GEOPOLYMERIZATION OF COPPER MINE TAILINGS

By

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ABSTRACT

Geopolymerization is a chemical reaction process, reacting SiO$_2$ and Al$_2$O$_3$ with alkaline solutions, which can transform aluminosilicate solids or particles to polymer materials. Geopolymers have many engineering applications such as cementation binders for construction and solidification or encapsulation of hazardous heavy metals. Mine tailings mainly consist of SiO$_2$ and Al$_2$O$_3$. Theoretically, mine tailings can be used as source materials for geopolymerization.

However, for most researchers, they use fly ash, metakaolin or furnace slag as source minerals, because these minerals are much more reactive with alkaline solutions. Mine tailings are naturally-forming minerals and are considered to be inert in geopolymerization. How are mine tailings to be activated through different reaction conditions? We conducted several tentative or preliminary experiments to study the geopolymerization process step by step.

We tried different methods to react mine tailings with alkaline solutions. Mine tailings were submerged into alkaline solutions in a plastic bucket for 6 days in room temperature (20-25°C). We wanted mine tailings to be activated by soaking. The results were not satisfying. Then we tried to react mine tailings with alkaline solutions at 60°C and 90°C. After analyzing, we found that the results were not satisfying either.

So, we conducted simplified geopolymerization experiments in order to better understand the chemical reaction mechanism. Pure SiO$_2$ and Al$_2$O$_3$, which were two major reactants, were employed to simplify and simulate the geopolymerization process. We drew some useful conclusions such as that geopolymerization took place at elevated temperatures; Al$_2$O$_3$ almost did not react with alkaline solutions at low temperatures, etc.

We conducted experiments at elevated temperatures (150°C, 180°C, 210°C). Different levels of pressure (5 MPa, 10 MPa, 20 MPa) were applied to make compact specimens. After many attempts, the results were successful. The highest mechanical strength was about 20 MPa. Most importantly, we obtained polymers produced from geopolymerization, which could be seen by naked eyes.

The experiment techniques such as scanning electron microstructure (SEM) imaging and X-ray diffraction (XRD), inductively-coupled plasma mass spectrometry (ICP-MS), and unconfined compression tests (UCS) were applied to study the geopolymerization reaction mechanism and the feasibility of using mine tailing-based geopolymers as construction materials.
1.1 Background

1.1.1 Mine tailings

Mining industries are fundamental to manufacturing industries. Mining relocates and generates large amounts of rock and tailings. Mine Tailings are the fine-grained residual material containing un-economic minerals. Tailings are stored in large tailings storage facilities. With the production rate becoming higher and higher, every year, there are a large amount of mine tailings disposed to tailings dams, for example, about 370 tons mine tailings being produced with 1 ton metal (0.3% ore grade, 90% total recovery). In 2000, the EPA Toxic Release Inventory (OIG-US EPA 2004) reported that the hard-rock mining industry was the largest producer of toxic waste that year, releasing 1.5 million metric tons, or 47% of the total waste released by the United States (US) industry [1].

Conventional methods for mine tailings treatment are to backfill to the underground voids for underground mining and re-vegetation reclamation for surface mining. These reclamation methods, which just “bury” the mine tailings into the impoundments, are not solving the problems completely. The problems such as occupying large hectares of lands, heavy metals leaching, dust pollution, and the potential threat from the tailing dam collapses still exist. Dry stack tailings technology is being implemented at some mines to allow for more reclamation options. We propose another approach which is to convert tailings to a construction material.

As we know, mine tailings contain some heavy metals such as copper, molybdenum, arsenic and uranium [2-8], which contaminate the ground water and soils, threatening plants and lives. If we want to recycle the mine tailings, heavy metals contained must be encapsulated and immobilized.

1.1.2 Geopolymerization

During the past few years, a new technique called geopolymerization has attracted attentions of researchers. According to Dr. Davidovits [9-14], who developed this technique, geopolymers, mineral polymers produced from geochemistry or geo-synthesis, are new materials for coating and adhesives, new binders for fiber composites, waste encapsulation and new cement for concrete.
Geopolymerization involves a chemical reaction between solid aluminosilicate oxides and alkali metal silicate solutions at alkaline conditions at certain temperatures, yielding amorphous to semi-crystalline polymeric structures, which consist of Si–O–Al and Si–O–Si bonds. Geopolymers are alumino-silicate macromolecules, which are formed under hydrothermal conditions in an alkaline medium.

According to Davidovits, Duxson et al. [9-14] and Dimas et al. [15-16], a two-step reaction theory is proposed for a better explanation of geopolymerization. The geopolymerization process includes the dissolution of minerals which contain alumina and silica in alkaline medium under certain temperature, and alumina-silica oligomers are formed. The second step is the poly-condensation of oligomeric macromolecules to generate 3-D polymer networks, and bond the un-reacted particles as well as toxic elements in the geopolymer matrix.

Dr. Davidovits and other researchers give the Poly (sialates -Si-O-Al-O-) an empirical formula, which consist of SiO4 and AlO4 tetrahedra linked alternately by sharing all the oxygen:

\[ \text{M}_n(\text{SiO}_2)\text{z-AlO}_2\text{n} \cdot \text{wH}_2\text{O} \]

Wherein “z” is 1, 2, 3 or higher; M is a monovalent cation such as potassium or sodium, and “n” is a degree of polycondensation.

Most researchers [5, 6, 17-19] used fly ash (coal combustion ash), kaolinite or metakaolinite, and blast furnace slag as alumina and silica sources for geopolymerization, which have higher reactivity with alkali solutions. Some researchers used tungsten mine tailings and copper mine tailings to conduct geopolymerization experiments [20-25].

Compared to ordinary Portland cement (OPC), geopolymer binders show some advantages such as high acid resistance, excellent adherence to aggregates, and immobilization of toxic and hazardous materials. Several researchers [2-8] reported that geopolymerization process could immobilize most of the toxic elements such as Cr\(^{6+}\), Cd\(^{2+}\), and Pb\(^{2+}\).

