A METHOD FOR MEASURING INTER-PARTICLE HAMAKER CONSTANTS IN MINERAL MATERIALS USING ATOMIC FORCE MICROSCOPY

HUA Q. YUAN[*], ZHI GE[†] AND HONG Z. ZHANG[†]

[*] School of Civil and Hydraulic Engineering, Ningxia University
Yinchuan 750021, PR China
e-mail: yuanhq@nxu.edu.cn

[†]School of Qilu Transportation, Shandong University
250002 Jinan, PR China
e-mail: zhige@sdu.edu.cn; hzzhang@sdu.edu.cn

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Abstract: The rheological properties of cement slurry are primarily influenced by the spatial distribution of particles and their interaction forces. The Hamaker constant plays a crucial role in quantifying these interactions; however, its study has been limited due to technical constraints. Atomic force microscopy (AFM) can measure probe-to-particle surface interaction forces via the microcantilever deformation during the extension and retraction process, but it cannot directly measure particle-to-particle interaction forces. In view of this limitation, this paper introduces an AFM-based test method to quantify the interaction force between particles and a new approach for calculating the Hamaker constant. Using these methods, the particle-to-particle Hamaker constants of cement and fly ash in various environments were investigated. The measured Hamaker constants of different mineral materials ranged from 22.79 to 38.26×10^{-20} J in air and from 4.79 to 14.47×10^{-20} J in water. The primary factors influencing Hamaker constant were the material properties and the test environment.

1 INTRODUCTION

Cement slurry constitutes a pivotal component within cement-based materials, playing a critical role in enhancing their fluidity and strength. Fresh cement slurry is described as a densely concentrated suspension of mineral particles ranging in size from 0.01 to 100 µm, dispersed uniformly within a continuous liquid phase. This polydispersity results in a series of microscopic interaction forces within the slurry, including van der Waals force, electrostatic force and capillary force. Typically, one or more of these forces dominate, thereby determining the macroscopic rheology of the slurry. Flatt et al. [1] identified van der Waals forces as the primary cause of mineral particles

agglomeration in the slurry, thereby resulting in poor flow properties. The Hamaker constant is a critical parameter for quantifying the van der Waals attraction energy and calculating the interaction force between particles [2, 3]. Therefore, accurately determining the interaction force and Hamaker constant between particles of different mineral materials in a complex environment is essential for fully understanding the generation and variation mechanism of the rheological behavior of cement slurry.

The interaction forces between mineral material particles cannot be quantified by conventional testing methods due to their nanometer-scale range of action. Atomic force microscopy (AFM), capable of measuring the interaction force between two objects, offers a

potential method for achieving this objective. However, conventional AFM tests only measure the interaction force between a probe and the test material; they cannot directly measure the interaction force between different particles. So far, the research conducted by Yuan et al. [4], Kauppi et al. [5], Fronczak et al. [6] have utilized AFM to investigate the interaction forces between probes and various mineral materials, including cement, slag, mica, and silica. The resulting data is then used to calculate the Hamaker constant. An integrated method is needed to connect the experimental testing method with the analytical model for determining interface forces.

In this paper, a novel AFM-based test method was proposed to directly quantify the interaction forces between different mineral particles. Additionally, a new method for calculating the Hamaker constant between particles was also introduced based on the elastic contact theory. This integrated approach enabled the determination of typical Hamaker constant values between different mineral particles in both air and water.

2 MATERIALS AND METHODS

2.1 Raw materials

The mineral materials used in this study were Type I Portland cement (P.I) and fly ash (FA). The chemical compositions and physical properties of used materials are given in Table 1. The specific surface area (SSA) of all raw materials was tested using a fully automated BET instrument. The density of P.I was 3129 kg/m3 with a median particle size (Dv50) of 17.38μm. Fly ash had a density of 2327 kg/m3 and a median particle size (Dv50) of 12.33μm.The particle size distributions and morphology of the raw materials are shown in Figure 1 and Figure 2, respectively. As can be seen from Figure 2 that FA were regular spheres, while P.I exhibited angular particles.

