Stability of kaolin particles subjected to elevated temperatures using various dispersing agents

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Abstract. The stability of kaolin particles is largely influenced by nature and the behaviour of dispersing agents introduced to the system. This study analysed the size of kaolin particles subjected to elevated temperatures by using various dispersing agents such as ultrapure water (UPW), acetone (Ace) and sodium hydroxide (NaOH). It was found that kaolin particles in UPW formed a stable dispersion compared to particles in Ace and NaOH without further aggregation. Interestingly, kaolin particles under UPW, Ace, and NaOH dispersants had a strong affinity for water and can be classified as possessing hydrophilic behaviour. The mean size of kaolin particles was reduced under UPW and Ace dispersion but increased under NaOH suspension. Under UPW dispersion, kaolin particles ranged from 141.8nm to 5560nm, creating a mid-range monodisperse size distribution (0.08 < PDI < 0.7) without any presence of agglomeration due to high potential energy barrier and electrostatic repulsion. Kaolin particles subjected to NaOH dispersant produced a narrow distribution of particle sizes ranging from 295.3nm to 1106nm but appeared to agglomerate because of Van der Waals interactions. In contrast, the Ace dispersant produced a very broad polydisperse particle size distribution (PDI > 0.7) of greater than 10µm in kaolin with a little aggregation but lacking consistency in terms of stability. However, all dispersants contributed to the kaolin particles dispersion but UPW shown more stability dispersion due to increase in number of hydroxyl groups in dispersant molecule. In conclusion, this simple and low cost methodology can be useful in characterising kaolin particle sizes with limited resources.

1. Introduction
Kaolin has always been widely used in many areas of applications such as arts, ceramics, chemicals, coatings, construction materials, cosmetics, paints, pharmaceuticals and treatments. In construction materials, kaolin is often pulverized to reduce its size and subjected to elevated temperatures in order to achieve a state of highly reactive particles for cementing applications [1-2]. This industry requires a stable, uniform and homogeneous colloidal system in order to meet the standard and quality of production [3-4]. Due to that reason, the stability of aqueous kaolin dispersion is important and often used as a decisive factor [5-6]. However, the stability of kaolin dispersion can be influenced by many factors such as the chemistry of dispersions, the properties of particles in the dispersants as well as process conditions [7].

Kaolin minerals are aluminosilicates containing hydroxyl structure groups that usually carry negative charges. Thus, effective dispersants for kaolin dispersion should be from the group of anionic...
solvents [8]. Most dispersants help to prevent the aggregation of kaolin particles through surface adsorption in order to induce electrostatic or steric repulsion forces between particles [9]. In addition, the aggregation of kaolin particles is caused by the interaction between positive and negative charges at the edges and on the basal face of the heterogeneous surface of kaolin particles while in contact with the surrounding environment [10]. Thus, the selection of dispersants is important so that the kaolin particles are successfully dispersed into the suspending solvent and to facilitate a stable dispersion without any form of aggregation [11].

Dynamic light scattering (DLS) is a fast and reliable tool in particle size analysis for determining the mean size, particle size distribution and polydispersity index (PDI) of particles. This method exploits the dynamic fluctuation of scattered light to measure the average size of particles. The particle size is measured by the assumption that each particle is a perfect sphere. Thus, this tool can be useful for deciding the condition of particle dispersion to observe the presence of particle agglomeration in the system.

In this study, the effects of different dispersants on the mean size, particle size distribution and PDI of kaolin particles were examined by using a DLS tool known as a Zetasizer particle size analyser. The dispersion behaviour and sedimentation performance of kaolin particles under different dispersants were also determined. This helps a lot in selecting the appropriate solvents and dispersing agents for better stability while reducing the tendency for agglomeration.

2. Experimental procedures

Kaolin (Malaysia) Sdn Bhd under the brand name KM65 commercialized the kaolin particles. The elemental analysis indicated that the kaolin particles contained 64.16% SiO$_2$, 28.59% Al$_2$O$_3$, 2.16% K$_2$O, 1.87% MgCO$_3$, 1.65% Fe$_2$O$_3$, 0.98% TiO$_2$, 0.35% CaCO$_3$, 0.13% P$_2$O$_5$, 0.08 % SO$_3$ and 2.47% loss on ignition. Kaolin particles were exposed to elevated temperatures of 600°C, 700°C and 800°C for durations of 3hr and 4hr in a general purpose industrial chamber furnace (Carbolite GPC1200, Carbolite Gero Limited, UK) as described in Table 1.

| Sample | Temperature (°C) | Duration (hr) |
|--------|-----------------|---------------|
| K      | 0               | 0             |
| MK 600-3 | 600            | 3             |
| MK 600-4 | 600            | 4             |
| MK 700-3 | 700            | 3             |
| MK 700-4 | 700            | 4             |
| MK 800-3 | 800            | 3             |
| MK 800-4 | 800            | 4             |