1.2 Literature review

In 2000, Xu and Deventer [26] drew conclusions from their experiments that the strength of geopolymers depended on the nature of the source materials, with geopolymers synthesized from calcined source materials, for instance, fly ash, slag and metakaolinite demonstrating a higher compressive strength than those formed from non-calcined materials such as kaolinite, mine tailings and naturally occurring
minerals. In their opinions, many industrial wastes, such as mine tailings, paper sludge and some naturally occurring minerals were inert in geopolymerization, so that the addition of calcined materials might activate these originally inert industrial wastes to form mechanically strong geopolymers.

In 2002, Xu and Deventer [27] studied the geopolymerization of multiple minerals. They selected three minerals, i.e. fly ash, kaolinite and albite to investigate various combinations. The results showed that when appropriate reaction parameters were used, the three component system gave geopolymers possessing the highest compressive strength and the lowest probability of cracking.

In 2007, Diop et al [28] conducted the geopolymerization experiments using tuffs under low temperature (40 °C, 80 °C, 120 °C) to create bricks. The highest mechanical strength they obtained was about 20 MPa.

In 2008, Torgal et al [23], they used thermally treated (950°C for 2 hours) tungsten mine waste to make hydration products, and the highest strength value was about 80 MPa.

In 2009, Mohsen and Mostafa [29] used thermally treated low kaolinitic clays to create geopolymer bricks. The alumino-silicate sources mineral, kaolinitic clays were pre-thermally treated at 700°C for 2 hours. The activation process was conducted at different temperatures (room temperature, 75°C, and 150°C). The results showed that samples cured at 75°C for 24 hours resulted in satisfactory mechanical properties. With increasing temperature from room temperature to 75°C, the reaction between the activation solution and calcined clays increased, but, increasing the curing temperature to 150°C caused a decline in compressive strength. The maximum strength value obtained by them was about 80 MPa.

In 2011, Saeed et al [17], conducted the geopolymerization based on copper mine tailings. In his papers, he studied the factors including Si/Al ratio, alkali concentration (10-15M), curing temperature (60-120°C), forming pressure (0-35 MPa), etc. The highest mechanical strength value was about 20 MPa, and they drew conclusions that copper mine tailings were promising sources materials for construction application.

1.3 Experiment objectives and goals

Among the researchers, who study on mine tailings geopolymerization, some of them [22-25, 29] employ high temperature (700°C-900°C) to activate mine tailings for about 2 hours. Their experiment method is the pre-thermal treatment with mine
tailings to increase the reactivity by calcinations. The others [19-21] choose lower temperature (90°C) or ambient temperature, and mine tailings are considered to be inert in geopolymerization process under a lower temperature.

Our experiment methods were different from the previous ones. Mine tailings in our experiments are from an open pit copper mine company. We used elevated temperatures (150°C, 180°C and 210°C) for soaking mine tailings in sealed bottles, and applied hydraulic pressures on the samples in molds. Mine tailings can be partially geopolymerized using the innovative geopolymerization technology and utilized as construction material.

The materials, such as mine tailings and pure SiO₂ and Al₂O₃ solids, were used in our experiments. The experiment techniques such as scanning electron microstructure (SEM) imaging and X-ray diffraction (XRD), inductively-coupled plasma mass spectrometry (ICP-MS), unconfined compression tests (UCS) were applied to study the geopolymerization reaction mechanism and the feasibility of using mine tailing-based geopolymer as construction material.

The major goal of our research is to enhance the understanding of the underlying mechanism of geopolymerization of mine tailings and to apply the utilization of mine tailings as construction material in large scale, contributing to sustainable development.

1.4 Experiment layout and report organization

Although intensive research on geopolymerization has been conducted by researchers all over the world, the exact mechanisms are still not fully understood. So, we conducted the geopolymerization experiments with tentative starting.

The results obtained from our experiments will be described in details from chapter 2 to chapter 4. Each chapter consists of an introduction, experiment and methods, results and discussion, conclusion and references sections.

Chapter 2 describes the geopolymerization experiments conducted at 60°C and 90°C with different activator/sodium hydroxide concentrations and different particle sizes. The UCS results are analyzed.

Chapter 3 reports the pure SiO₂ and Al₂O₃ solids reaction with sodium hydroxide solutions at different temperatures. The kinetics of SiO₂ and Al₂O₃ dissolution rate is discussed based on the results from ICP-MS leaching tests. And the dry products are examined by SEM.
Chapter 4 describes the experiments conducted at elevated temperatures (150°C, 180°C and 210°C) with different hydraulic pressures applied on specimens. The UCS test results are discussed.

Chapter 5 lists the possible future experiments. It is suggested that some future works should be studied to apply mine tailing based geopolymers to construction industries.
References:


CHAPTER 2 MINE TAILING BASED GEOPOLYMERIZATION
AT LOW TEMPERATURES

2.1 Introduction

Many alumino-silicate materials can be used as a single precursor or a combination for geopolymerization [1-6, 21], such as kaolinite, metakaoline, fly ash and furnace slag. Compared to these conventional geopolymer source materials, mine tailings contain relatively higher Si and lower Al content.

Xu and Deventer [7-9] drew conclusions from their experiments that the strength of geopolymers depended on the nature of the source materials. Mine tailings and some naturally occurring minerals were considered to be inert in geopolymerization process. Geopolymers synthesized from mine tailings demonstrated a lower compressive strength than those formed from calcined materials such as fly ash, furnace slag and metakaolinite.

In 2007, Diop and Grutzeck [10] made durable alkali-activated aluminosilicate brick with aluminosilicate soils cured in a solar heated enclosure. The high strength of bricks was a result of a chemical reaction that took place at a relatively low temperature.