Table 1: The chemical compositions and physical properties.

Materials		P.I	FA
Chemical composition	CaO	63.43	4.34
	SiO_2	20.07	51.05
	MgO	2.05	0.46
	Al_2O_3	5.09	30.30
	Fe_2O_3	3.81	7.88
	K_2O	-	1.34
	SO_3	2.33	1.8
	Na_2O	0.55	0.28
	TiO_2	-	1.55
	LOI (%)	2.15	0.45
Physical properties	Density (kg)	3122	2321
	SSA (m^2/kg)	359	588
Median particle diameter	D_v50 (μm)	17.38	12.33

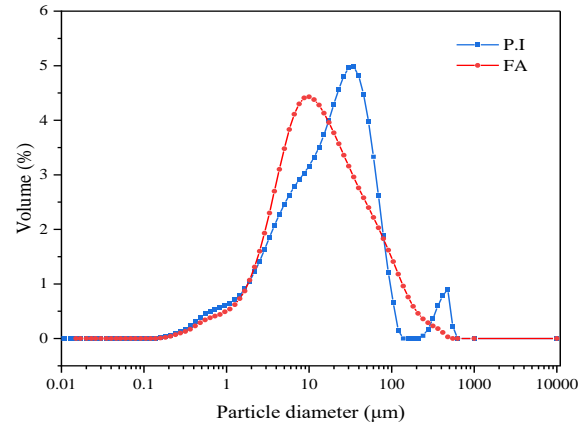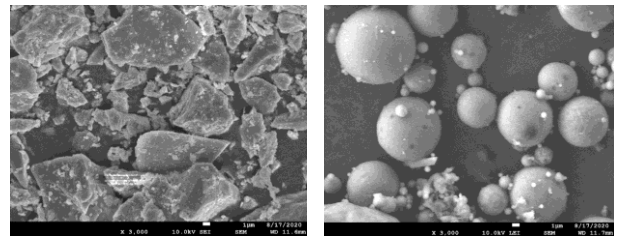

Figure 1: Particle size distributions.

(a) P.I   (b) FA

Figure 2: Morphology of the used materials.

2.2 Sample preparation

For tests of adhesion between the probe and

particles, the test samples were prepared by mixing the particles with the epoxy resin in the ratio of 1:25 by weight and cured at room temperature for 24 h. Then the samples were sanded, polished and cleaned to expose the particles to the sample surface.

For particle-to-particle adhesion tests, as depicted in Figure 3, a single mineral particle was affixed to the tip of a commercial silicon nitride probe using epoxy resin, serving as a new testing tip. Test samples were prepared on a microscope slides (Figure. 3b), where individual mineral particles were securely attached to the slide using UV adhesive.
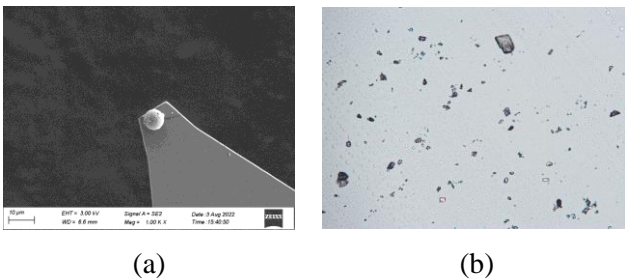

(a)   (b)

