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# Calcium Leaching of Reinforced Concrete with Fly Ash

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**ABSTRACT**

*This study discusses how Leaching of calcium ions increases the porosity of cement-based materials, consequently resulting in a negative effect on durability since it provides an entry for aggressive harmful ions, causing reinforcing steel corrosion. This study investigates the effects of leaching behavior of calcium ions on the compression and durability of cement-based materials. Since the parameters influencing the leaching behavior of cement-based materials are unclear and diverse, this paper focuses on the influence of added mineral admixtures (fly ash, slag and silica fume) on the leaching behavior of calcium ions regarding compression and durability of cemented-based materials. Ammonium nitrate solution was used to accelerate the leaching process in this study.*

Keywords: leaching, calcium ion, durability, cement-based materials, mineral admixture

## 1.0 INTRODUCTION.

When a cement-based material experiences humidity for a long time period, water may penetrate into the material, causing leaching of calcium hydroxide. Leaching of calcium ions increases the porosity of cement-based materials, consequently resulting in a negative effect on durability since it provides an entry for aggressive harmful ions, causing reinforcing steel corrosion.

During the leaching process, calcium hydroxide was found to be the first hydration product leached from the cement-based material due to its solubility. Calcium hydroxide is slightly soluble, and can be leached out because of enlarging capillary pores. Leaching of calcium ions increases the porosity of cement-based material, thus resulting in degradation including damage to the pore structure. Increasing porosity results in a weakened matrix and lower compressive strength of the cement-based material. Leaching of calcium ions also has a detrimental effect on durability, since the occurrence provides an entry for aggressive harmful ions into the cement-based material, causing reinforcing steel corrosion. While cement-based material is degraded by the leaching of calcium ions, compressive strength drops dramatically. Furthermore, the degradation volume of the cement-based material can be increased with the leaching progression of calcium ions, and has a linear relationship with the loss in compressive strength.

This study utilized an ammonium nitrate solution to accelerate the leaching process of the cement-based materials. Leaching durations were set to 56 days, 91 days, and 140 days, investigates the effects of leaching behavior of calcium ions on the compression and durability of cement-based materials. Since the parameters influencing the leaching behavior of cement-based materials are unclear and diverse, this paper focuses on the influence of added mineral admixtures (fly ash, slag and silica fume) on the leaching behavior of calcium ions regarding compression and durability of cemented-based materials. Ammonium nitrate solution was used to accelerate the leaching process in this study

**2.0 Test Method.**

In this study, we cast a total of 30 specimens. Each testing values reported are the average of five specimens. The 150 mm × 150 mm × 150 mm cubical specimens of each mix were prepared for the compressive strength test, accelerated leaching test, initial surface absorption test, ultrasonic pulse velocity measurement and x-ray diffracton test.**4.1 Mix Design of the Cement-Based Material.**The specimens prepared for this study are based on the requirements of ASTM C109. The water/binder (w/b) ratio is fixed at 0.55 for all specimens in this study, while the cement/sand ratio is set at 1:3.

**3.0 Plan of test and specimen making.**

The concrete mixtures were prepared in a laboratory. The materials were placed in the mixer in the following order, first coarse aggregates and sand, followed by cement, other cementitious material and water reducer agent. After all materials are ready, mix it for 3 minutes.

The water used in the production of the RC mixtures was fresh and clean water, free from any harmful substance such as oil, acid, salt, alkali, organic matter, and other substances deleterious to the hardening of RC.

Once mixing was completed, the fresh mortar was placed in steel molds in two layers; each layer was compacted in 25 strokes by metal stick and then put the molds to the vibrostand steel plate vibrator for 25 seconds. The Vebe test was used to evaluate the workability of the fresh mixture.

Before casting, the entire test specimen molds were cleaned and oiled properly. These were securely tightened to correct dimensions before casting.

After casting, the specimens were allowed to remain in the mold for 48 h at room temperature (20 ± 5 C) covered by plastic sheet to keep the moist.