In 2009, Mohsen and Mostafa [11] used thermally treated low kaolinitic clays to create geopolymer bricks. The activation process was conducted at different temperatures (room temperature, 75°C, and 150°C). The results showed that samples cured at 75°C for 24 hours resulted in satisfactory mechanical properties. With increasing temperature from room temperature to 75°C, the reaction between the activation solution and calcined clays increased. However, when cured at higher temperature to 150°C, the samples had a lower mechanical strength.

In 2011-2012, Saeed [12-13] studied the copper mine tailings based geopolymerization. He conducted experiments at four different curing temperatures such as 60°C, 75°C, 90°C, 120°C. The research conclusions were that the UCS increased with the curing temperature up to a certain level and then decreased with the curing temperature. For the copper mine tailings studied in his paper, the optimum curing temperature was around 90°C.

The main objective of this study is investigating the effects of sodium hydroxide concentration, water content, and particle sizes on the mechanical properties at low temperature such as 90°C. The tests investigate how the content of sodium hydroxide, and the content of water affects the strength of the geopolymerized mine tailings.
The macro-scale study focused on the investigation of mechanical properties of geopolymerized mine tailings. Unconfined compression tests were conducted to investigate the mechanical properties of copper mine tailings based geopolymers produced at different reaction conditions.

The results of this study provide some information for recycling and utilization of copper MT as construction material through the geopolymerization technology at low temperature.

2.2 Materials and methods

2.2.1 Materials

The materials used in the experiments included reagent grade 98% sodium hydroxide pellets/flakes (NaOH) from Alfa Aesar Company and the distill water. The mine tailings were provided by a local open pit copper mine.

Table 1 and table 2 show the major elemental composition and chemical composition of mine tailings, feed ore, respectively. What the differences between the mine tailings and feed ore in chemical composition were only the copper and molybdenum.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>31.60</td>
</tr>
<tr>
<td>Al</td>
<td>7.31</td>
</tr>
<tr>
<td>Ca</td>
<td>1.53</td>
</tr>
<tr>
<td>Fe</td>
<td>1.8</td>
</tr>
<tr>
<td>S</td>
<td>0.96</td>
</tr>
<tr>
<td>K</td>
<td>3.82</td>
</tr>
<tr>
<td>Mg</td>
<td>0.417</td>
</tr>
</tbody>
</table>

Table 1 Major Element Composition of mine tailings

The mineralogy analysis of the copper mine tailings showed that the tailings had about 28.42% (weight percentage) quartz, 31% Plagioclase and 26.22% K-feldspar, and little amount of muscovite and pyrite. After mineral extraction, the valuable minerals such as chalcopyrite would be selected, the wastes were mine tailings.
<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>28.42</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>26.22</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>31.39</td>
</tr>
<tr>
<td>Muscovite</td>
<td>4</td>
</tr>
<tr>
<td>Biotite</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorite</td>
<td>1.08</td>
</tr>
<tr>
<td>Swelling Clay</td>
<td>2.37</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.08</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.77</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.81</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>0.74</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 2: Chemical Composition of feed ore

Figure 2 shows the XRD analysis results of mine tailings. From the XRD graph, the mine tailings are in the crystalline phase, consisting large amount of quartz, albite.

![Image](image.png)

Figure 1: the grain size distribution of mine tailings

Figure 1 shows the grain size distribution of mine tailings. The particle size analysis shows that 40% (weight percentage) of tailings is finer than 100 mesh (150 μm) and 20% is finer than 100 μm.
2.2.2 Methods

Firstly, dissolving certain amount of sodium hydroxide pellets in the distill water, the solution was stirred up by a plastic mixer for 3-5 minutes and should not be exposed to the open air for more than 15 minutes to preventing the reaction between the solution with CO₂, which would decrease the alkalinity.

Secondly, the activator-alkaline solution was slowly poured to the mine tailings. The mixture paste was stirred by a mixer to make homogenous paste.

Thirdly, the homogenous paste was poured in cylindrical molds, which are 34.5mm in diameter and 86.25mm in length to make specimens. The filled mold was shaked for a couple of times to release the potentially trapped air bubbles.

Fourthly, the molds were covered and put into an oven at 90°C temperature. After being cured for about 24 hours, the specimens were de-molded, and then put into the oven for prolonged curing. After about 7 days curing, the specimens were taken out of the oven, cooled down in ambient condition and got ready for the tensile strength test.

Before being tested on the loading machine, both ends of the specimens were polished by a piece of sand paper a little bit to make sure that they were flat enough for the consecutive compression test.

In present study, a Verso Master loading system has been applied for the tensile strength test. The measurement error associated with the loading machine is about 41 kPa and the value is neglectable in our experiments.
2.3 Results and discussion

Geopolymerization was totally new research topic for me and we knew little about it. After reviewing papers, I knew that geopolymerization was a chemical reaction process that could transform aluminosilicate solids or particles to polymer materials. Geopolymeric binders were sound alternatives for Ordinary Portland Cement (OPC). Geopolymerization process could consume less energy and generate much less CO₂ [2, 14-17].

So, the major principle for us to design geopolymerization experiments was low energy consumption.

First, we tried to soak mine tailings into alkaline solutions in a plastic bucket for 1 day, 3 days, 6 days in room temperature (20-25°C), respectively. Mine tailings were submerged in alkaline solutions. We wanted mine tailings to be activated by soaking for a long time. But, pastes were put into molds for curing 7 days at 90°C, we found that the mechanical strength was too low and specimens were fragile. So, this method of activating mine tailings was failed.

After that, we conducted geopolymerization experiments at 60°C. After several days’ attempts, the mechanical strength was too low and specimens were fragile also. And the specimens consisted of particles like original mine tailings, there were no geopolymers produced.

We tried again at low temperature (90°C), because water would be at boiling phase above 100°C. The followings were some tentative or preliminary experiment results.