Figure 3: (a) Particle probe; (b) Sample preparation

2.3 Adhesion test

AFM from Bruker was employed to measure particle-to-particle normal surface interaction forces. As show in Figure 4, this was accomplished by maneuvering the test sample towards and away from the probe tip using its piezoelectric crystal scanner, and recording the resulting force-distance curves (Figure. 5). During the extend process, the attractive force gradient between the probe and particle gradually exceeded the stiffness of the probe, causing the probe to deflect. As the probe continued to approach, the force would increase linearly to a preset maximum value ensuring full contact between the probe and particle. After that, the probe retracted away from the particle, and the stiffness of the probe would overcome the attractive force at a location close to separation. Thus, the probe backed to its undeflected position, and the force change in this process was the particle's adhesion force. To accommodate the non-homogeneity of the chemical composition and microstructure of the mineral materials, at least three particles of each material were

selected for testing. A total of 256 (16×16) measurement points were selected within the range of 5 μm×5 μm on each particle, ensuring collection of at least 768 force-distance curves. For in-water testing, approximately 1 mL of water was added to the sample surface to fully submerge both the test particle and the probe.
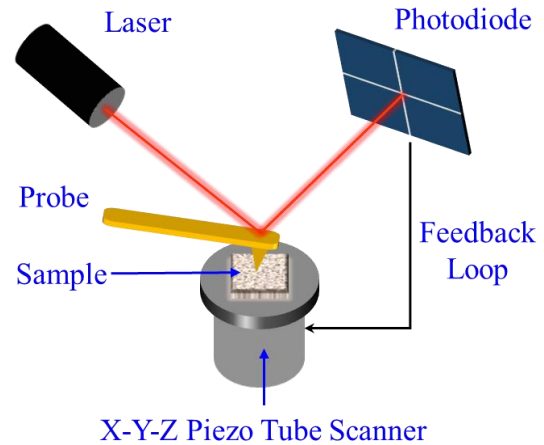
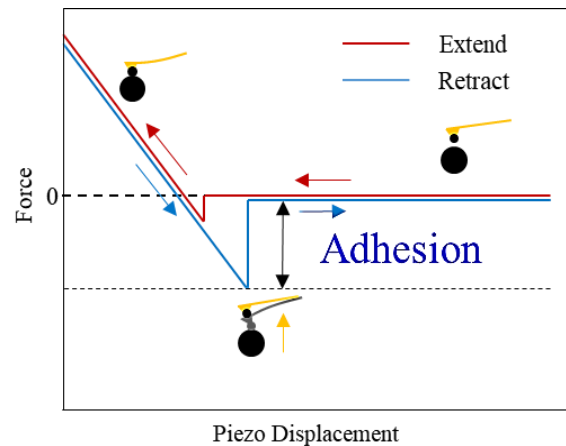

Figure 4: Diagram of AFM scanning.

Figure 5: Force-piezo displacement curve.

2.4 Hamaker constant calculation

In traditional AFM testing, the Hamaker constant between probe and particle is proportional to the adhesion, which can be calculated using Eq. (1).

To determine the particle-to-particle Hamaker constant, the key is to establish the inter-particle contact area. For simplicity in calculation, spherical particles adhered to the probe were assumed, and their equivalent radius was derived based on the principle of area equivalence. Additionally, it was also assumed that: a) the material is homogeneous

and isotropic; b) the deformation occurs within the material's elastic limit. According to the Hertz elastic contact theory[10], when two spheres come into contact under external force, a circular contact surface forms near the contact point due to local deformation. The radius of this contact surface can be mathematically calculated using Eq. (2). Therefore, by substituting Eq. (2) into Eq. (1), the particle-to-particle Hamaker constant can be determined, as shown in Eq. (3).

$$A_{12} = \frac{12 D_0^2 F_{12}}{c r} \quad (1)$$

$$r = \left(\frac{3}{4} R_0 \left(\frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \right) F \right)^{\frac{1}{3}} \quad (2)$$

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Where: A_{12} is Hamaker constant; F is the adhesion; D_0 is the cut-off distance, with a recommended value of 0.165 nm; c is a constant, which is 2 in the DMT model; r is the radius of the contact surface.