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**Figure 1:** specimen making

Then the specimens were demolded and placed in the curing room for 28days.

**4.0 Leaching test**

The calcium leaching of concrete is an extremely slow physical and chemical process, which must be accelerated in order to simulate in the laboratory. At present, there are mainly two methods to accelerate concrete dissolution: $NH_4CL$ solution chemical acceleration method and applied voltage acceleration method. Due to the applied voltage acceleration method should be applied voltage on both sides of specimen, between layers of RC and leakage dissolution process in an airtight container, it is difficult to applied voltage, and therefore, this method will not be considered.

$NH_4CL$ solution chemical acceleration method was first proposed by French scholar Christophe Carde, which is the most commonly, used acceleration method to study the corrosion of concrete.

This experiment required utilizing the chemical solution immersion approach to accelerate the leaching of calcium ions.

The aggressive solution was prepared as a concentration of 1mol/L (53.491g/L) of Ammonium Chloride solution.

1mol/L as a trail of the more aggressive solution. Such a solution leads to acceleration of the leaching

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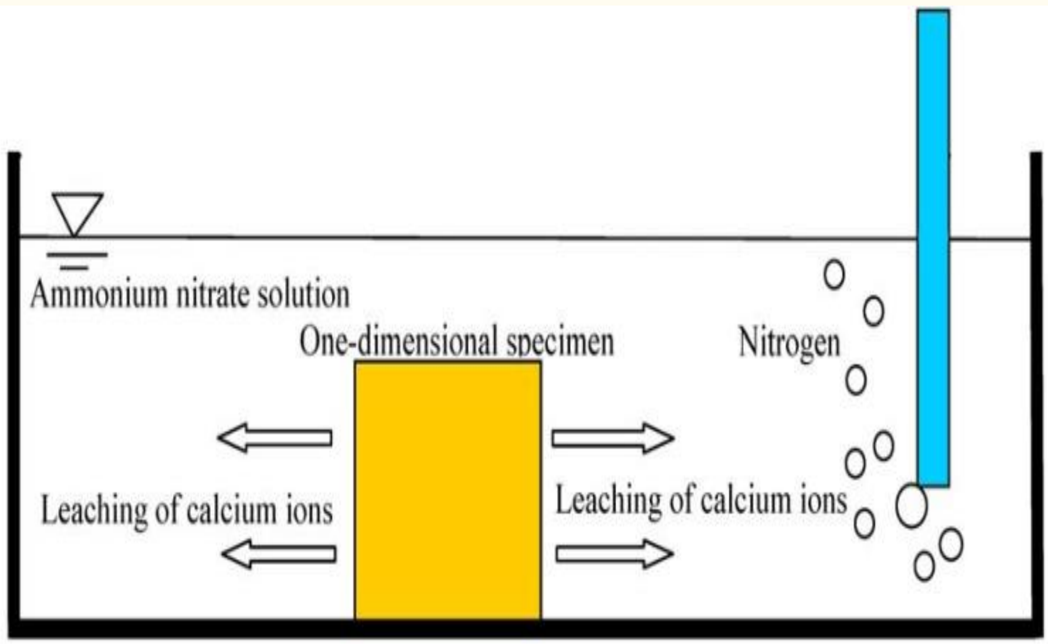
process by hundreds of times compared to deionized water. The leached calcium ions were then extracted every 10, 20, and 28days.

The test specimen for accelerated leaching test is designed as a one-dimensional approach to study the leaching behavior. To control the specimen to a one-dimensional path of leaching out, the other sides of the specimen require sealing with anti-acid adhesive tape. Thus, the effects from the leaching depth to the compressive strength, porosity, wave velocity, and chemical compounds can be explored. The scheme describing the accelerated leaching protocol using ammonium nitrate solution is illustrated in the Figure 2.




Scheme describing the accelerated leaching protocol using ammonium nitrate solution.