2.3.1 Water content effect:

The water content values are on weight ratios. The water to the mine tailings solids ratio varies from 25% to 35% for the non- sieved mine tailing sample. As to -200 mesh mine tailing samples, 45% to 60% water content were used.
Figure 3 Mechanical strength VS. Water content (the whole MT (non-sieved))

Figure 3 describes the UCS results obtained from the samples reacted with 10 M sodium hydroxide solution at 90°C curing temperature. From the figure, one can see that the optimal water content for the non-sieved mine tailings was 35% at which the highest mechanical strength was achieved and the value was about 11 Mpa. The paste or mixture had a bad workability if less water included. The geopolymerization process took place at watery alkaline medium.

Figure 4 Mechanical strength VS. Water content (-200 mesh MT)

Figure 4 describes the UCS results got from the samples produced at 10 M sodium hydroxide concentration, 90°C curing temperature. The samples were made from very fine particle (-200 mesh) mine tailings.

The particle sizes were finer and the surface areas were larger, so much more water needed to make good workability paste.
From this graph, the optimal water content for -200 mesh mine tailings was about 50%. The samples made at this condition were much more compact. The highest mechanical strength was about 21 MPa.

2.3.2 Particle size effect:

The finer mine tailings had a higher reactivity. The finer solids facilitated the geopolymerization process. The higher strength values could be obtained from finer solids.

Figure 5 Mechanical strength VS. Particle size

Figure 5 describes the UCS results got from the samples produced at 10 M sodium hydroxide concentration, curing temperature 90℃. The samples were made from three different sizes of mine tailings.

After curing in the oven for about 7 days, the specimens were took out and left in room temperature to cool down. Polishing the ends by sand papers, if the ends of the specimens were tilt or rugged, then the parameters of the samples were measured by a scale and a venire caliper.

The mechanical strength tests were conducted on the cylindrical samples with Verso Master loading machine. The tests were performed to measure the unconfined compressive strength (UCS) of the geopolymer samples produced at different conditions.
2.4 Conclusions

For geopolymerization process at low temperature (90°C), several factors affected the mechanical strength, among them were particle size, water content and alkaline concentrations.

If too much water involved in the chemical reaction, specimens were less compact. So the mechanical strength was lower.

Finer particles had larger surface areas. So, making pastes with good workability needed much more water. Obviously, at the same time finer particles could react with alkaline solutions much more easily.

However, after several months’ attempts, we found that the repeatability was low and specimens were likely to collapse. Most importantly, there were no signs about geopolymers produced. We thought that mine tailing based geopolymerization did not take place at such conditions such as 90°C.

Although many researchers studied the geopolymerization, most of them conducted experiments by reacting fly ash, metakaolin, and slag with alkaline solutions. These aluminosilicate materials were much more reactive.

So, the underlying chemical reaction mechanisms of mine tailing based geopolymerization were still obscure for us, because mine tailings were natural forming minerals, which were different from fly ash or metakaolin, and considered to be inert in geopolymerization process.

After analyzing the results from this chapter, we wanted to conduct simplified geopolymerization in order to understand the chemical reactions deeply.

So, in the chapter 3, pure SiO₂ and Al₂O₃, which were two major reactants, were employed to simplify and simulate geopolymerization process.
References:


CHAPTER 3 PURE SiO₂ AND Al₂O₃ SOLIDS REACTION WITH ALKALINE SOLUTION AT DIFFERENT TEMPERATURES

3.1 Introduction

Although intensive researches on geopolymerization have been conducted, the general reaction mechanisms during geopolymerization process are still not totally understood, such as the dissolution rate of Si and Al and the geopolymer reaction temperature. Some researchers applied the accumulated knowledge about zeolite synthesis to explain the geopolymerization process.

In 2011, Saeed el at. [1] studied the production of bricks from copper mine tailings through geopolymerization. In his paper, he discussed that increasing water content at constant NaOH concentration required more NaOH, which resulted in dissolution of more Si. Since and quartz was more stable than the other minerals, increasing alkalinity may help incorporate more Si in geopolymerization.

Xu and Deventer. [2-4] studied the geopolymerization of different kinds of aluminosilicate minerals. The results showed that higher curing temperature was more favorable for releasing Al. Appropriately raising curing temperature accelerated dissolution and condensation rate, causing higher strengths of samples. For some natural forming minerals, the amount of Al was not enough to produce geopolymeric precursors.

As we know, the geopolymerization process includes two steps [5-9], the first is the dissolution of minerals which contain alumina and silica and the second is the poly-condensation to generate polymers. After dissolution, the dissolved and free SiO₄ and AlO₄ tetrahedral units are released in solution. The tetrahedral units are linked to polymeric precursors by sharing oxygen atoms forming geopolymers.

From the research results obtained by Xu and Van Deventer [2-4,10], the geopolymerization process started with the production of soluble Al(OH)₄⁻ and –OSi(OH)₃ from Al-Si source materials, then forming an undefined gel. The gel would be hardening into geopolymers. Consequently, knowledge on the extent of dissolution of natural Al-Si minerals and formation of individual anions Al(OH)₄⁻ and –OSi(OH)₃ is necessary for an understanding of geopolymerization reaction mechanism.
Xu and Van Deventer [2] selected 16 natural Si-Al minerals to study the geopolymization. After studying the extent of dissolution of the thirteen minerals (sodalite, augite, andalusite, etc.) in alkaline medium, they found that the rate of dissolution of Al from the natural alumino-silicates was often small. It was not sufficient to produce a geopolymeric precursor. In such cases, they found that the addition of kaolinite was necessary.

As for the geopolymer reaction temperatures, different researchers conducted geopolymerization experiments at different temperatures. Some researchers thought [1,12-15] that the geopolymer products could be obtained at ambient or 60-90℃ temperatures, they made bricks by geopolymerization at low temperature. But, from the experiment results obtained by Dr. Davidovits [16-19], he used kaolinite as Si-Al source mineral and conducted the experiment at 100-150℃. He also chose a natural kaolinite/quartz blend (50/50 weight ratio) to react with caustic soda at 130-180℃. And generally speaking, the zeolite can be obtained at high temperature (e.g. 220℃) at high pressures.