Ultrapure water (ELGA PURELAB®, Option-R, ELGA LabWater, UK), acetone (anhydrous, 99.5%, Bendosen Laboratory Chemicals, Malaysia) and sodium hydroxide (50%, RDeH Chemicals, Malaysia) denoted as UPW, Ace, and NaOH respectively were tested as dispersing agents for kaolin particles. The dispersion procedures involved a mixing process between kaolin particles and dispersing agents at a ratio of 0.05 in a 10ml graduated cylinder with a stopper in accordance with ISO 148887: 2000 [12]. The mixtures were manually agitated for at least 1hr at room temperature until a complete settlement. The particle size in liquid suspension was measured at a temperature of 25°C using a particle size analyser (Zetasizer Nano ZS, Malvern Instruments, UK), at a backscatter angle of 173°. The refractive index for the material and dispersing agents was 1.57 for kaolin, 1.33 for ultrapure water, 1.356 for acetone, and 1.358 for sodium hydroxide. The mean size value was reported as the mean diameter of kaolin particles using a cumulants analysis together with the effective sizes of D10, D50 and D90 using particle distribution analysis. The polydispersity index (PDI) was determined based on the classification: <0.05 is monodisperse, 0.08 to 0.7 is nearly to mid-range monodisperse,
and $>0.7$ is polydisperse. The dispersion stability of kaolin particles under various dispersing agents were determined by using sedimentation test under gravity condition that recorded daily.

3. Results and discussion

3.1. Effects of Various Dispersing Agents on the Dispersion Behaviour

Figures 1 (a) and (b) present the dispersion behaviour of kaolin particles subjected to elevated temperatures using various dispersing agents. The results indicated that kaolin particles under UPW, Ace and NaOH dispersants had a strong affinity for water and can be classified as possessing a hydrophilic behaviour. Under hydrophilic behaviour, as observed visual, a stable suspension formed by mixing the particles in UPW, Ace or NaOH aqueous solution to separate the particles from large agglomeration. The critical stage in the production of kaolin particles is making sure the primary particles disperse in the suspension solvents and a stable dispersion can be achieved during separation without aggregation [11]. The degree of particle dispersion in the suspension can be defined by the ability of individual particles to separate from one another in the liquid medium to achieve an optimum dispersant requirement that depends upon particle properties and dispersion medium. The stability of the particles depend on the main chain length, the size, position and number of branching chains on the adsorbed layer thickness of kaolin particles in the solvents as well as the solvency of the medium [13]. Dry kaolin particles are aluminosilicates containing hydroxyl groups that are often associated with tightly bound aggregates of particles when in contact together before dispersion [11]. The formation of aggregates is dependent upon the chemistry of particle surfaces. The increase in the number of hydroxyl groups in the dispersant molecules also helps to improve the sedimentation of kaolin particles in terms of packing density. In this study, the dispersing agents used in the preparation of a stable liquid suspension for kaolin particles subjected to elevated temperatures are considered homogeneous and can be further analysed with DLS.

![Figure 1](a) Initial, (b) after dispersion of kaolin particles with (A) UPW - hydrophilic, (B) Ace - hydrophilic and (C) NaOH – hydrophilic

The mean sizes of kaolin particles were reduced under elevated temperature using various dispersing agents of UPW (from $3.55E5\pm4.94E5$nm to $4635\pm1841$nm) and Ace (from $1.16E6\pm1.30E6$nm to $1.36E5\pm1.25E5$nm) dispersions but increased under NaOH suspension (from $632\pm98$nm to $1121\pm128$nm). Types of dispersing agents have an influence on the mean size of kaolin mineral particles. Under UPW and Ace suspensions, small kaolin particles are caused by the electrostatic repulsion developed between particles and dispersant that can be identified as deflocculated suspension particles that can settle slowly [14-15]. In contrast, the increase in the mean size of kaolin particles in the NaOH dispersion or often known as flocculated suspension particles create aggregates caused by Van der Waals interactions to settle fast [14]. The increase in kaolin particle size is also often associated with problems such as agglomeration, flocculation and sedimentation because of high surface area, microparticles or nanoparticles forming aggregates, and agglomerates due to Van der Walls or other attractive forces such as hydrogen bonding [16]. This is
because pH, surface charge of particles and surfactants, zeta potential and particle surface coatings affects the stability, particle interactions, sizing and dispersion behaviour of kaolin particles [17].

3.2. Effects of Various Dispersing Agents on the Particle Size Distribution

Figures 2(a), (b), (c), (d), (e), (f) and (g) indicate the particle size distribution of kaolin particles subjected to elevated temperatures using various dispersing agents.