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**Figure 2:** Leaching Test

### 5.0 Ultrasonic Pulse Velocity

This study also measured leaching of cement-based material specimen through the horizontal surface. The measuring procedure required placing the transducers on both sides of the specimen surface to measure the longitudinal wave velocity through the specimen. This test utilizes ultrasonic pulse velocity measurement travelling between two transducers to explore the influence of the leaching property of different specimens.

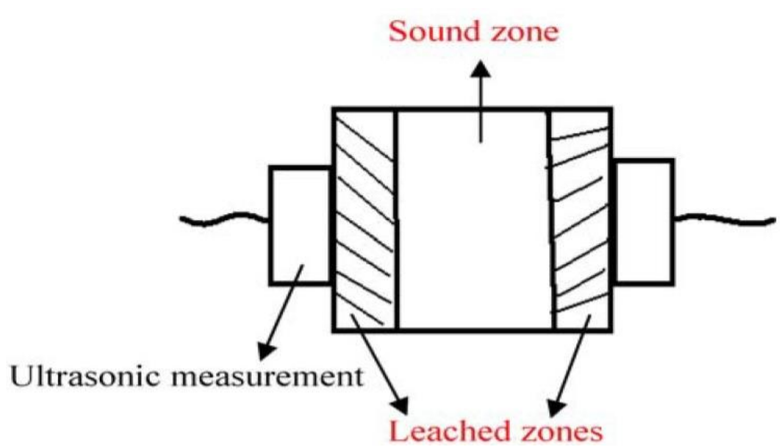


**Figure 3:** Leached zones

A pulse of longitudinal vibrations is produced by an electro-acoustical transducer, which is held in contact

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with one surface of the concrete under test. When the pulse generated is transmitted into the concrete from the transducer using a liquid coupling material such as grease or cellulose paste, it undergoes multiple reflections at the boundaries of the different material phases within the concrete. A complex system of stress waves develops, which include both longitudinal and shear waves, and propagates through the concrete. The first waves to reach the receiving transducer are the longitudinal waves, which are converted into an electrical signal by a second transducer. Comparatively higher velocity is obtained when concrete quality is good in terms of density, uniformity, homogeneity etc. Electronic timing circuits enable the transit time T of the pulse to be measured.

Longitudinal pulse velocity (in km/s or m/s) is given by:

$v=L/T$

where

where v = is the longitudinal pulse velocity, in km/s or m/s

L = is the path length, in m or km.

**6.0 Splitting tensile test**

The tensile strength of concrete is one of the basic and important properties. Splitting tensile strength test on concrete is a method to determine the tensile strength of concrete. The concrete is very weak in tension due to its brittle nature and is not expected to resist the direct tension. The concrete develops cracks when subjected to tensile forces. Thus, it is necessary to determine the tensile strength of concrete to determine the load at which the concrete members may crack. Figure 4.3 shows split test and also the splitted specimens.

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**Figure 3:** Split test

**Figure 4:** splitted specimens

## 7.0 Calculation

The splitting tensile strength of the specimen shall be calculated as follows:

$$f(ct) = \frac{2P}{\pi l d}$$

where:

- $f(ct)$= splitting tensile strength, N/mm^2

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- P = maximum applied load indicated by the testing machine, kN
- *l*= length of the specimen, mm, and
- d= diameter of the specimen, mm.

**8.0Carbonation test**

Carbonation of concrete is associated with the corrosion of steel reinforcement and with shrinkage. However, it also increases both the compressive and tensile strength of concrete, so not all of its effects on concrete are bad. Carbonation is the result of the dissolution of CO2 in the concrete pore fluid and this reacts with calcium from calcium hydroxide and calcium silicate hydrate to form calcite (CaCO3). Aragonite may form in hot conditions. Within a few hours, or a day or two at most, the surface of fresh concrete will have reacted with CO2 from the air. Gradually, the process penetrates deeper into the concrete at a rate proportional to the square root of time. After a year or so it may typically have reached a depth of perhaps 1 mm for dense concrete of low permeability made with a low water/cement ratio, or up to 5 mm or more for more porous and permeable concrete made using a high water/cement ratio.
The affected depth from the concrete surface can be readily shown by the use of phenolphthalein indicator solution. Phenolphthalein is a white or pale yellow crystalline material. For use as an indicator it is dissolved in a suitable solvent such as alcohol in a 1% solution.

