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# An integrated microstructural-nanomechanical-chemical approach to examine material-specific characteristics of cementitious interphase regions

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ABSTRACT

Effective properties and structural performance of cementitious mixtures are substantially governed by the quality of the interphase region because it acts as a bridge transferring forces between aggregates and a binding matrix and is generally susceptible to damage. As alternative binding agents like alkali-activated precursors have obtained substantial attention in recent years, there is a growing need for fundamental knowledge to uncover interphase formation mechanisms. In this paper, two different types of binding materials, i.e., fly ash-based geopolymer and ordinary portland cement, were mixed with limestone aggregate to examine and compare the microstructures and nanomechanical properties of interphase region. To this end, microstructural characteristics using scanning microscopies, nanomechanical properties by nanoindentation tests, and spatial mapping of chemical contents based on the energy dispersive spectroscopy were integrated to identify and investigate the interphase region formed by the case-specific interactions between the matrix materials and limestone. The integrated microstructural-nanomechanical-chemical approach was effective to better understand links between material-specific properties of cementing phases. More specifically, the fly ash-based geopolymer paste was usually well bonded to the aggregate surface with a rich formation of N-A-S-H gel, while interfacial debonding was often observed between aggregate surface and paste in ordinary portland cement concrete. However, when a good bonding between aggregate and paste is formed, interphase region in PCC did not show any considerable difference in nanomechanical properties compared to the bulk paste.

## 1. Introduction

Cementitious materials are the backbone of the world's infrastructure, used in vast amounts to construct roads, buildings, bridges, and other structures. In cementitious mixtures, paste works as a glue that binds aggregate particles together and forms a strong whole. Effective properties and structural performance of the mixture are substantially dependent on the quality of the interphase region which exists between the aggregate and paste.

In conventional portland cement concrete (PCC), the interphase region is usually called Interfacial Transition Zone (ITZ) which is believed to act as a weak link between aggregate and paste and is susceptible to damage [1]. Due to the lower strength and stiffness of the interphase region, the first microcracks resulting from mechanical loads will appear in this region and will impact the overall mixture behavior [1–3]. Many studies, by using scanning electron microscopy (SEM), have identified the microstructural characteristics of the interphase region in concrete and shown that ITZ is extremely heterogeneous and distinct from the surrounding paste [2,4–8]. The higher porosity of the ITZ can significantly reduce the mechanical properties and durability of cementitious mixtures by allowing easier penetration of aggressive species into the mixtures [9]. Recently, nanoindentation which is a useful tool to derive the local nanomechanical properties of the materials, has been widely used to directly characterize the nanomechanical properties of the interphase region [10–16]. Although there are a lot of studies which have investigated the microstructure and mechanical properties of interphase region in PCC, studies on investigating chemical properties and integrating with mechanical and microstructural features of this region are limited. The adhesion between paste and aggregate particles has been characterized at the microscale by using particle probe scanning force microscopy [17,18] for different types of materials.

In addition to the weak ITZ, the high emission of carbon dioxide ($CO_2$) during the production of portland cement [19] is another drawback of the PCC mixtures. Recently, many studies have sought alternative pastes in concrete mixtures to reduce the $CO_2$ emission.

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Geopolymer, which is an alkali-activated binder that can be obtained from industrial byproducts such as fly ash, has obtained particular attention in civil engineering as an alternative to portland cement due to its low emission of $CO_2$ without compromising mechanical properties [20–25]. In low calcium fly ash-based geopolymer material, sodium aluminosilicate hydrate (N-A-S-H) gel is the main reaction product and has similar elastic modulus to low density calcium silicate hydrate (C-S-H) which is the main reaction product in PCC [26–28]. In spite of an increasing attention towards the use of geopolymer concrete (GPC) as an alternative cementitious mixture, few studies have investigated the interphase between the geopolymer paste and aggregates [29,30].

## 2. Research Objective and Scope

The primary objective of this study is to investigate the microstructural, nanomechanical, and chemical characteristics of the interphase region in cementitious mixtures with two representative binding agents: fly ash-based geopolymer and portland cement. For this purpose, three different aspects of investigation; geometrical, mechanical, and chemical; were integrated. Geometrically, scanning electron microscopy (SEM) and laser scanning microscopy (LSM) were used to examine the microstructure of the interphase region. Mechanically, nanoindentation tests were conducted to evaluate the nanomechanical response of the material. Chemically, energy dispersive spectroscopy (EDS) was used to obtain information about the influence of the material chemical composition on the formation of the bond between aggregate and paste in the interphase region.

## 3. Materials and Laboratory Tests

### 3.1. Materials and Mixture Ratios

Class F fly ash, whose chemical composition is given in Table 1, was used in this study as an aluminosilicate source material for making geopolymer concrete. Class F fly ash obtained from Boral, Colorado was produced from the combustion of pulverized bituminous or Texas lignite coal. The specific gravity of the fly ash is 2.37. The alkaline activator solution was a mixture of sodium hydroxide and sodium silicate solutions. Sodium hydroxide solution of 12 M concentration was prepared by dissolving sodium hydroxide pellets with a purity of 98% in distilled water. Sodium silicate solution (28% $SiO_2$, 9% $Na_2O$, and 63% water) was chosen for this study. The mass ratio of sodium silicate to sodium hydroxide solutions was kept 1.0. Ordinary portland cement Type I, with the chemical compositions shown in Table 1, was used to produce the conventional concrete for comparison. Crushed limestone with a maximum aggregate size of 19 mm was used for mixing with each binding material.

The GPC and PCC samples were prepared with the same amount of binder and aggregate. Geopolymer specimens were prepared with an alkali solution to fly ash ratio of 0.4, and PCC specimens were prepared with water to cement (w/c) of 0.4. The fly ash and local crushed limestone were dry-mixed for 3 min, and then the alkaline solution was added and mixed for another 5 min. The GPC and PCC specimens were cast in 100 mm by 200 mm concrete cylinder molds. The GPC specimens were covered and cured at 60 °C for 24 h in a laboratory oven, then demolded and stored in a controlled temperature of 23 ± 2 °C. PCC specimens had different curing regimes where specimens after casting were sealed using lids and plastic bags to prevent excessive moisture loss. After 24 h, PCC specimens were demolded and placed in water for 28 days.

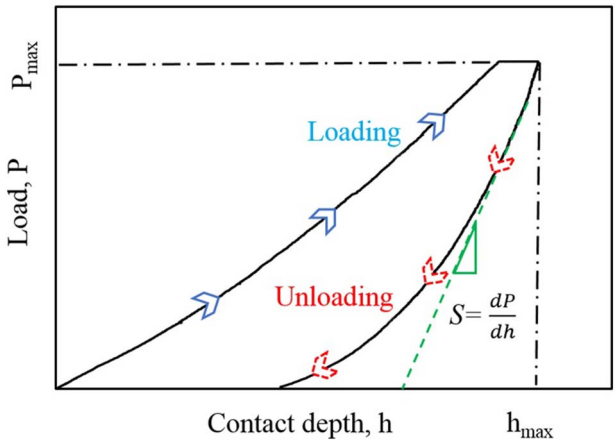


**Fig. 1.** Schematic of load–displacement curve from nanoindentation.

### 3.2. Specimen Preparation

Since analysis of nanoindentation experiments assume that the indentation occurs on a flat surface, smoothening the surface and reducing the roughness to a tolerable level is critical for receiving accurate results [31]. Therefore, once each mixture was fully cured, the center part of the mixture specimen was extracted and then each piece was cut with MTI digital low speed diamond saw into small slices of approximately 10 mm × 10 mm cross section and 4-mm thickness. Before grinding and polishing, which are necessary to achieve a flat surface, samples were vacuum impregnated with a low viscosity epoxy resin. Epoxy fills the pores of the sample and when it gets hardened, it maintains the microstructure unchanged and enables it to tolerate the stresses induced from grinding and polishing procedure without alteration [32]. After epoxy impregnation, silicon carbide abrasive papers of 400, 600, 800, and 1200 grit were used to remove material by grinding. After grinding with the 1200 grit paper, for removing the scratches resulted from sawing and grinding, the surface was polished using a sequence of successively finer alumina suspension particles (1 μm, 0.3 μm, and 0.05 μm). Finally, the samples were cleaned in an ultrasonic bath in ethanol to remove all foreign particles that remained from the polishing process.

### 3.3. Laser Scanning Microscopy (LSM)

Laser Scanning Microscopy (LSM) is a type of optical microscopy which uses a focused beam of a laser that can scan the sample and reflect intensity that is displayed as a function of position. A digital reflected light image of the sample can be created as a result. LSMs are able to collect both an optical image and high-resolution surface data by combining white light with a laser light source. Since the resolution is determined by the position of the beam rather than the pixel size of the detector, nanometer-level resolution digital images of any material can be generated by using LSM. By analyzing the intensity of the returned laser light relative to the z-position of the laser, nanometer-level

**Table 1**
Chemical composition of materials (%).

| Component | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $SO_3$ | $Na_2O$ | $Na_2O_3$ | L.O.I.* |
|---|---|---|---|---|---|---|---|---|---|---|
| Class F fly ash | 51.82 | 23.07 | 13.02 | 2.79 | 0.85 | 2.52 | 1.23 | 0.71 | – | 2.41 |
| Portland cement Type I | 20.99 | 6.19 | 3.86 | 65.96 | 0.22 | 0.6 | 0.55 | – | 0.17 | 1.46 |

* L.O.I. loss on ignition.