Another example for the reaction temperature is the extraction of alumina from bauxite ore. The extraction method was invented by Karl Josef Bayer, an Austrian citizen. Bauxite (Al₂O₃-nH₂O) is treated with NaOH (5 M) at 140-240 °C at a pressure of 3-5 atm. The alumina contained in the ore is dissolved to form sodium aluminate. The silica in the bauxite reacts and precipitates from solution as sodium-aluminum-silicate. From this method, we know that alumina can react with NaOH solution at 140-240 °C when high pressure being applied.

As we know, the reactants in the geopolymerization process are mainly alumina and silica. In order to study the geopolymerization reaction mechanism completely, we chose the pure SiO₂ and Al₂O₃ solids to simplify and simulate the reaction process.

3.2 Materials and experiments

The materials used in this section of experiments were pure SiO₂, Al₂O₃ and Ca(OH)₂ solids or powder, distill water and sodium hydroxide pellets. The sodium hydroxide reagent grade is 97% and the calcium hydroxide reagent grade is 95%. These two chemical was bought from the Alfa Aesar company. The aluminum oxide reagent grade is larger than 98%, and the silica is silica fume. These two minerals were bought from the Sigma-Aldrich company.

The reactants (SiO₂, Al₂O₃, Ca(OH)₂) were put into 50 ml plastic containers, and 40 ml solutions with different NaOH concentrations (5M,10M) were added to the reactants. The containers were shaked for a while and then put into an oven for cuing
about 4 hours at different temperatures. After 4 hours’ curing, the containers were
took out and placed in room temperature condition to cool down.

The product solution was filtered with 0.2µm filters. The filtered solution was
diluted to 100,000 times by distill water. The samples were sent to do leaching
analysis. The ICP-MS (inductively coupled plasma mass spectrometry) technique was
used to measure the concentration of silicon and aluminum in the filtrate.

The product solids were drying completely and sent for Scanning electron
microscopy (SEM) and X-ray diffraction (XRD) analysis, studying the microstructure
and phase composition of the solids.

A Hitachi S2700 scanning electron microscope was used and equipped with a
solid backscattered detector and a Rontec energy dispersive (EDS) X-Ray
microanalysis system. X-ray powder diffraction patterns (from 10 to 70 (2θ)) were
recorded on a Scintag XDS 2000 diffractometer using Cu Ka as a radiation source and
a scanning rate of 2.00 degree/min.

Table 1 shows the experiment parameters designed for different temperatures,
NaOH concentrations and different reactant content.

<table>
<thead>
<tr>
<th>H₂O</th>
<th>NaOH</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Ca(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>1 g</td>
<td>0.5 g</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>1 g</td>
<td>0.5 g</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>1 g</td>
<td>0 g</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>1 g</td>
<td>0 g</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>0 g</td>
<td>0.5 g</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>0 g</td>
<td>0.5 g</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 M</td>
<td>16 g</td>
<td>1 g</td>
<td>0.5 g</td>
</tr>
</tbody>
</table>

Table 1
The quantities of NaOH, SiO₂, Al₂O₃ and Ca(OH)₂ in this section of experiments
3.3 Results and discussion

3.3.1 Soaking temperature effect:

<table>
<thead>
<tr>
<th>Temperature(℃)</th>
<th>NaOH</th>
<th>[Si]</th>
<th>[Al]</th>
<th>[Si]/[Al] ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>10M</td>
<td>1561</td>
<td>14</td>
<td>112</td>
</tr>
<tr>
<td>150</td>
<td>10M</td>
<td>4229</td>
<td>202</td>
<td>21</td>
</tr>
<tr>
<td>190</td>
<td>10M</td>
<td>19383</td>
<td>2726</td>
<td>7</td>
</tr>
<tr>
<td>210</td>
<td>10M</td>
<td>23990</td>
<td>5874</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2 Dissolved [Si] and [Al] concentration (ppm) and [Si]/[Al] ratio

The reaction conditions were: 1 g SiO₂, 0.5 g Al₂O₃, 10M NaOH solution, curing 4 hours. The [Si] and [Al] concentrations were shown in the above drawing.

Both concentrations were increased with soaking temperature increasing. However, the [Si] concentration increased less compared to the [Al] concentration from 90 ℃ to 210 ℃. It is much easier for SiO₂ reacts with NaOH solutions than Al₂O₃ does at lower temperature such as 90 ℃ or ambient temperatures.

As for Al₂O₃, it almost doesn’t react with alkaline solutions at lower temperatures. Therefore, much more Al were liberated at elevated soaking.
temperatures such as 190°C and 210°C. Table 2 shows that the [Si]/[Al] ratios were kept on decreasing from 112 to 4, the dissolved Al content increased dramatically. Higher curing temperature was more favorable for releasing Al.

### 3.3.2 Geopolymerization simulation and Ca(OH)$_2$ effect:

<table>
<thead>
<tr>
<th>NaOH</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Ca(OH)$_2$</th>
<th>[Si]</th>
<th>[Al]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M</td>
<td>1 g</td>
<td>-</td>
<td>-</td>
<td>19383</td>
<td>-</td>
</tr>
<tr>
<td>10 M</td>
<td>1 g</td>
<td>-</td>
<td>1 g</td>
<td>2578</td>
<td>-</td>
</tr>
<tr>
<td>10 M</td>
<td>-</td>
<td>0.5 g</td>
<td>-</td>
<td>-</td>
<td>2726</td>
</tr>
<tr>
<td>10 M</td>
<td>-</td>
<td>0.5 g</td>
<td>1 g</td>
<td>-</td>
<td>745</td>
</tr>
<tr>
<td>10 M</td>
<td>1 g</td>
<td>0.5 g</td>
<td>1 g</td>
<td>2796</td>
<td>281</td>
</tr>
</tbody>
</table>

Table 3 190°C [Si] and [Al] concentrations (ppm) with Ca(OH)$_2$

![XRD graph on Sodium Carbonate](image)

Figure 2  XRD graph on Sodium Carbonate
From table 3, we can see that the [Si] content decreased from 19383 ppm to 2578 ppm, because Ca(OH)$_2$ reacted with SiO$_2$ at alkaline conditions. Therefore, calcium silicate was produced from this process and it is precipitant. Then the dissolved [Si] content dropped.