The phenolphthalein indicator solution is applied to a fresh fracture surface of concrete. If the indicator turns purple, the pH is above 8.6. Where the solution remains colorless, the pH of the concrete is below 8.6, suggesting carbonation. A fully-carbonated paste has a pH of about

**9.0 Scanning Electron Microscopy (SEM)**

Scanning electron microscopy utilizes an electron gun firing system exciting electron beams to hit cement-based materials. The specimen surface of the cement-based material can animate a reflecting signal, which is sent through a signal amplifier and subsequently to a cathode-ray tube, before being displayed on a screen. The screen can be used to observe the cement-based material by the surface microcrystalline phase.

The purpose of the scanning electron microscope (SEM) is investigation of cementitious materials and concrete microstructure. SEM imaging offers comprehensive images of the microstructure .The primary advantages are the high-contrast images of the microstructure, the high spatial resolution of the images, and the ability to perform simultaneous imaging and chemical analysis.

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This part presents an overview of the SEM and includes specimen sample preparation, and image analysis. The SEM scans a focused shaft of light of electrons across the sample and measures any of several signals resulting from the electron beam interaction with the sample. Computer-based image processing and analysis make routine quantitative imaging possible.

Moreover, understanding of the basic chemical reactions and physical occurrence as well as microstructures of the hardened mass produced by the hydration and hydrolysis of cement is one of the fundamental conditions for the most advantageous use of cement in building materials.

## 10. Test Results and Discussion

### 10.1 Leaching test

The specimens are put into 1mol/L $NH_4CL$ solution. Such a solution leads to acceleration of the leaching process by hundreds of times compared to deionized water. The leached calcium ions were then extracted every 10, 20 and 28days.

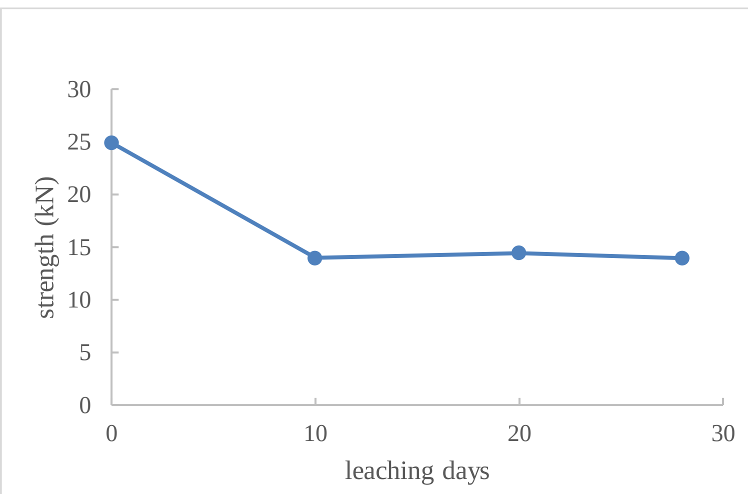


**Figure 5 :** The figure shows that leaching can reduce the tensile strength of concrete depending on the leaching duration time. But the 10d, 20d and 28d do not show obvious difference on split tests. So , we suppose to do it longer.

