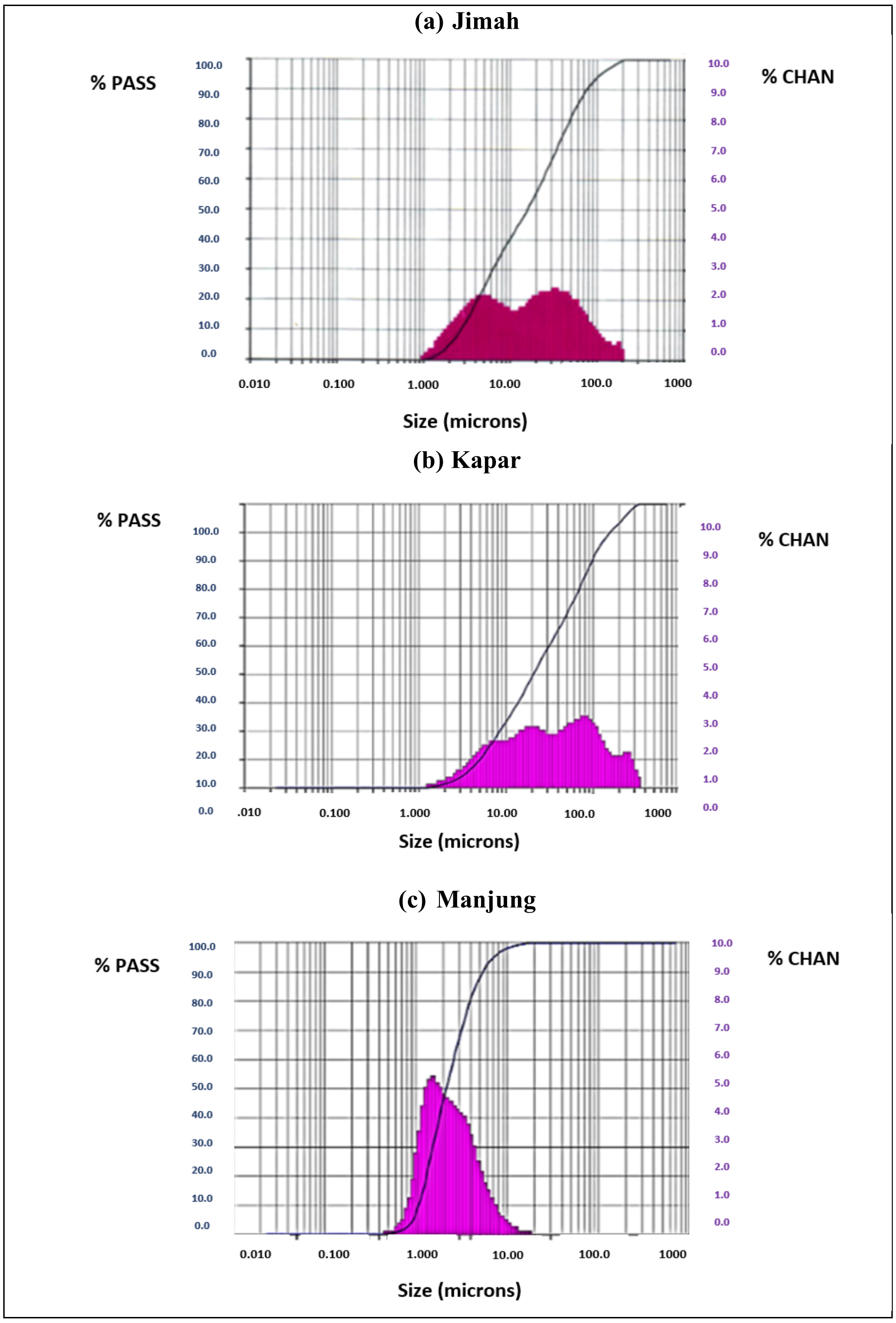

FIGURE 5. PSA images for FA from Jimah, Kapar and Manjung

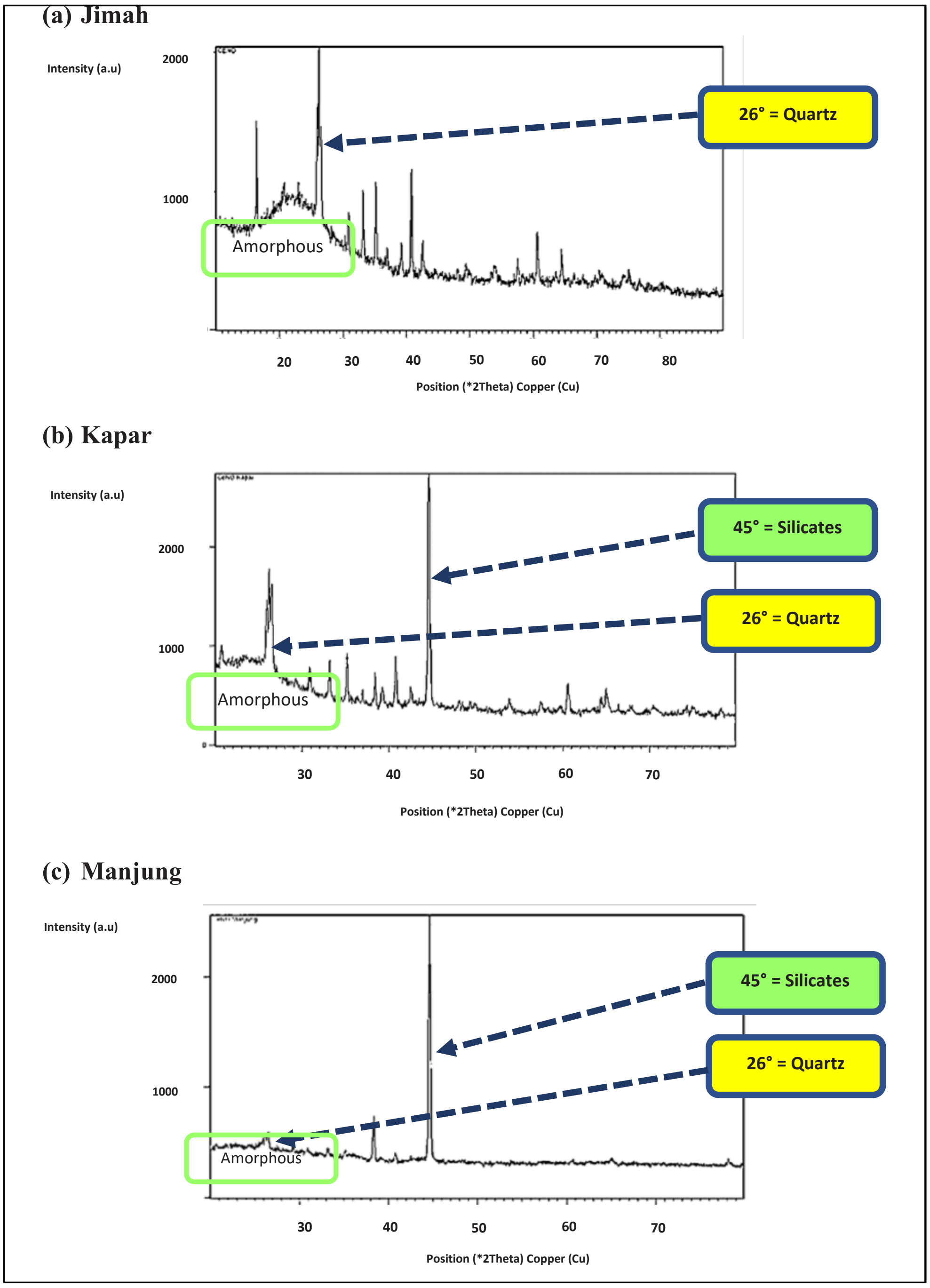

FIGURE 6. The XRD analysis for cenospheres from Jimah, Kapar and Manjung

Notes: 26°: quartz (SiO_2), 45° : Silicates (i.e. Ca_2O_4Si, $Ca_2Mg(Si_2O_7)$, $Ca_2Al(AlSi)O_7$, $Ca_2(Al,Mg,Fe)((Al,Si,B)SiO_7)$, or quartz ($SiO_2$))