From figure 4, the XRD analysis shows that calcium silicate does exist in the products. As for Al$_2$O$_3$, Ca(OH)$_2$ reacted with Al$_2$O$_3$ at alkaline conditions also. The precipitant calcium aluminate was produced. The dissolvable [Al] content was decreased.
Figure 5 XRD graph on Calcium Aluminum Silicate

From XRD analysis on the solid products, from figure 5, we can see that Calcium Aluminum Silicate was produced at such conditions as 10M NaOH, 1g SiO₂, 0.5 g Al₂O₃, 1 g Ca(OH)₂ and 190°C. And other researchers [21] reported that in geopolymerization process, the geopolymer chain could be linked as -Ca-Al-Si- form. And the CaO content of source material appeared to strengthen the geopolymer by forming amorphously structured Ca-Al-Si gel during geopolymerization.

The lime or Ca(OH)₂ was widely used in cement industry because of its availability. The Calcium silicate and calcium aluminate are two components in the cement. In cement production, lots of Ca(OH)₂ were added to increase the strength. And other researchers [22] reported that adding certain amount of Ca(OH)₂ to the geopolymer process would increase the strength of the results products. But, when calcium hydroxide percentages above 10% were used, strength decrease after 14ᵗʰ curing day was noticed.

How the addition of calcium hydroxide affects geopolymerization process? More experiments were needed for further research.
3.3.3 SEM analysis on geopolymer products:

Figure 6  The SEM micrographs of the solid products (10M NaOH, 1g SiO$_2$ and 0.5 g Al$_2$O$_3$, 190°C)

Figure 6 shows the SEM micrographs of the solid products (10M NaOH, 1g SiO$_2$ and 0.5 g Al$_2$O$_3$,190°C,4 hours) . From this graph, we can see that the materials are not individual particles; they are linked together by chains, so we can say that these materials are polymers (macromolecule).
Figure 7 shows the SEM micrographs of the solid products (10M NaOH, 1g SiO₂, 0.5 g Al₂O₃ and 1 g Ca(OH)₂, 190°C). This picture showed that the geopolymers and un-reacted particles. Compared to Figure 6, geopolymers produced at the presence of Ca(OH)₂ had shorter links and much more compact.

3.4 Conclusions:

Geopolymerization process takes place at higher temperatures, because the Al₂O₃ has difficulty in reacting with alkaline solutions at lower temperatures. The dissolving rate of Al becomes higher at elevated temperatures such as 190°C. And Dr. Davidovits used kaolinite as Si-Al source mineral and conducted the experiment at 100-150°C. He also chose a natural kaolinite/quartz blend(50/50 weight ratio) to react with caustic soda at 130-180°C. As for mine tailings, the soaking temperature should be about 190°C. Soaking temperature is a major factor.

Raising the soaking temperature can adjust the Si/Al ratios. Adding Ca(OH)₂ can adjust the Si/Al ratios also. It is reported [1, 20] that the optimum Si/Al ratio is about 2. So, much more geopolymeric precursors would be produced at optimum Si/Al ratio. And, the CaO content of source material appeared to strengthen the geopolymer by forming amorphously structured Ca-Al-Si gel during geopolymerization [21].

From the XRD and SEM analysis of the pure SiO₂ and Al₂O₃ solids geopolymerization at elevated temperatures, we find that the products are polymers.

After XRD analysis on geopolymerization products from mine tailings, Calcium Aluminum Silicate Hydrate was detected and this mineral didn’t exist in the original mine tailings.
References:


CHAPTER 4 MINE TAILING BASED GEOPOLYMERIZATION AT HIGHER TEMPERATURES

4.1 Introduction

The chapter 2 and 3 discussed that mine tailings reaction with alkaline solutions under lower temperature (say 90°C) and geo-polymerization chemical reaction mechanism via pure SiO₂ and Al₂O₃ solids reacting with alkaline solutions under different conditions.

From chapter 2, we found that the mechanical strength of samples was low and the repeatability was not satisfying. The resulted samples, which were hardened by them-selves without pressure being applied, couldn’t get a good mechanical strength. To obtain a better mechanical strength and a higher repeatability, we applied forming pressures on specimens.

In chapter 3, we studied geo-polymerization chemical reaction mechanism. Pure SiO₂ and Al₂O₃ solids represented the two major reactants during geo-polymer process. As for mine tailings, they were natural rock-forming minerals and had different mineral components. Experiments about mine tailings reacting with alkaline solutions at elevated temperatures such as 150-210°C should be conducted to study the reaction kinetics of the natural rock-forming minerals in alkaline condition.

In addition, the optimum Si/Al ratio in geo-polymerization process is about 2 [1-3]. The Si/Al ratio of mine tailings is around 5-6, which is too large for geo-polymerization. Whereas the ultimate Si/Al ratios in geo-polymerization process mainly depends on the reactivity of Al-Si, because not all the silica and alumina are reactive.

We know that the rate of dissolution of Al from Al₂O₃ is small at lower temperature from conclusions in chapter 3. The content of dissolved Al is insufficient to produce geo-polymer precursors. If the concentrations of Si are higher than the corresponding Al, sodium silicate (water glass) will be easily produced at alkaline conditions. Sodium silicate has a bad influence on mechanical strength. The external Al source is necessary to supply enough dissolved Al to form polymer links. In our experiments, pure Al₂O₃ solids were added to supply external Al for geo-polymer precursors.

From the figure about chemical components of mine tailings, we know that calcium hydroxide exists in mine tailings. From chapter 3, we know that calcium hydroxide reacts with silicates and aluminates to produce precipitant such as calcium
silicate and calcium aluminate. The existence of calcium hydroxide has effects on geo-polymerization to some extent. In our experiments, we studied the mechanical strength of samples with addition of certain amount of calcium hydroxide.