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### 10.2 Ultrasonic Pulse Velocity Test

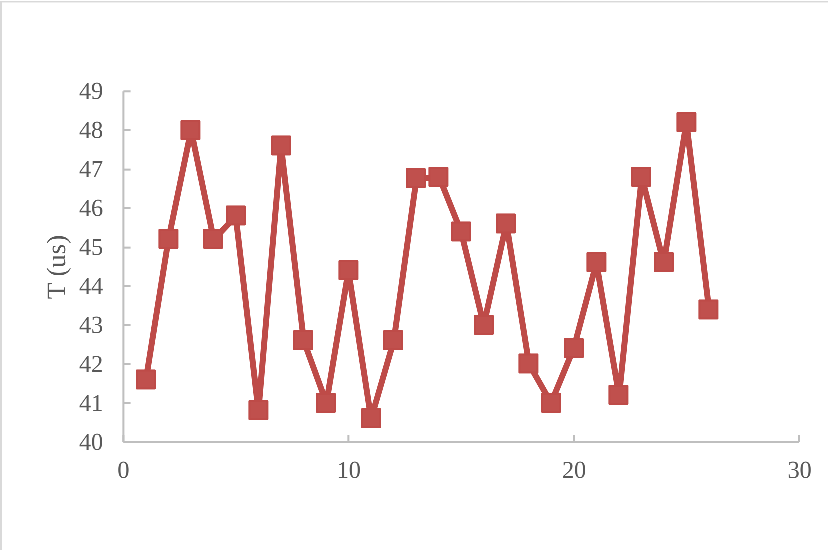


**Figure 6:** 30 specimens have been done by ultrasonic pulse velocity tests (UPV).

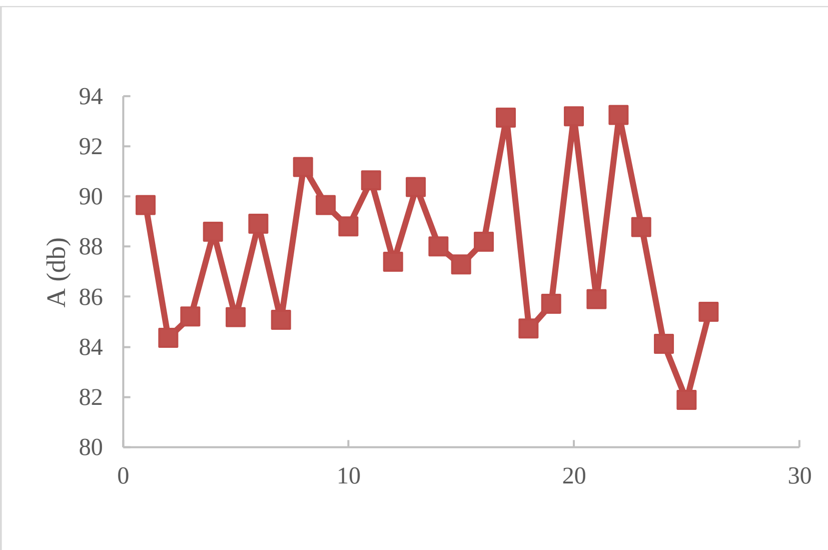


**Figure 7:** The data shows the reduce of the A(db) and T(us).

### 10.3 Splitting tension Result

With the cube or cylinder specimen in specimen between upper and lower bearing surface and press platen, add a washer to form specimens and the corresponding bar loaded, specimen center along the cube or cylinder diameter section of fracturing, will split the force value conversion can get the axial tensile strength of concrete.

The splitting tensile strength of the specimen shall be calculated as follows:

$$f(ct) = \frac{2P}{\pi l d}$$

where:

- $f(ct)$= splitting tensile strength, N/mm^2
- P = maximum applied load indicated by the testing machine, N
- $l$= thickness of the specimen, mm, and
- d= diameter of the specimen, mm.

### 10.4 Carbonation Result

The value of concrete carbonation depth can indirectly reflect the durability of concrete, and the value of carbonation depth will also be determined in the structural entity test to deduce the carbonation depth of concrete. 1.5% dense phenolphthalein agent is used in this study. Figure shows the spraying of phenolphthalein on Concrete.

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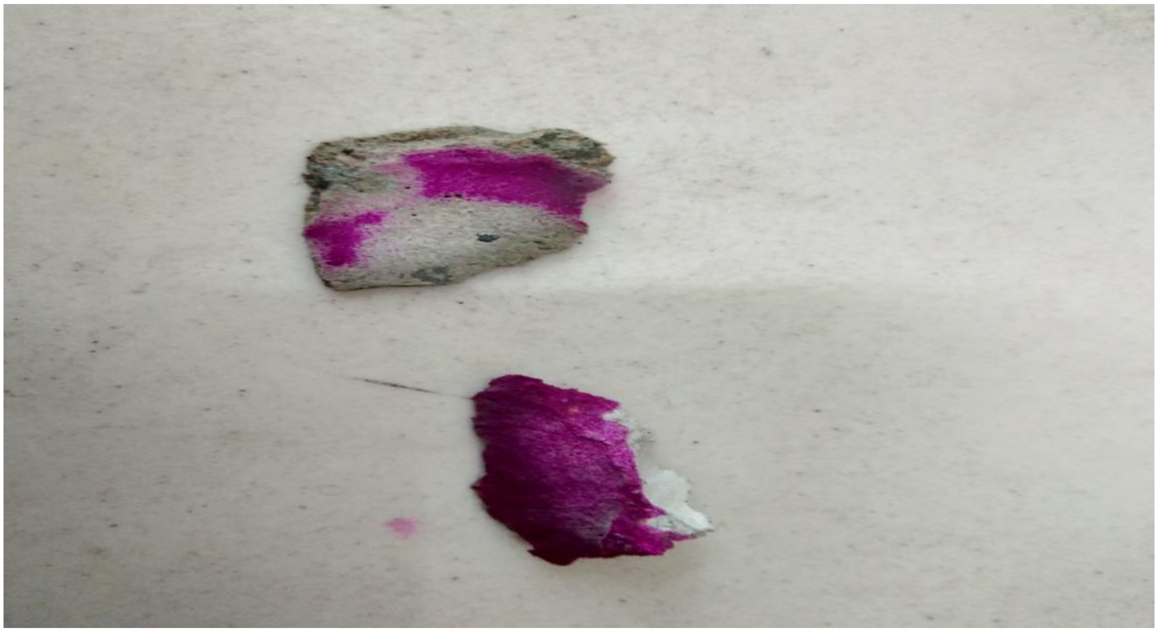

**Figure 8:** the spraying of phenolphthalein on Concrete.

### 10.5 Scanning Electron Microscope Result

The SEM was used to examine the microstructure of growing cement pastes in this experiment. Sample blocks of RC specimen were taken to dry in an oven at a low temperature of 50 °C in the oven for 24h before using. The samples were taken out of the oven when they finished the time of drying and then the SEM test was done .Computer-based image processing and analysis may also be used to extract information from images, or combinations of images.

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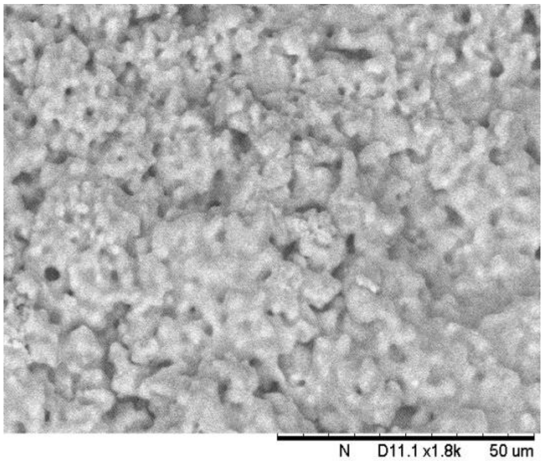
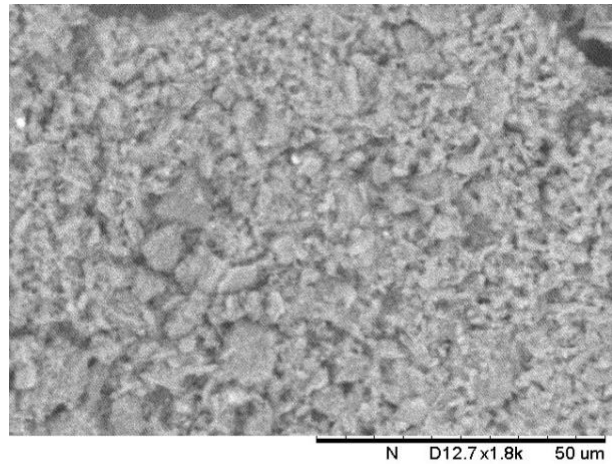
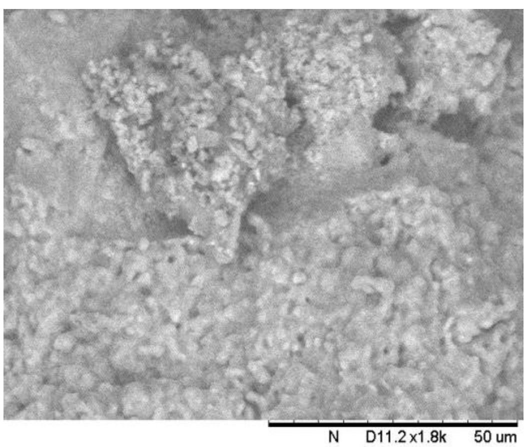