3 RESULTS AND DISCUSSION

3.1 Reliability analysis

Figure 6 shows 256 force-distance curves obtained from a single AFM test, demonstrating consistent shapes and values across all curves. Further statistical analysis of the adhesion distribution is presented in Figure 7. The analysis reveals that the adhesion predominantly ranged between 4.0~4.8 nN, exhibiting a log-normal distribution. Notably, 90% of the adhesion values were concentrated within 4.1~4.5 nN, affirming the robustness and reliability of the particle interaction force testing method proposed in this study.
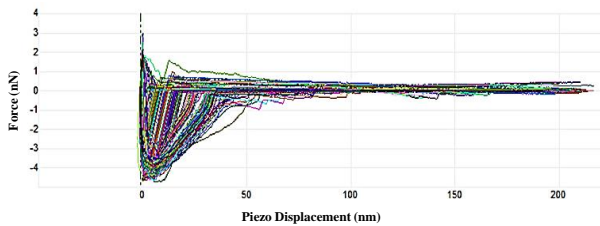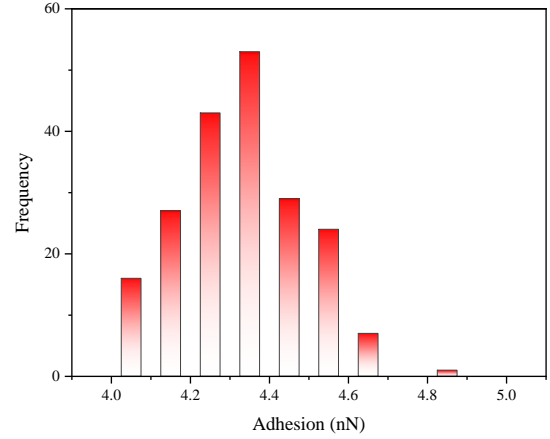

Figure 6: The force-distance curves.

Figure 7: The adhesion distribution.

3.2 Probe-particles Hamaker constant

Table 2 shows the Hamaker constant between probe and different materials. The measured Hamaker constant for probe and P.I was up to 15.45×10^{-20} J, which was in agreement with the existing results [11] and confirmed the accuracy of the test method in this paper. The Hamaker constant between probe and FA was 7.59×10^{-20} J, which was 0.5 times that of Hamaker constant between probe and P.I. A higher Hamaker constant for a cementitious material means a higher adhesion force between particles. This confirms that there are significant differences in the Hamaker constants of different mineral materials. The cause of the discrepancy could be due to the intrinsic properties of the material such as chemical composition, mineral phase and surface energy.

Table 2: Hamaker constant between probe-particles

Material	Adhesion force (nN)	Hamaker constant ($\times 10^{-20}$ J)
P.I	7.57	15.45
FA	3.72	7.59

3.3 Particles-particles Hamaker constant

Typical force-distance curves between mineral particles in air and water are shown in Figure 8 and Figure9. Initially, the force increased linearly from 0 to a predetermined value upon particle-to-particle contact, then gradually decreased to 0 during separation. Subsequently, the attraction between the

particles caused the probe cantilever to deform in the opposite direction, resulting in a negative measured force. The maximum negative force represented the particle-to-particle adhesion, effective up to 50 nm. In a water environment, the adhesion between the same two mineral particles was significantly reduced. In addition, long range repulsive forces were observed in the force-distance curve. A similar phenomenon had been reported in the literature[11].
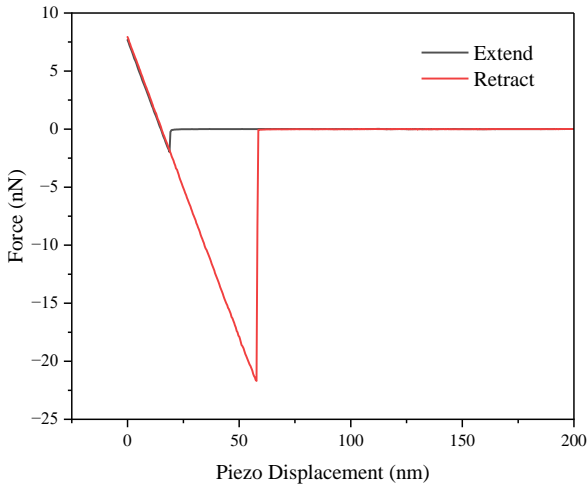