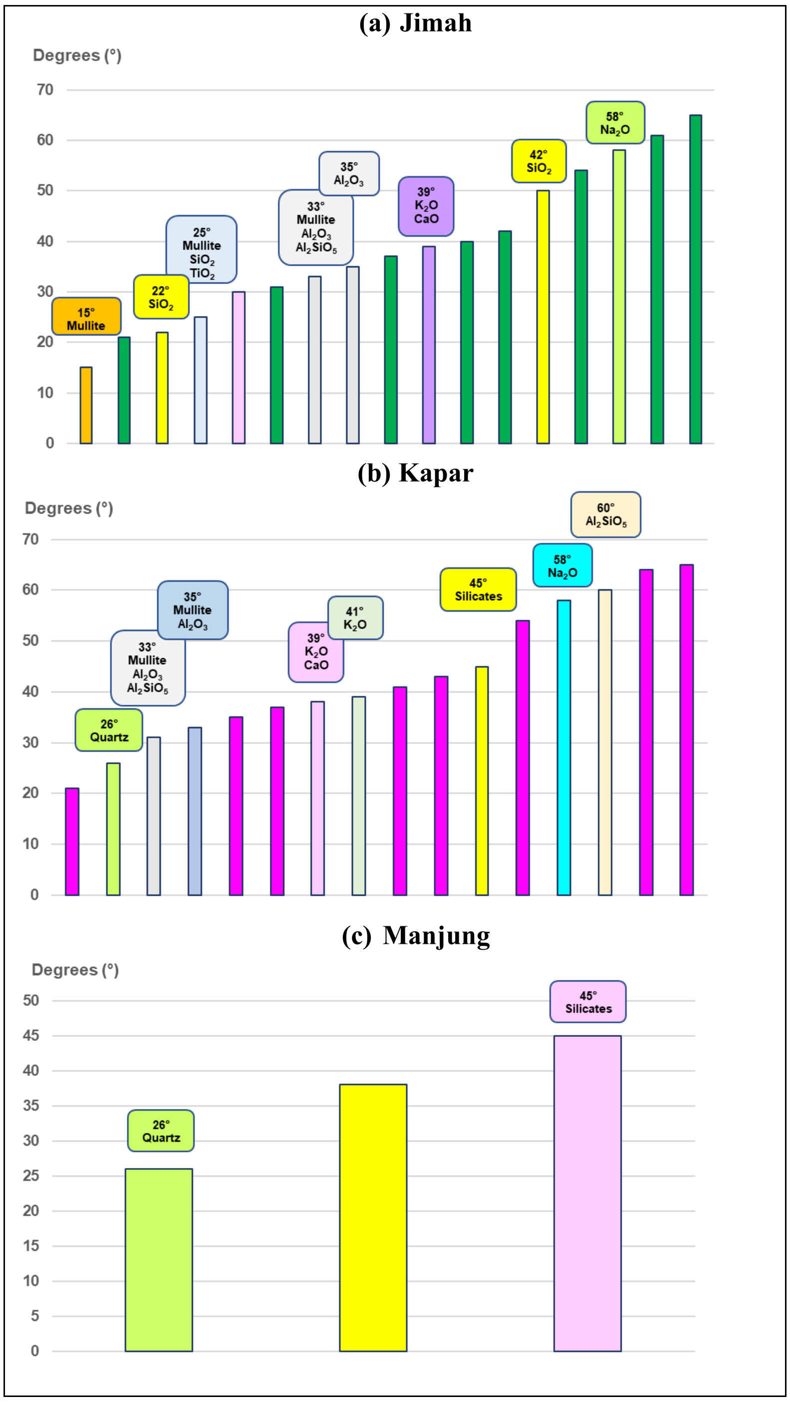

FIGURE 7. The diffraction peaks identification from XRD analysis of cenospheres from Jimah, Kapar and Manjung

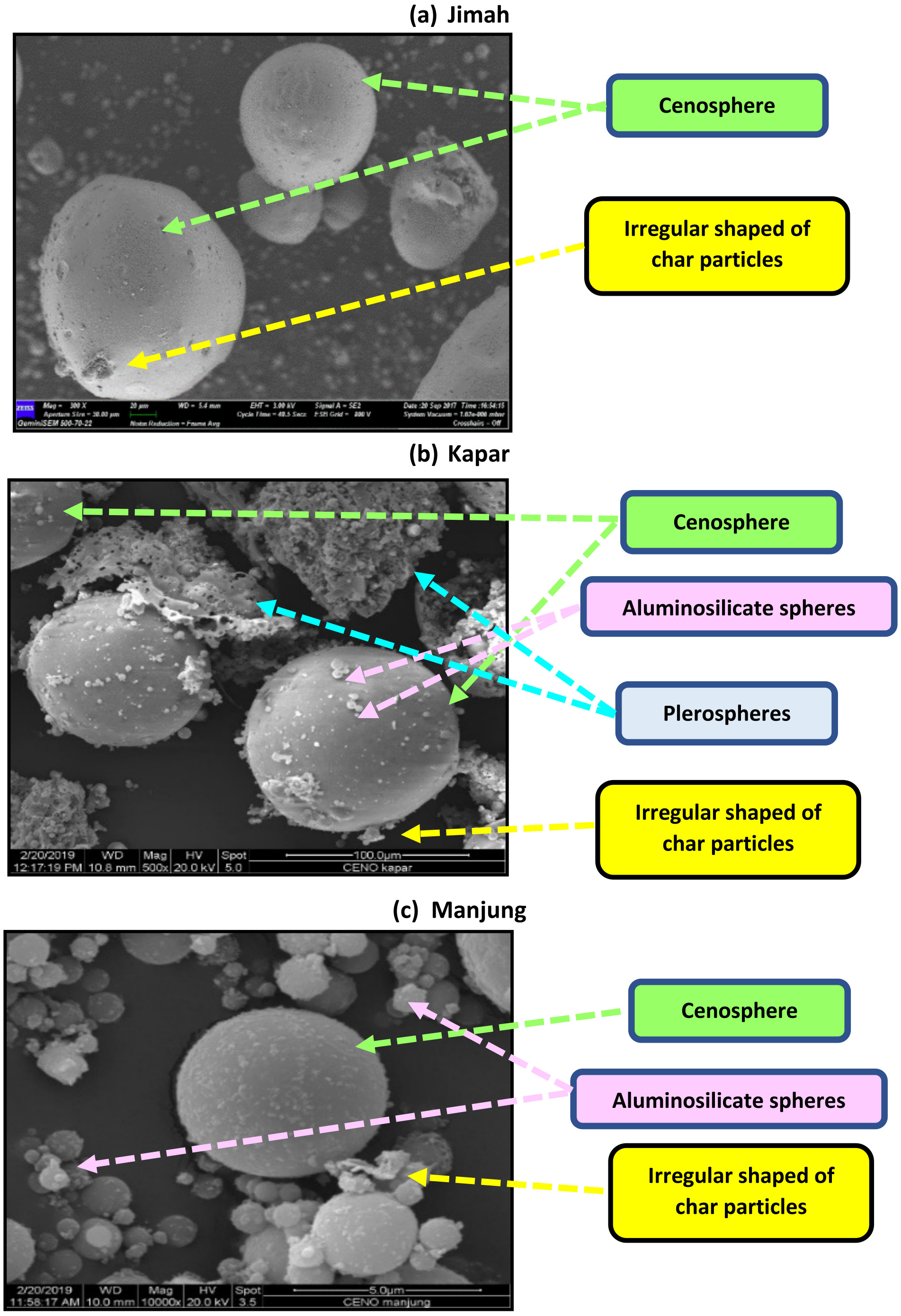

FIGURE 8. The SEM images of cenospheres from Jimah, Kapar and Manjung

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DECLARATION OF COMPETING INTEREST

None

REFERENCES

Abd Manan, T.S.B., Beddu, S., Mohamad, D., Mohd Kamal, N.L., Wan Mohtar, W.H.M., Khan, T., Jusoh, H., Sarwono, A., M. Ali, M., Che Muda, Z., Mohamed Nazri, F., Isa, M.H., Ghanim, A.A.J., Ahmad, A., Wan Rasdi, N., Basri, N.A.N., 2021. Physicochemical and Leaching Properties of Coal Ashes from Malaysian Coal Power Plant. Chem. Phys. Lett. 138420. https://doi.org/10.1016/j.cplett.2021.138420

American Society for Testing and Materials, 1994. ASTM C618-05: Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete, in Annual book of ASTM standards, vol 04.02 1994. United States of America.

Banerjee, D., Suresh, K.G., Nigam, A.K., 2008. Effect of Y substitution on the structural and magnetic properties of Dy1-xYxCo5 compounds. J. Magn. Magn. Mater. 320, 374–378. https://doi.org/10.1016/j.jmmm.2007.06.011

Beddu, S., Abd Manan, T.S.B., Zainoodin, M.M., Khan, T., Wan Mohtar, W.H.M., Nurika, O., Jusoh, H., Yavari, S., Kamal, N.L.M., Ghanim, A.A., Pati, S., Abdullah, M.T., 2020. Dataset on leaching properties of coal ashes from Malaysian coal power plant. Data Br. 31, 105843. https://doi.org/10.1016/j.dib.2020.105843

Beddu, S., Zainoodin, M., Basri, A., Itam, Z., Ahmadi, R., Abd Manan, T.S., 2021. The potential of cenospheres production from Malaysian coal power plants. IOP Conf. Ser. Mater. Sci. Eng. 1101, 012012. https://doi.org/10.1088/1757-899x/1101/1/012012

Beddu, S., Zainoodin, M., Kamal, N.M., Mohamad, D., Nabihah, S., Nazri, F.M., 2018. Material characterization of coal combustion product (cenosphere) generated from coal - Fired power plant in Malaysia, in: AIP Conference Proceedings. American Institute of Physics Inc., p. 020259. https://doi.org/10.1063/1.5066900

Blissett, R., 2015. COAL FLY ASH AND THE CIRCULAR ECONOMY. The University of Birmingham.

Brooks, A.L., Shen, Z., Zhou, H., 2020. Development of a high-temperature inorganic synthetic foam with recycled fly-ash cenospheres for thermal insulation brick manufacturing. J. Clean. Prod. 246, 118748. https://doi.org/10.1016/j.jclepro.2019.118748

Canadian Standards Association, 2004. Cementitious Materials Used in Concrete CAN/CSA-A3001-13 [See A3000-13]. Canada.

Ćwik, A., Casanova, I., Rausis, K., Koukouzas, N., Zarębska, K., 2018. Carbonation of high-calcium fly ashes and its potential for carbon dioxide removal in coal fired power plants. J. Clean. Prod. 202, 1026–1034. https://doi.org/10.1016/j.jclepro.2018.08.234

Dimitrova, S. V, Mihailova, I.K., Nikolov, V.S., Mehandjiev, D.R., 2012. Adsorption capacity of modified metallurgical slag, Bulgarian Chemical Communications.

Goodarzi, F., Sanei, H., 2009. Plerosphere and its role in reduction of emitted fine fly ash particles from pulverized coal-fired power plants. Fuel 88, 382–386. https://doi.org/10.1016/j.fuel.2008.08.015

Guo, H., Yuan, P., Zhang, B., Wang, Q., Deng, L., Liu, D., 2021. Realization of high-percentage addition of fly ash in the materials for the preparation of geopolymer derived from acid-activated metakaolin. J. Clean. Prod. 285, 125430. https://doi.org/10.1016/j.jclepro.2020.125430

Hanif, A., Diao, S., Lu, Z., Fan, T., Li, Z., 2016. Green lightweight cementitious composite incorporating aerogels and fly ash cenospheres - Mechanical and thermal insulating properties. Constr. Build. Mater. 116, 422–430. https://doi.org/10.1016/j.conbuildmat.2016.04.134

Hanif, A., Lu, Z., Sun, M., Parthasarathy, P., Li, Z., 2017. Green lightweight ferrocement incorporating fly ash cenosphere based fibrous mortar matrix. J. Clean. Prod. 159, 326–335. https://doi.org/10.1016/j.jclepro.2017.05.079

Hirajima, T., Petrus, H.T.B.M., Oosako, Y., Nonaka, M., Sasaki, K., Ando, T., 2010. Recovery of cenospheres from coal fly ash using a dry separation process: Separation estimation and potential application. Int. J. Miner. Process. 95, 18–24. https://doi.org/10.1016/j.minpro.2010.03.004

Hoy, M., Horpibulsuk, S., Arulrajah, A., Mohajerani, A., 2018. Strength and Microstructural Study of Recycled Asphalt Pavement: Slag Geopolymer as a Pavement Base Material. J. Mater. Civ. Eng. 30, 04018177. https://doi.org/10.1061/(asce)mt.1943-5533.0002393

Jiang, F., Zhang, L., Mukiza, E., Qi, Z., Cang, D., 2018. Formation mechanism of high apparent porosity ceramics prepared from fly ash cenosphere. J. Alloys Compd. 749, 750–757. https://doi.org/10.1016/j.jallcom.2018.03.303

Kosari, M., Seayad, A.M., Xi, S., Kozlov, S.M., Borgna, A., Zeng, H.C., 2020. Synthesis of Mesoporous Copper Aluminosilicate Hollow Spheres for Oxidation Reactions. ACS Appl. Mater. Interfaces 12, 23060–23075. https://doi.org/10.1021/acsami.0c03052

Łach, M., Korniejenko, K., Hebdowska-Krupa, M., Mikuła, J., 2018. The Effect of Additives on the Properties of Metakaolin and Fly Ash Based Geopolymers, in: MATEC Web of Conferences. EDP Sciences. https://doi.org/10.1051/matecconf/201816306005

Li, J., Zhang, D., Gao, Q., Xu, Y., Wu, D., Sun, Y., Xu, J., Deng, F., 2011. Hollow mesoporous aluminosilicate spheres with acidic shell. Mater. Chem. Phys. 125, 286–292. https://doi.org/10.1016/j.matchemphys.2010.09.036

Mandal, A.K., Verma, H.R., Sinha, O.P., 2017. Utilization of aluminum plant's waste for production of insulation bricks. J. Clean. Prod. 162, 949–957. https://doi.org/10.1016/j.jclepro.2017.06.080

Markandeya, Dhiman, N., Shukla, S.P., Kisku, G.C., 2017. Statistical optimization of process parameters for removal of dyes from wastewater on chitosan cenospheres nanocomposite using response surface methodology. J. Clean. Prod. 149, 597–606. https://doi.org/10.1016/j.jclepro.2017.02.078

Mohamad, D., Beddu, S., Nabihah Sadon, S., Liyana Mohd Kamal, N., Itam, Z., Mohamad, K., Mohd Sapua, W., 2017. Self-curing Concrete using Baby Diapers Polymer. Indian J. Sci. Technol. 10, 1–7. https://doi.org/10.17485/ijst/2017/v10i4/110895

Mohd Kamal, N.L., Shafiq, N., Alaloul, W.S., Beddu, S., Abd Manan, T.S.B., 2021. Application of Response Surface Methodology for the Optimization of Mix Design Concrete Using Coal Bottom Ash as Cement Replacement Material. Lect. Notes Civ. Eng. 132, 396–404. https://doi.org/10.1007/978-981-33-6311-3_45

Noor-Ul-Amin, 2014. A multi-directional utilization of different ashes. RSC Adv. https://doi.org/10.1039/c4ra06568a

Oh, T.H., 2010. Carbon capture and storage potential in coal-fired plant in Malaysia - A review. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2010.06.003

Raask, E., 1985. Mineral Impurities in Coal Combustion: Behavior, Problems, and Remedial Measures. United States.

Ramme, B.W., Noegel, J.J., Rohatgi, P.K., 2013. Separation of Cenospheres from Fly Ash. US8,520,210 B2.

Sadon, S.N., Beddu, S., Naganathan, S., Mohd Kamal, N.L., Hassan, H., 2017. Coal Bottom Ash as Sustainable Material in Concrete - A Review. Indian J. Sci. Technol. 10, 1–10. https://doi.org/10.17485/ijst/2017/v10i36/114595

Sen, S., 2014. PHYSICAL PROPERTIES OF CENOSPHERE. National Institute of Technology Rourkela, Rourkela.

Shibaoka, M., 1986. Carbon content of fly ash and size distribution of unburnt char particles in fly ash. Fuel 65, 449–450. https://doi.org/10.1016/0016-2361(86)90314-5

Sokol, E. V., Kalugin, V.M., Nigmatulina, E.N., Volkova, N.I., Frenkel, A.E., Maksimova, N. V., 2002. Ferrospheres from fly ashes of Chelyabinsk coals: Chemical composition, morphology and formation conditions. Fuel 81, 867–876. https://doi.org/10.1016/S0016-2361(02)00005-4

Thunuguntla, C.S., Gunneswara Rao, T.D., 2018. Appraisal on Strength Characteristics of Alkali-Activated GGBFS with Low Concentrations of Sodium Hydroxide. Iran. J. Sci. Technol. - Trans. Civ. Eng. 42, 231–243. https://doi.org/10.1007/s40996-018-0113-4

Wang, J.Y., Zhang, M.H., Li, W., Chia, K.S., Liew, R.J.Y., 2012. Stability of cenospheres in lightweight cement composites in terms of alkali-silica reaction. Cem. Concr. Res. 42, 721–727. https://doi.org/10.1016/j.cemconres.2012.02.010

Wang, L., Zhang, B., Zhang, J., Jiang, Y., Wang, W., Wu, G., 2021. Deformation and energy absorption properties of cenosphere-aluminum syntactic foam-filled tubes under axial compression. Thin-Walled Struct. 160, 107364. https://doi.org/10.1016/j.tws.2020.107364

Wrona, J., Żukowski, W., Bradło, D., Czupryński, P., 2020. Recovery of Cenospheres and Fine Fraction from Coal Fly Ash by a Novel Dry Separation Method. Energies 13, 3576. https://doi.org/10.3390/en13143576

Xi, B., Zhou, Y., Yu, K., Hu, B., Huang, X., Sui, L., Xing, F., 2020. Use of nano-SiO2 to develop a high performance green lightweight engineered cementitious composites containing fly ash cenospheres. J. Clean. Prod. 262, 121274. https://doi.org/10.1016/j.jclepro.2020.121274

Xu, B., Ma, H., Hu, C., Li, Z., 2016. Influence of cenospheres on properties of magnesium oxychloride cement-based composites. Mater. Struct. Constr. 49, 1319–1326. https://doi.org/10.1617/s11527-015-0578-6

Yadav, V., 2021. Fly Ash | Encyclopedia [WWW Document]. Sch. Community Encycl. URL https://encyclopedia.pub/item/revision/5bbd5a240a21a0d9e706b166342b24ac (accessed 4.20.21).

Yadav, V., Choudhary, N., Mallik, P., Khan, S.H., Rajendran, S., Inwati, G.K., 2020. Recovery of natural nanostructured minerals-Ferrospheres, Plerospheres, Cenospheres, and Carbonaceous particles from fly ash, Handbook of Research on Emerging Developments and Environmental Impacts of Ecological Chemistry. IGI Global.

Yadav, V.K., Fulekar, M.H., 2020. Advances in Methods for Recovery of Ferrous, Alumina, and Silica Nanoparticles from Fly Ash Waste. Ceramics 3, 384–420. https://doi.org/10.3390/ceramics3030034

Yahya, A.A., Ali, N., Mohd Kamal, N.L., Shahidan, S., Beddu, S., Nuruddin, M.F., Shafiq, N., 2017. Reducing Heavy Metal Element from Coal Bottom Ash by Using Citric Acid Leaching Treatment. MATEC Web Conf. 103, 01004. https://doi.org/10.1051/matecconf/201710301004

Yoriya, S., Intana, T., Tepsri, P., 2019. Separation of cenospheres from lignite fly ash using acetone-water mixture. Appl. Sci. 9, 3792. https://doi.org/10.3390/app9183792

Zhao, Y., Zhang, J., Tian, C., Li, H., Shao, X., Zheng, C., 2010. Mineralogy and chemical composition of high-calcium fly ashes and density fractions from a coal-fired power plant in China. Energy and Fuels 24, 834–843. https://doi.org/10.1021/ef900947y

Zyrkowski, M., Neto, R.C., Santos, L.F., Witkowski, K., 2016. Characterization of fly-ash cenospheres from coal-fired power plant unit. Fuel 174, 49–53. https://doi.org/10.1016/j.fuel.2016.01.061