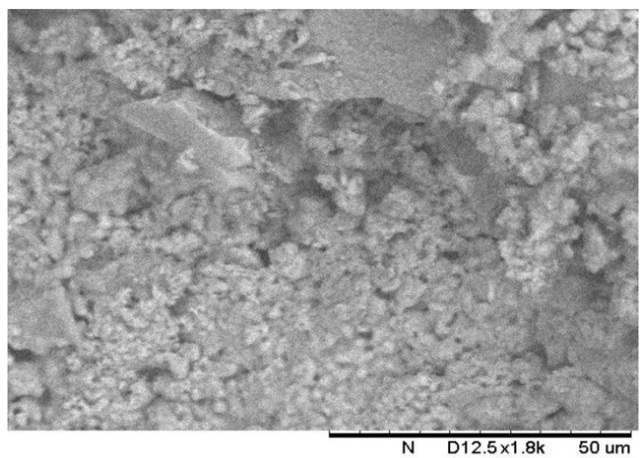

a) G1 Edge




b) G1 Middle




c)G2 Edge




d)G2 Middle

**Figure 9:** The microstructures cement paste was investigated with SEM and been observed with a magnification of times 1800. The images are shown in Figure

A **diffractometer** is a measuring instrument for analyzing the structure of a material from the scattering pattern produced when a beam of radiation or particles (such as X-rays or neutrons) interacts with it.

Because it is relatively easy to use electrons or neutrons having wavelengths smaller than a nanometer, electrons and neutrons may be used to study crystal structure in a manner very similar to X-ray diffraction.