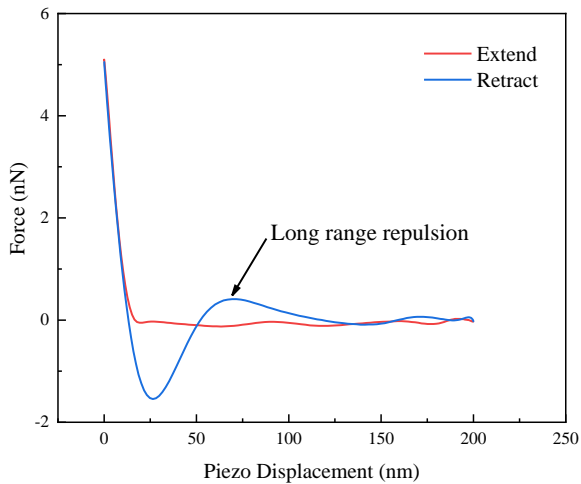**Figure 8**: Typical force-distance curves in air.

Figure 9: Typical force-distance curves in water.

The Hamaker constants between P.I and FA particles in air and water are shown in Figure 10. It is evident that the Hamaker constants between different mineral materials vary significantly within the same environment. In air, the Hamaker constants for P.I-P.I, FA-FA,

and P.I-FA ranged from 22.79 to 38.26×10^{-20} J, with P.I-FA having the smallest value and FA-FA the largest. In contrast, the Hamaker constant in water was much smaller, ranging from 4.79 to 14.47×10^{-20} J, which is closely related to presence of water molecules around the particles[12]. Specifically, the adsorbed and film water around the particles help to balance a large part of the van der Waals forces. Additionally, the water layer increases the distance between particles, thereby reducing the adhesion between them and significantly decreasing the inter-particle Hamaker constant. Due to the different surface properties of the particles and the varying thickness of the adsorbed water layer depending on the mineral composition or hydrophilicity, the Hamaker constants between different particles exhibit significant variations.
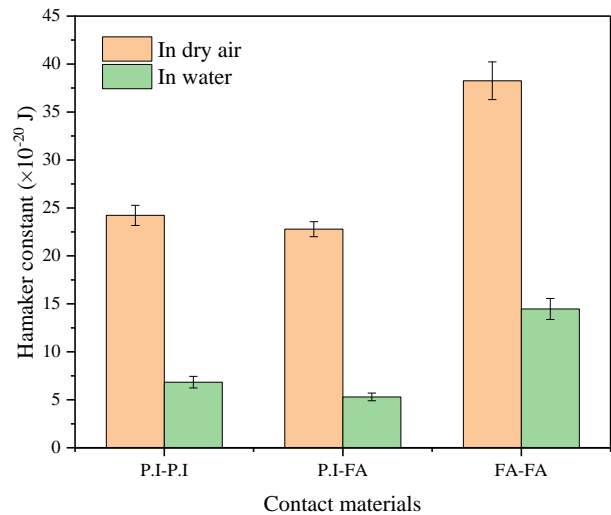

Figure 10: Hamaker constant between particles and particles.

4 CONCLUSIONS

In this paper, a novel method for measuring the interaction force between particles of mineral materials based on AFM is introduced together with an analytical model for calculating the Hamaker constant. In view of this, the adhesion and Hamaker constant between P.I-P.I, P.I-FA, and FA-FA in both air and water were studied. The results indicate significant differences in the adhesion and Hamaker constant between different mineral materials, likely due to the variations in chemical composition and synthesis conditions

of mineral particles. The Hamaker constant in air ranged from 22.79 to 38.26 × 10-20 J, significantly higher than that in water, which ranged from 4.79 to 14.47 × 10-20 J. A test on well-established particle interaction sample would be carried out in the future for the method validation of the proposed method.

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