In our experiments, hydraulic pressures were used to make samples. The samples were made from 5MPa, 10MPa and 20MPa respectively. Forming pressures were applied to the samples gradually.

The UCS and XRD analysis was performed on geo-polymer specimens to study the mechanical strength and phase compositions. Specimens were prepared in accordance with ASTM for measurement of compressive strength. A Verso Master loading system has been applied for the tensile strength test. The measurement error associated with the loading machine is about 41 kPa, which is neglectable in our experiments. The XRD analysis was performed with a scintag XDS 2000 PTS Diffraction using Cu Ka Radiation at 2.00 degree/min ranging from 10.00 to 70.00 degrees with 0.600s count time.

### 4.2 Materials and methods

#### 4.2.1 Materials

The materials used in the experiments included reagent grade 98% sodium hydroxide pellets/flakes (NaOH) from Alfa Aesar Company and the distill water. Mine tailings were provided by a local open pit porphyry copper mine. The grain size distribution and chemical compositions of mine tailings are shown in the figure 1 and table 2 in chapter 2. The XRD analysis of mine tailings was shown in the figure 2. From the XRD graph, the mine tailings are in the crystalline phase, consisting large amount of quartz, albite.

Some seamless cylindrical molds, which are 34.5mm in diameter and 63.5mm in length and made from copper metal, were used to make specimens. Some mold accessories such as plates and pushers were also needed.

One set of hydraulic pressure apparatus was used for compressing samples. The apparatus could be loaded to 30MPa maximum value. Some accessories such as porous stones and pushers were also used in this compressing process.

Some PTFE plastic bottles with volume of 2 L were employed as containers for mine tailings and alkaline solutions. The bottles could be withstanding high pressures. Steel frames were equipped to fix the bottles for safety consideration.
4.2.2 Methods

Dissolving certain amount of sodium hydroxide pellets in the distill water, the solution was stirred up by a plastic mixer for 3-5 minutes and should not be exposed to the open air for more than 15 minutes to preventing the reaction between the solution with CO₂, which would decrease the alkalinity.

Certain amount of mine tailings were put into PTFE bottles and poured the alkaline solutions with required concentrations also. The bottle was capped and screwed up tightly. Then, the bottles were shaked for a while. The filled bottles were put into an oven with steel frames for reacting at different conditions.

After reacting for required hours, cooling down the bottles gradually and taking out the supernatant. The remaining paste was stirred by a mixer to make homogenous paste and then poured into cylindrical molds.

The filled molds were placed on the compressing machine. The samples were gradually compressed to the desired pressure such as 10MPa. Water was squeezed outward.

The compact samples were pushed out from molds and then put into an oven for prolonged curing at lower temperature such as 90°C.

After being cured for about 7 days, the specimens were taken out of the oven, cooled down in ambient condition and got ready for the tensile strength test.

Before being tested on the loading machine, both ends of the specimens were polished by a piece of sand paper a little bit to make sure that they were flat enough for the consecutive compression test.

4.3 Results and discussions

Several factors influence the measured mechanical strength; among them are temperature, pressure, surface area (particle size), alkaline solution concentration and reacting time, etc.

The filled bottles were heated at elevated temperatures such as 150-210°C. The internal pressure would be 3-5atm roughly; water is not at boiling stage at such conditions, remaining liquid phase.

Poly-condensation is best affected in the presence of water. Evaporation of water from the mixture during poly-condensation is undesirable.
4.3.1 Curing time effect:

The resulted paste was produced at 180°C and reacting for about 3 hours. And forming pressure was about 10 MPa. The samples were kept in an oven for different days such as 3, 5 and 7 days. The samples with different curing days were tested for mechanical strength. The strength values were shown in Figure 1.

![Figure 1 Mechanical strengths VS. Curing days](image1.png)

From this figure, we can see that there is no big difference in terms of mechanical strength between samples. After about 3 days curing, the samples were harden enough and could reach 90% of final strength value. So, in our experiments, the curing time for hardening samples was 7 days.

4.3.2 Reacting temperature effect:

Experiments were conducted to determine the optimum soaking temperatures. Different samples were soaked in different temperatures such as 150°C, 180°C and 210°C for about 1 hour. The strength results were shown in the figure 2.

![Figure 2 Mechanical strength VS. Soaking temperature](image2.png)
Mine tailings reacted at conditions such as 210°C and 1 hour soaking can get a better mechanical strength than others. The results can be explained that mine tailing based geo-polymers were produced much more than others at higher temperature. So, we chose 210°C as reacting temperature.

4.3.3 Forming pressure effect:

The mine tailing and alkaline mixtures were put into bottles and reacted at 210°C for about 3 hours. The products were poured into molds and then applied different forming pressures on the specimens. The experiment results about mechanical strength were shown in the figure 3.

![Figure 3 Mechanical strength VS. Forming pressures](image)

The optimum forming pressure was about 10 MPa. The higher forming pressure such as 20 MPa squeezed water out from specimens. Poly-condensation was best affected in the presence of water. Evaporation of water from the mixture during poly-condensation is undesirable.

4.3.4 Addition of more Al effect:

The Si/Al ratio of mine tailings was around 5-6, which was too large for geo-polymerization. The external Al source is necessary to supply enough dissolved Al to form polymer links. Xu and Van Deventer [4-7] found that the addition of kaolinite to the natural alumino-silicates was necessary to produce a geo-polymeric precursor.

In our experiments, 15 grams of Al₂O₃ solids were added to the mixture. And mixtures were reacted at 210°C for about 3 hours. The products were poured into
molds and then applied different forming pressures on the specimens. The experiment results about mechanical strength were shown in the figure 4.