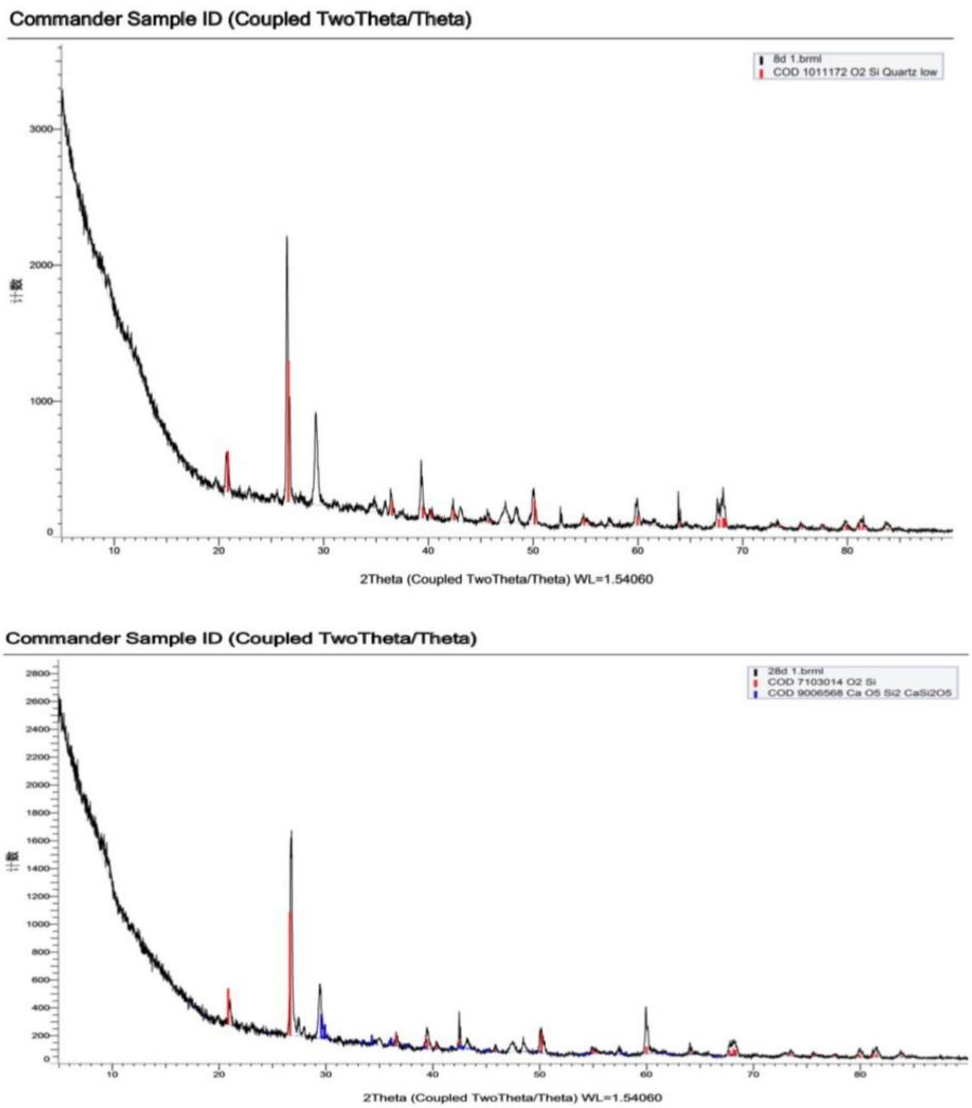



**Figure 10:** X-ray diffraction Test

## Conclusions

This study illustrated the effects of leaching behavior of calcium ions on compression and durability of cement-based materials with various mineral admixtures. The conclusions are as follows:

1. Cement-based materials with mineral admixtures can facilitate trimming down the degradation process because an appropriate mineral admixture can produce C–S–H gels by consuming calcium

hydroxide content. Due to denser C–S–H gels, the leaching process of calcium ions decelerates, slowing the deterioration of compressive strength of the specimens. Therefore, adding appropriate mineral admixtures into cement-based materials not only helps increase compressive strength, but also provides resistance to the leaching process from porosity generation. In brief, the mineral admixtures reduce calcium hydroxide quantity and refine pore structure via pozzolanic reaction, thus enhancing the compressive strength and durability of the cement-based materials.

2. The mineral admixture replacing cement results in a post-production pozzolanic reaction, resulting in the production of C–S–H gel, which is able to enhance specimen density, reducing the porosity in the specimen and also affecting the pore size distribution. The leaching depths of the cement-based material specimens with mineral admixtures over 140 days are less than those of specimens without mineral admixtures. Adding an appropriate amount of mineral admixture facilitates a reduction in the leaching depth of the cement-based material.

3. The SEM images showed that the hydration products of the cement-based material with mineral admixtures significantly decreased and resulted in increasing porosity.

4. The experimental results show that the capillary porosity and gel porosity of the cement-based materials with mineral admixtures increased with the leaching process, based on mercury intrusion porosimetry, while the velocity decreased, based on ultrasonic pulse velocity.

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