**Figure 2.** (a) Kaolin, (b) MK600-3, (b) MK600-4, (d) MK700-3

Under UPW dispersion, kaolin particles ranged from 141.8nm to 5560nm to create a mid-range size distribution while the Ace dispersant produced a very broad particle size distribution greater than 10µm (Figures 2 (d), (e), (f) and (g)). Kaolin particles subjected to elevated temperatures under the NaOH dispersant have produced a narrow distribution of particle sizes ranging from 295.3nm to 1106nm as shown in Figures 3 (e), (f) and (g).
The particle size distribution tends to be broader if the particle formation is longer and continues beyond a certain period [18]. The colloidal stable suspensions produced higher packing densities and a narrower pore size distribution when compared to strongly flocculated suspensions [19]. In order to produce kaolin particles which meets the standard, a narrow-sized distribution and uniform inter-particle pores are essential [11]. A decrease in particle size influences the dispersion stability in connection with the sedimentation rate due to an increase in the tendency of particle settlement packing as observed in kaolin particles under NaOH suspension [20]. As particle size decreases, the size distribution becomes more monodisperse due to an increase in the hydrophilicity behaviour of the dispersant and ion group effects [18]. The type of dispersant agent, pH and the presence of other substances influences kaolin particle distribution [17]. However, particles subjected to higher molecular weight stabilise more effectively but has a tendency to produce polydisperse particles because of the high viscosity and different grafting probability in dispersants [18].

3.3. Effects of Various Dispersing Agents on the Polydispersity
The polydispersity index indicates whether individual particles have separated from the bigger particle clusters to form monodisperse particles. In the UPW suspension, kaolin particles exhibited a broad range of polydispersity (PDI > 0.7) in the original kaolin sample to mid-range monodispersity (0.08 <
PDI < 0.7) for kaolin samples subjected to elevated temperatures through DLS characterisation without any presence of agglomeration. In contrast, the NaOH dispersant displayed a mid-range monodispersity (0.08 < PDI < 0.7) for original kaolin particles to a broad range of polydispersity (PDI > 0.7) for kaolin undergoing calcination treatment which caused the particles to agglomerate. However, kaolin particles under the Ace suspension displayed an inconsistency in dispersion stability, showing interchangeably between a broad range of polydispersity (PDI > 0.7) and mid-range monodispersity (0.08 < PDI < 0.7). The existence of a potential energy barrier between particles led to interactions between the electrical double layers and van der Waals energy that are responsible for the stable dispersions [5]. Under Ace and NaOH dispersants, kaolin particles appeared to agglomerate due to the small potential energy barrier but stabilised in the UPW suspension due to the high potential energy barrier. Besides, kaolin particles are unable to attain high packing density (i.e. tends to agglomerate) are often associated with failures in terms of achieving of deagglomeration and a complete dispersion of dry particles into the solvent, particles setting in the liquid media without agglomeration caused by inter-particle interactions, a surface charge and thick layer on particles to prevent agglomeration and a high mobility and low friction within the sediment to allow optimum packing [11, 21].

3.4. Effects of Various Dispersing Agents on the Sedimentation

Figures 3 (a), (b), (c), (d), (e), (f) and (g) show the sedimentation height of kaolin particles subjected to elevated temperatures using various dispersing agents. The settling rate of the sediments went very fast during the first day but started to settle more slowly in the second to seventh days of experiment as shown in Figures 2 (b), and (c).

![Figure 3](image-url)
This type of sedimentation rate known as fast settlement due to interface between the supernatant liquid and consolidation sediment to move down at rapid speed [21]. The suspensions indicated opaque and cloudy portions containing flocs in the first day but fine particles gradually settled down from second day onward. All the dispersants contributed to the kaolin particles dispersion but UPW shown more stability dispersion due to increase in number of hydroxyl groups in dispersant molecule [11].

**Figure 3:** (e) MK700-4, (f) MK800-3, and (g) MK800-4

4. Conclusions and recommendations
From the experiments, kaolin particles subjected to elevated temperatures works well with dispersing agents in the following order: UPW > NaOH > Ace. Kaolin particles under UPW, Ace and NaOH suspensions has the same affinities toward water and are categorised as having hydrophilic behaviour. They are often considered homogeneous and stable particles. However, the DLS detection indicated some agglomerations. The mean sizes of kaolin particles were reduced under UPW and Ace dispersions but increased under NaOH suspension due to electrostatic repulsion, Van der Walls interactions and hydrogen bonding. Under Ace and NaOH dispersants, kaolin particles appeared to agglomerate due to the small potential energy barrier but stabilised in the UPW suspension due to the high potential energy barrier. In case of sedimentation, all dispersants contributed to the kaolin
particles dispersion but UPW shown more stability dispersion due to increase in number of hydroxyl groups in dispersant molecule. For future studies, further understanding the contact angle and zeta potential of particles under dispersants can help to identify optimal condition for kaolin particles. With the presence of large particles or agglomerates, certain methods are needed to break down the attached particles into single ones (e.g. ultrasonic, centrifugation). Agglomeration conformity can be identified by understanding the flocculation and sedimentation of kaolin particles under various dispersants. In addition, kaolin particles under good dispersants can be useful for many applications such as ultra-high performance concrete, pervious concrete [22-23], water and wastewater treatment which may lead to some interesting results.

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