![Figure 4 Mechanical strength VS. Forming pressures with addition of Al₂O₃](image)

Comparing the figure 4 to the figure 3, we found that adding certain amount of Al₂O₃ solids could increase the mechanical strength. The highest strength values were about 20 MPa at conditions such as 10 MPa forming pressure.

Adding much more source of Al could produce more mine tailing based geo-polymers, because the Si/Al ratio of mine tailings was about 5-6. At the same time, fewer amounts of sodium silicates were produced. Sodium silicates had bad influences on mechanical strength.

4.3.5 Over-reaction of mine tailing based geo-polymerization:

In order to find out the optimum soaking time for mine tailing based geo-polymers, experiments about 7 -10 hours soaking time were conducted. But, in our experiments, we found that the samples were easily to collapse for 7 hours soaking. Even if samples could stand without failure, the strength value was less than 1 MPa.
After analyzing, we found that mine tailing based geo-polymers were over-reacted. Larger amounts of sodium silicates were produced because mine tailings contain too much SiO₂ to react in geo-polymerization process. So, we planned that mine tailings should be partially reacted to get better mechanical strength. The samples should contain certain amount of un-reacted particles or gravels to ensure a good mechanical strength.

4.4 Mine tailings based geo-polymers:

Mine tailings reacted with 10 M NaOH solutions at 210°C for about 10 hours, the products were put into tap water, large amount of polymers were emerged and floated in the surface.
The produced geo-polymers were visible by naked eyes in the pan (30.5cm*20.3cm). Geo-polymers contained relatively large units of alumino-silicate macromolecules. The length of polymer chains was in the range of 10cm-20cm, which was much longer than 10-20 nanometers found by Dr. Davidotas [8-12].

Geo-polymer links (-Si-O-Al-O-Si-) could be interconnected to a longer chain under reaction conditions such as compression pressures, long soaking times or elevated temperatures.

![Figure 5 Comparisons of XRD diagraph between Geo-polymer and MT](image)

Geo-polymerization, can transform mine tailing solids into polymers. We call them geo-polymers. Geo-polymers are inorganic polymer materials in amorphous phase. So, the XRD diagraph of amorphous material such as geo-polymers has low peaks compared to a diagraph of crystalline materials such as mine tailings. In other words, geo-polymerization can transform crystalline materials into amorphous ones.

After comparing two XRD diagraphs of geo-polymers and mine tailings, we found that XRD diagraph of geo-polymers had lower peaks than corresponding components of mine tailings. However, mine tailings were partially reacted, so un-reacted solids or particles were absorbed or locked in geo-polymer matrix. That’s why the XRD diagraph of geo-polymers had relatively high peaks such as peak zone of quartz.
4.5 Conclusions:

In our experiments, curing temperatures were considered the major factor that affecting the chemical reaction of geo-polymerization. So, we used the constant alkaline concentrations such as 10M. The elevated curing temperatures (180-210°C) and higher internal pressures such as 3-5atm roughly in sealed PTFE bottles could facilitate and accelerate chemical attacking on minerals.

Mine tailing based geo-polymerization was designed to react partially, the un-reacted particles or aggregates accounted for higher mechanical strength. So, the other factor accompany with temperatures was curing time. If curing time was too long, we would have problems such as over-reaction or collapse of specimens.

After considering curing temperature and time, we draw a conclusion in our experiments that the better curing temperature and time were 210°C and 3 hours, respectively.

It was necessary that applying forming pressures on specimens to increase compactness and repeatability. As for forming pressure values, 10 MPa was considered a better option. If forming pressure was too large, water inside specimens would be squeezed outward completely, which has adverse influence on condensation of geo-polymerization. Certain amount of water could help specimens to obtain a better mechanical strength.

It was necessary that adding certain amount of Al sources to mine tailings to facilitate geo-polymerization, because mine tailings had a relatively higher Si/Al ratio and a weaker reactivity with alkaline compared to meta-kaolin or fly ash. If we added additional Al sources to mine tailings, much more geo-polymer precursors would be produced. At the same time, less sodium silicates was produced, which was good for mechanical strength of specimens. The mechanical strength would be achieved to a higher value.

After comparing mechanical strength and displacement between geo-polymeric specimens produced at low temperature (90°C) and specimens produced at elevated temperature(210°C), we found that specimens produced at elevated temperature and forming pressures had higher mechanical strength value and good repeatability. Besides, the strain had a larger value. Geo-polymer chains with un-reacted particles accounted for larger strain values, because much more polymers and longer polymer chains were produced at condition such as elevated temperatures and forming pressures.
After analyzing geo-polymerization process under different temperatures in our experiments, we found that geo-polymerization could take place at higher temperature only, or the geo-polymeric chemical reaction could take place more efficiently at elevated temperatures only, because we did find that large amount of polymers were produced, whereas there were no polymer materials produced at low temperatures.
References:


CHAPTER 5 FUTURE STUDIES

Time is not enough to study the geo-polymerization experiments completely, so, I propose the future works as follows:

1. It is suggested that one can use an autoclave as a container for the reactants at high temperature condition. If an autoclave will be employed in the geo-polymerization experiments, the pressures inside the container will be easily controlled and adjusted. In addition, use seamless steel molds and steel porous stone.

2. It is proposed that it is important to cover specimens with plastics during the poly-condensation or curing process of geo-polymers. Covering specimens is preventing water evaporation too fast. So, I propose that plastic films should be used in the curing stage of geo-polymers.

3. It is necessary to add fly ash or metakaolin to mine tailings, studying the combined materials based geo-polymerization effect. In addition, I propose that experiments about addition of certain amount of calcium hydroxide should be conducted to study the effects on mechanical strength.

4. It is necessary to decrease the quantities of sodium hydroxide usage. It is not practical for mine tailings based geo-polymerization when consuming large amount of sodium hydroxide. The geo-polymerization should be conducted in a friendly and greenly way.

5. Experiments on leaching tests should be conducted to study the durability of the mechanical strength of samples in water and the encapsulation conditions of heavy metals.
REFERENCES:


