

# Characterizations of mine tailings to explore their potential beneficiation in cementitious or alkali-activated materials

Zuobang Yao<sup>1</sup>, Haemin Song<sup>2</sup>, Ali Kashani<sup>3</sup>, Adrian Russell<sup>4</sup>, Taehwan Kim<sup>5</sup>

<sup>1</sup>PhD Candidate, Centre for Infrastructure Engineering and Safety, School of Civil and Environmental Engineering, UNSW Sydney, Australia

<sup>2</sup>Research Fellow, Centre for Infrastructure Engineering and Safety, School of Civil and Environmental Engineering, UNSW Sydney, Australia

<sup>3</sup>Senior Lecturer, Centre for Infrastructure Engineering and Safety, School of Civil and Environmental Engineering, UNSW Sydney, Australia

<sup>4</sup>Professor, Centre for Infrastructure Engineering and Safety, School of Civil and Environmental Engineering, UNSW Sydney, Australia

<sup>5</sup>Senior Lecturer, Centre for Infrastructure Engineering and Safety, School of Civil and Environmental Engineering, UNSW Sydney, Australia

## Abstract

The mining industry is a crucial sector in the Australian economy; however, there is a growing concern about the environmental impact related to mine tailings which is a disposed waste product from the mining process. The utilization of tailings in construction has been proposed to resolve tailings-associated environmental issues. Although using tailings as aggregate has been investigated, the possibility of reusing these tailings as supplementary cementitious materials have not been thoroughly investigated.

This study investigated the potential of tailings to function as supplementary cementitious materials (SCMs) or precursors in the alkali activation process. Several characterization methods were utilized to investigate the chemical characteristics of three raw tailings. Chemical composition and mineralogical content were characterized with X-ray fluorescence (XRF) and X-ray diffraction (XRD). Furthermore, the decomposition of minerals was investigated using thermogravimetric analysis (TGA). In addition, their potential properties for SCMs were investigated using the newly developed rapid, relevant, and reliable (R<sup>3</sup>) test methods.

The characterization results indicate that the main element in the gold and copper tailings is silicon (Si), which exists in the form of quartz (SiO<sub>2</sub>). On the contrary, aluminium hydroxide and aluminium oxide hydroxide crystalline phases are the significant components of bauxite tailings. The R3 test methods showed the heat flow and accumulated heat of bauxite tailings were greater than those obtained from the other two tailings. As observed from TGA, clear mass drops are related to a few mineral phase decompositions, and this implies that the reactivity of tailings may be improved through several pretreatment methods, including thermal or mechanochemical treatment.

## 1. Introduction

The annual global carbon dioxide emissions have continuously increased since 2015. One main contribution to this carbon dioxide emission is the production of cement clinker (IEA, 2022), where the thermal decomposition of raw limestone and clay in a kiln under 900°C release carbon dioxide (Gao et al., 2016). As the requirement of sustainable development, more researchers have focused on looking for industry waste that can be used as a binder to replace Portland cement fully or partially. Slag and fly ash are the typical types of industrial waste used as supplementary cementitious materials (SCMs). However, more types of waste can be sources of alternative SCMS but have not been thoroughly investigated, such as tailings from the mining industry (Juenger et al., 2019).

Tailings are mining by-products resulting from waste after extracting valuable fractions from ores. These mine wastes are often disposed of in large tailings dams, which can induce the significant environmental risk of river pollution and dam failure (Komnitsas et al., 1998). Using tailings in the construction field can help reduce carbon emissions, mitigate environmental risks, reduce storage and disposal costs, and create economic benefits. However, to use mine tailings as SCMs, their potential reactivity is crucial and thus has

to be evaluated. Generally, the reactivity of SCMs relates to their physical and chemical characteristics (Simonsen et al., 2020), including elemental (or oxide) composition, mineral composition, particle size, surface area, and contents of amorphous or crystalline phases.

Therefore, the characterization of mine tailings as SCMs is an important step to investigate the reactivity of mine tailings and thus this study can potentially improve sustainable material development using mine tailings. Recent studies have shown that certain types of mine tailings have the great potential to be used as SCMs. However, these materials' complex mineralogy and chemistry make the characterization process challenging (Simonsen et al., 2020a). Additionally, different types of tailings can behave very differently. Therefore, it is essential to use effective methods to characterize the reactivity of mine tailings and identify the most suitable tailings for use as SCMs (Obenaus-Emler et al., 2020).

The present study investigated bauxite, copper, gold, and lead tailings to evaluate their potential reactivity to be used as SCMs or precursors in the alkali activation process. Raw tailings were evaluated by particle size distribution test, XRF, XRD, TGA, dissolution test, and R<sup>3</sup> isothermal calorimetry test. In particular, the XRF test assessed their oxide content, while the XRD test estimated their qualitative crystalline analysis. The concentrations of dissolved aluminum and silicon ions were examined by R<sup>3</sup> isothermal calorimetry test, given that those ions are significant indications for assessing their potential reactivity as SCMs or precursors in the alkali activation process.

## 2. Experimental

Of these four materials, bauxite and lead tailings were rock, while others were powder. To compare all tailings in the following analyses, they were dried at 105°C for three days, followed by being pulverized using a ring mill (RM2000, Scott, New Zealand) for five minutes. Then, their particle size was evaluated by the laser diffraction particle size analyzer (Mastersizer 2000, Malvern Panalytical, UK).

The chemical oxide compositions of powder tailings were analysed using a wavelength-dispersive XRF spectrometer (PANalytical AXIOS, Malvern Panalytical, United Kingdom). Their mineralogical contents were investigated by an X-ray diffraction (XRD) (PANalytical Empyrean 2, Malvern Panalytical, United Kingdom) equipped with a Co-K $\alpha$  radiation source with a wavelength of 1.79 Å with angular scans from 5 to 100° 2 $\theta$ . To support the minerals identified through XRD analysis, a thermogravimetric analyzer (Q600, TA instrument, United States) was used to investigate the weight losses of all tailings from room temperature to 1,000 °C at 10 °C/min under N<sub>2</sub> gas.

A dissolution test was also carried out to relatively compare their reactivity in a highly alkaline environment. In this test, 4.0 grams of each tailing were mixed with 400 ml of 1 M sodium hydroxide (NaOH) solution in the glass bottle, followed by sealing and storing in a 40°C furnace. At each specific time interval (i.e., 4, 20, 24, 44, 48, and 168 hours), 2.0 mL of the filtered solution was collected using a syringe filter (pore size 0.22  $\mu$ m) and diluted with 4% nitric acid (HNO<sub>3</sub>) for the ICP-OES analysis. In addition, an additional 2 ml of 1 M NaOH solution was refilled into each container to maintain the same quantity of solution.

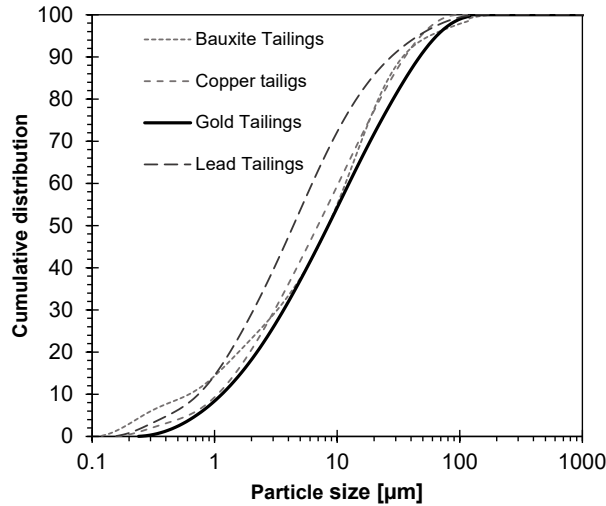
The cementitious reactivities of these tailings were investigated using the R<sup>3</sup> test (Snellings et al., 2019). The R<sup>3</sup> tests are a series of simplified tests to evaluate the reactivity of SCMs by simulating a similar condition in hydrated blended cement. Among the tests involved in the R<sup>3</sup> test, isothermal calorimetry analysis was conducted in this study. For the R<sup>3</sup> test, 1.0 g of tailings was mixed with 3.0 g of calcium hydroxide (Ca(OH)<sub>2</sub>) and 0.5 g of calcium carbonate (CaCO<sub>3</sub>) in a potassium solution using a constant speed mixer at 1,600 rpm for 2 mins. The potassium solution was prepared by dissolving 4.0 g of potassium hydroxide (KOH) and 20.0 g of potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) in 1.0 l of reagent water. The heat flow and total accumulated heat of the R<sup>3</sup> mixture were recorded at 40°C using an isothermal calorimeter (TAM Air, TA instrument, United States) for 7 days.

## 3. Results

### 3.1. Particle size distribution

**Figure 1** shows the particle size distribution (PSD) of four tailings after 5 minutes of ring milling. The lead tailings have the finest PSD ( $d_{10}$  = 0.83  $\mu$ m,  $d_{50}$  = 4.37  $\mu$ m, and  $d_{90}$  = 26.30  $\mu$ m), while the gold tailings have

a coarser size distribution ( $d_{10} = 1.10 \mu\text{m}$ ,  $d_{50} = 8.71 \mu\text{m}$ , and  $d_{90} = 30.20 \mu\text{m}$ ). The remaining tailings have a very similar  $d_{50}$  range, ranging from  $7.59 \mu\text{m}$  to  $8.71 \mu\text{m}$ . It was also observed that bauxite tailings tends to have a higher percentage of particles below  $1 \mu\text{m}$  in size. Generally, the ground tailings prepared in this study have similar PSDs as shown in **Figure 1**.



**Figure 1.** Particle size distributions of tailings after milling

### 3.2. Oxide compositions by XRF

The chemical oxide composition of the tailings is summarized in **Table 1**, investigating their chemical characteristics. Calcium oxide, silicon oxide, aluminium oxide, magnesium oxide, and iron oxide are the important chemical oxides studied in this research. The supplementary cementitious materials can be classified into three groups according to the calcium oxide and silicon oxide content. In this study, except for bauxite tailings, all tailings were listed in the group identified with low calcium and high silicon oxides. This group could exhibit pozzolanic reactivity when functioning SCMs (Simonsen et al., 2020b). The bauxite tailings exhibit the highest loss on ignition and aluminium oxide content, which is not listed in any groups. Therefore, it is difficult to be classified the bauxite tailings into one of the already existing groups in SCMs, but its unique chemical characteristic (high aluminium content) seems to make the bauxite tailings a potential supplement for precursors in geopolymer paste (Ye et al., 2017). Copper, gold, and lead tailings contain high silicon oxide content ranging from 38.97-64.48%. The mineralogical form of silicon oxide plays a crucial role in determining the reactivity of these tailings.

**Table 1.** X-ray fluorescence chemical composition of different types of tailings

Oxide (wt.%)	Bauxite	Copper	Gold	Lead
Al <sub>2</sub> O <sub>3</sub>	55.65	9.77	15.42	5.04
SiO <sub>2</sub>	12.68	64.48	63.38	38.97
Fe <sub>2</sub> O <sub>3</sub>	9.25	16.93	5.12	13.73
TiO <sub>2</sub>	3.62	0.36	0.75	0.12
ZrO <sub>2</sub>	0.18	<0.01	<0.01	<0.01
MgO	0.16	3.11	3.00	7.24
P <sub>2</sub> O <sub>5</sub>	0.06	0.08	0.17	0.07
V <sub>2</sub> O <sub>5</sub>	0.04	<0.01	0.01	<0.01
SO <sub>3</sub>	0.04	0.59	0.32	7.35

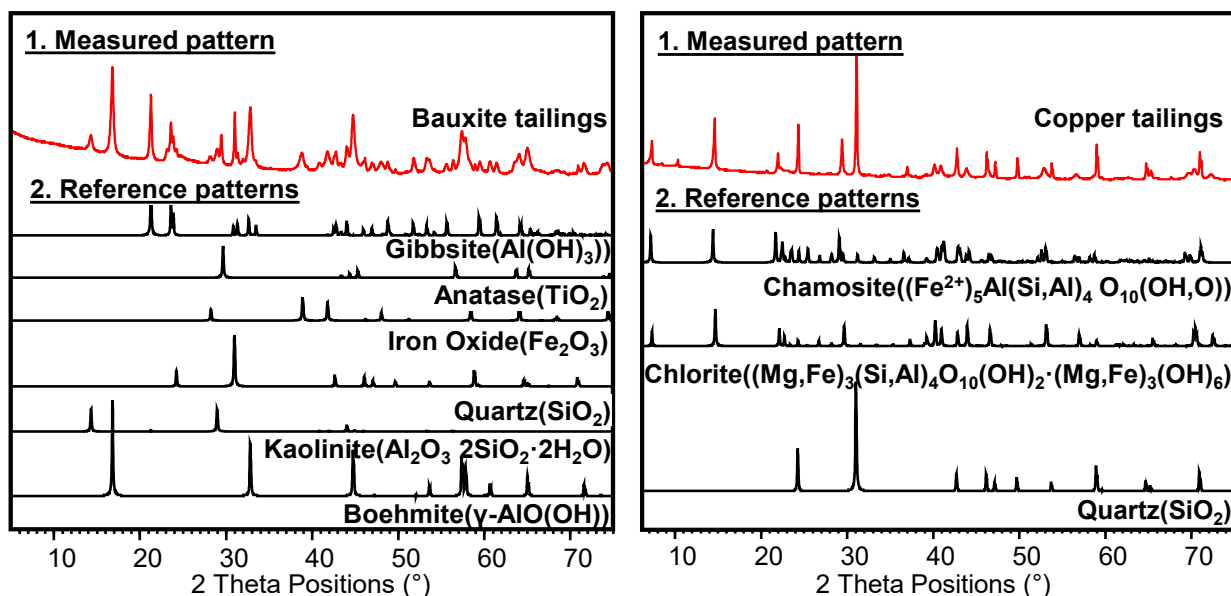
Mn <sub>3</sub> O <sub>4</sub>	0.04	0.24	0.06	0.49
Na <sub>2</sub> O	0.03	0.04	3.50	0.16
K <sub>2</sub> O	0.02	0.45	1.62	1.90
CaO	0.01	0.44	4.93	10.38
L.O.I.	18.22	3.43	1.72	13.59
TOTAL	100.00	100.00	100.00	100.00

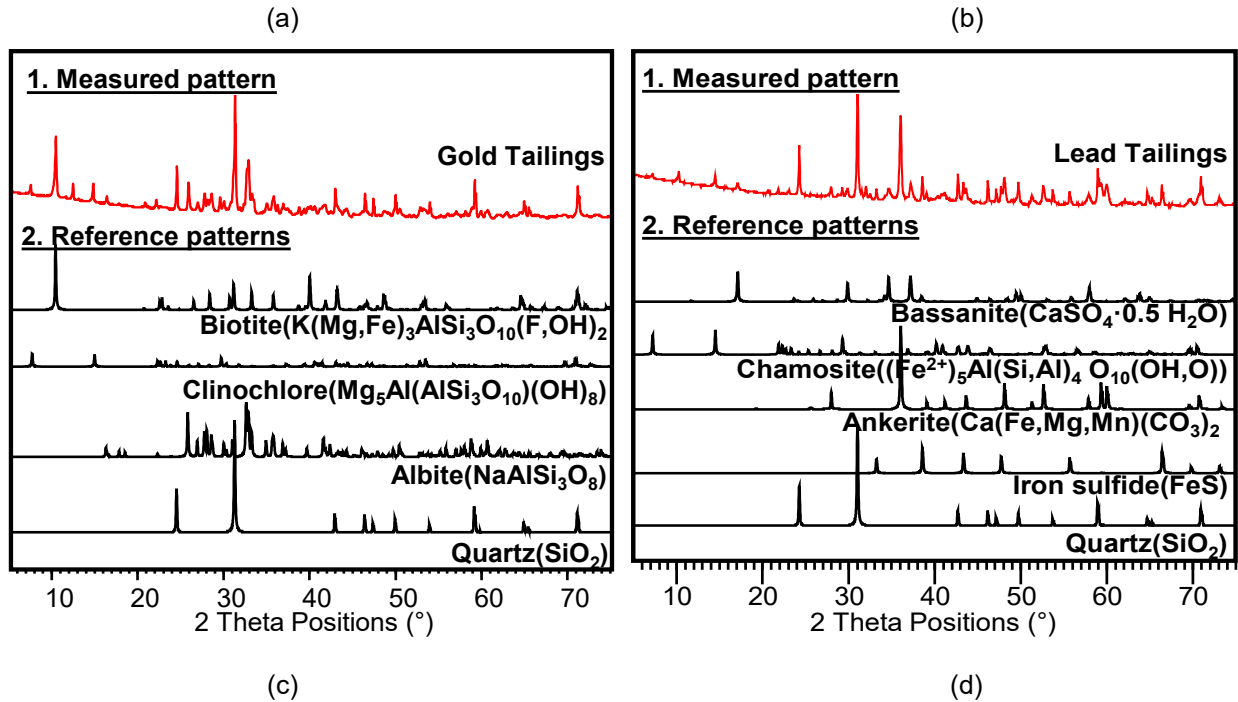
### 3.3. Mineralogical analysis by XRD

The XRD phase identification results are shown in **Figure 2**. Cobalt (Co) was used as an X-ray source instead of a copper (Cu) X-ray source since the high content of iron oxide (Fe<sub>2</sub>O<sub>3</sub>) in all tailings (see **Table 1**) can make noise in the background of the scanning when copper (Cu) is used as an X-ray source (Mos et al., 2018).

Quartz (SiO<sub>2</sub>) was detected in all types of tailings. It is well known that quartz is not reactive in most cementitious systems. Except for bauxite tailings, a large amount of quartz (**Figure 2**) was the main mineral in the remaining tailings. Albite [NaAlSi<sub>3</sub>O<sub>8</sub>] and ankerite [Ca(Fe, Mg, Mn)(CO<sub>3</sub>)<sub>2</sub>] were found in copper and lead tailings, respectively. Albite is sodium aluminosilicate, a type of feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) which extremely low solubility (Blake and Walter, 1999). Ankerite is a combined group of carbonates, including calcium, iron, magnesium, and manganese. Copper tailings have a high amount of quartz, as well as chlorites [(Mg, Fe)<sub>3</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·(Mg, Fe)<sub>3</sub>(OH)<sub>6</sub>] and chamosite [(Fe<sup>2+</sup>)<sub>5</sub>Al(Si, Al)<sub>4</sub>O<sub>10</sub>(OH, O)]. Chamosite is a subgroup of chlorite. As chlorite generally does not dissolve in alkaline solutions (Lowson et al., 2007), the cementitious performance of copper tailings was expected to be very low or negligible. In addition, the reactivity of the gold tailings used in this study may be also very low like that of copper tailings because quartz and albite are the main minerals of gold tailings, however both of these two minerals are stable crystallines. Bauxite tailings have a high content of alumina hydroxides which are boehmite [Al(OH)<sub>3</sub>] and gibbsite [γ-Al(OH)<sub>3</sub>], which can be heated and partially dissolved in sodium hydroxides (Pereira et al., 2009).

The typical mineral phases of gold, copper, and lead tailings indicated that those tailings did not seem to be sufficiently reactive in the cementitious systems. However, bauxite tailings contained gibbsite and boehmite which were reported to have a certain degree of reactivity when mixed with sodium hydroxide. It also supports the concepts generated from XRF results (Pereira et al., 2009). This idea will be further supported by the following dissolution test results.

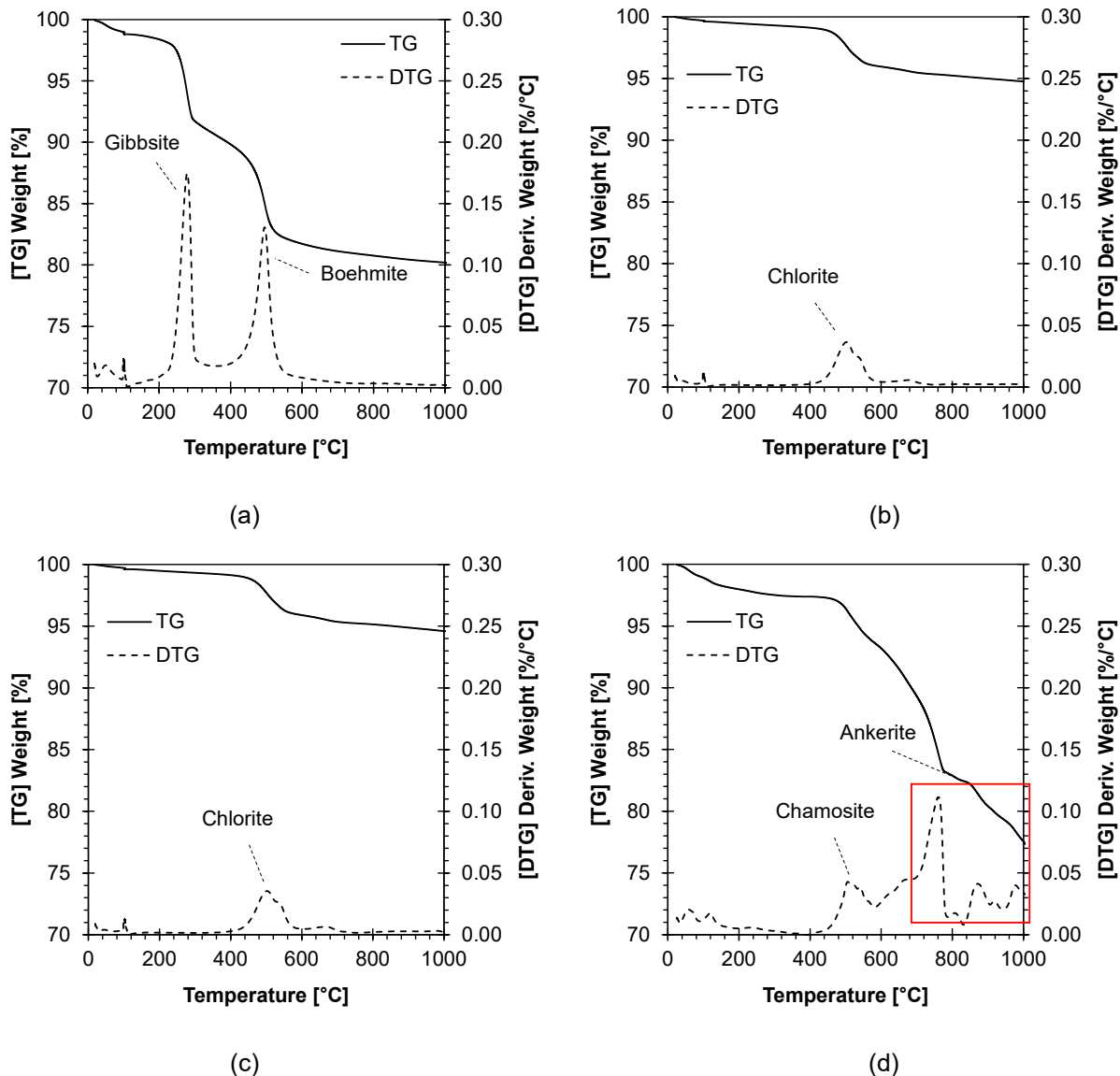




**Figure 2.** Powder XRD patterns and identifiable phases: (a) bauxite, (b) copper, (c) gold, and (d) lead.

### 3.4. Thermogravimetric analysis

Thermogravimetric analysis was performed to understand the characteristic decomposition temperature of different minerals in all tailings. **Figure 3** shows the weight and derived weight loss of four tailings ranging from 0-1050°C. For gold and copper tailings, chlorite is the only mineral containing a hydroxide group and decomposed at about 500°C (Laskou et al., 2006). The weight losses of chlorite in gold and copper are very close. Bauxite tailing shows two distinctive DTG peaks related to the gibbsite and boehmite decomposing at 280°C and 500°C respectively; it is clear to find almost 18% weight loss due to the decomposition (Klopogge et al., 2002). Lead tailings have ankerite, and chamosite will be decomposed; chamosite shows a similar decomposition temperature as gold and copper tailings, but ankerite shows there are three peaks related to a different stage of decomposition: i) First stage occurred at 760 °C: the decomposition of ankerite results in release magnesium calcite, magnesium oxide, iron oxide and liberating carbon dioxide ii) the second stage at 870 °C: an iron oxide interacts with magnesium oxide and forms magnesioferrite. Also, the solid-state reaction between magnesium calcite or calcite and magesioferrite can form diacalciumferrite with liberating carbon dioxide iii) the remaining is calcite decomposed at 980°C, and carbon dioxide released (Milodowski et al., 1989).

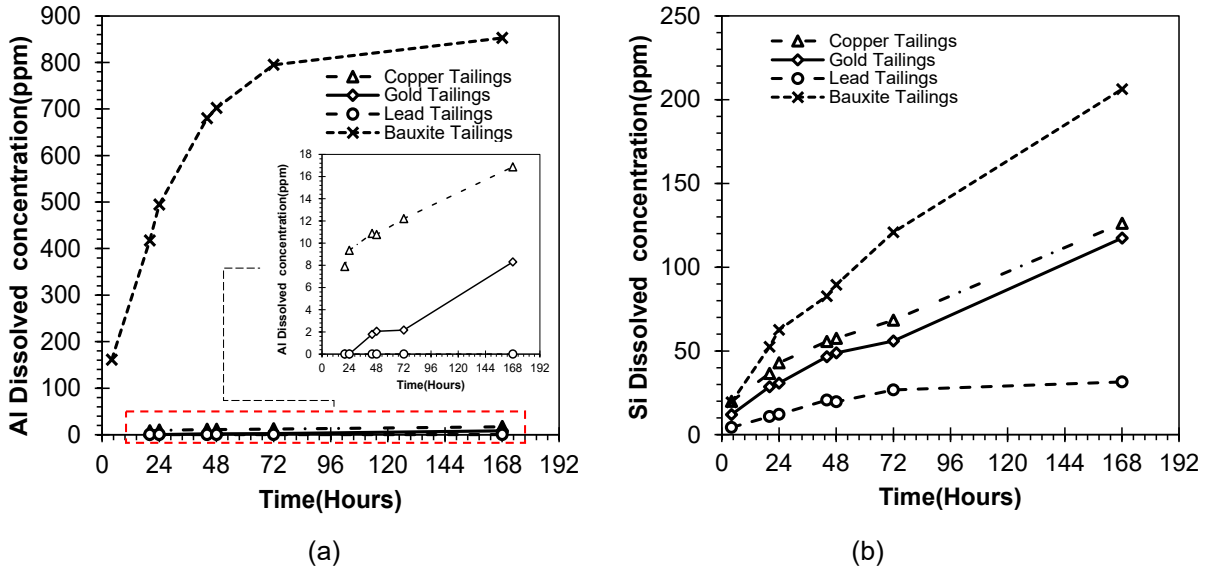


**Figure 3.** Thermal gravity analysis of tailings: (a) Bauxite, (b) Copper, (c) Gold, and (d) Lead.

### 3.5. Dissolution test

(a) shows the dissolution test results of four tailings in 1M sodium hydroxide solution for 7 days. The concentration of dissolved aluminum in bauxite tailings is markedly higher than in other tailings, reaching a maximum of 900 ppm at 168 hours (7 days). This finding suggests that the bauxite tailings have a greater dissolved aluminum concentration, which can be a potential source of aluminum in cementitious materials.

In (a) and (b) the leached solution of lead tailings showed no detectable aluminium through ICP-OES analysis and exhibited the lowest silicon concentration at 31 ppm. The gold and copper tailings exhibited similar dissolved aluminum and silicon levels due to their mineralogical compositions. However, the gold tailings showed an abundance of albite, a stable mineral that led to lower solubility. In the dissolution test, gold tailings demonstrated the lowest solubility of aluminum and silicon. According to XRF results (see **Table 1**), The dissolution test results demonstrated the highest concentrations of dissolved silicon despite bauxite tailings exhibiting a low silicon content. Consequently, bauxite tailings may possess a higher potential for reactivity than other tailings, which can prove this bauxite tailings might be able to function as an alumina supplement in geopolymer paste.

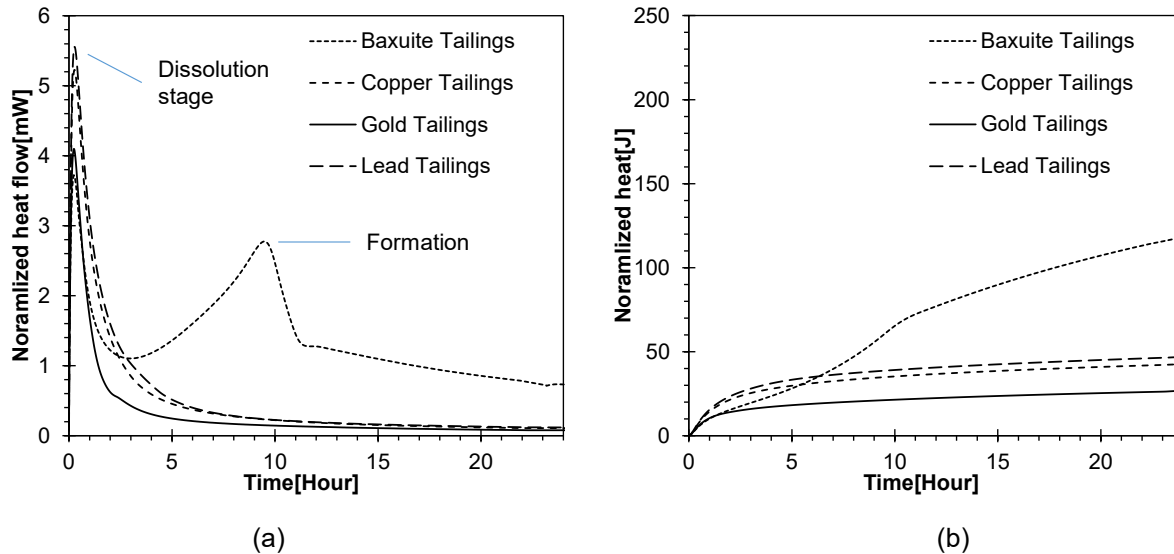


**Figure 4.** Dissolution test results: (a) Al concentration, (b) enlarged Al concentration, and (c) Si concentration.

### 3.6. Reactivity test by $R^3$ isothermal calorimetry test

The reactivities of four tailings were examined through isothermal calorimetry. The specific mixture design is denoted  $R^3$  mixture, which provides enough calcium hydroxide and blends with supplementary cementitious material under an alkaline environment. The heat generated from this mixture design can indicate the reactivity of SCMs.

**Figure 5(a)** presents the normalized heat flow of four different  $R^3$  tailings mixtures. The first peak position in the first 1 hour relates to the dissolution and wetting stage. The second peak was only observed from bauxite tailings, which correlates to the hydration product formation (Avet et al., 2016). **Figure 5(b)** shows the normalized accumulated heat released from the tailings mixtures. The gold tailings mixture released the lowest heat flow and accumulated heat. Although lead tailings dissolution performance was poor, it generated similar heat flow and accumulated heat with copper tailings. As mentioned, the performance of bauxite tailings is prior to other tailings, which have been examined through  $R^3$  isothermal calorimetry test. The reactivity of these tailings will be ranked in the following order: Bauxite tailings > Copper tailings  $\approx$  Lead tailings > Gold tailings.



**Figure 5.** Normalized heat flow and normalized cumulative heat generated by different types of tailings R<sup>3</sup> mixture.

#### 4. Conclusion

The characterization results indicate that the main element in the lead and copper tailings is silicon, which exists in the form of quartz. Gold tailings also contain high silicon in the form of albite and quartz, and they are stable minerals that cannot be involved in cementitious reactions. In addition, gibbsite and boehmite are aluminium hydroxides which are significant components of bauxite tailings. In future studies, gibbsite and boehmite can be heated and transferred into alumina form, improving the reactivity of bauxite tailing. (IEA, 2022)

The R<sup>3</sup> isothermal calorimetry test shows both the heat flow and accumulated heat of bauxite tailing prior to the other tailings. This result also agreed with the dissolution test. It should be noted that bauxite tailing shows higher aluminium and silicon solubility prior to other tailings. Therefore, bauxite tailings seems to be the best candidate for working as supplementary cementitious materials among these four tailings. However, these bauxite tailings' low silicon oxide composition makes it better to behave as an alumina supplement in a geopolymer precursor. As observed from TGA, clear mass drops are related to a few mineral phase decompositions. This implies that the reactivity of other tailings may be improved through several pretreatment methods, including thermal or mechanochemical treatment, which will be investigated in further study.

#### 5. Acknowledgements

The authors are grateful for the supply of two tailings (gold and bauxite), which are being studied as a part of TAILLIQ (Tailings Liquefaction). TAILLIQ is an Australian Research Council (ARC) Linkage Project (LP160101561) supported by financial and in-kind contributions from Anglo American, BHP, Freeport-McMoRan, Newmont, Rio Tinto and Teck. The TAILLIQ project is being carried out at The University of New South Wales, The University of South Australia, The University of Western Australia (lead organisation) and The University of Wollongong. The authors acknowledge the support and contributions of project personnel at each of the supporting organisations.

#### 6. Reference

AVET, F., SNELLINGS, R., DIAZ, A. A., HAHA, M. B. & SCRIVENER, K. 2016. Development of a new rapid, relevant, and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. *Cement and Concrete Research*, 85, 1-11.

- BLAKE, R. & WALTER, L. J. G. E. C. A. 1999. Kinetics of feldspar and quartz dissolution at 70–80 C and near-neutral pH: effects of organic acids and NaCl. 63, 2043-2059.
- GAO, T., SHEN, L., SHEN, M., LIU, L. & CHEN, F. 2016. Analysis of material flow and consumption in the cement production process. *Journal of Cleaner Production*, 112, 553-565.
- IEA 2022. Cement. Paris: IEA.
- JUENGER, M. C., SNELLINGS, R. & BERNAL, S. A. 2019. Supplementary cementitious materials: New sources, characterization, and performance insights. *Cement and Concrete Research*, 122, 257-273.
- KLOPROGGE, J. T., RUAN, H. D. & FROST, R. L. 2002. Thermal decomposition of bauxite minerals: infrared emission spectroscopy of gibbsite, boehmite, and diaspore. *Journal of materials science*, 37, 1121-1129.
- KOMNITSAS, K., KONTOPOULOS, A., LAZAR, I. & CAMBRIDGE, M. 1998. Risk assessment and proposed remedial actions in coastal tailings disposal sites in Romania. *Minerals Engineering*, 11, 1179-1190.
- LASKOU, M., MARGOMENOU-LEONIDOPOULOU, G. & BALEK, V. 2006. Thermal characterization of bauxite samples. *Journal of Thermal Analysis and Calorimetry*, 84, 141-146.
- LOWSON, R. T., BROWN, P. L., COMARMOND, M.-C. J. & RAJARATNAM, G. J. G. E. C. A. 2007. The kinetics of chlorite dissolution. 71, 1431-1447.
- MILODOWSKI, A., MORGAN, D. & WARNE, S. S. J. 1989. Thermal analysis studies of the dolomite-ferroan dolomite-ankerite series. II. Decomposition mechanism in flowing CO<sub>2</sub> atmosphere. *Thermochimica acta*, 152, 279-297.
- MOS, Y. M., VERMEULEN, A. C., BUISMAN, C. J. & WEIJMA, J. J. G. J. 2018. X-ray diffraction of iron containing samples: the importance of a suitable configuration. 35, 511-517.
- OBENAU-EMLER, R., FALAH, M. & ILLIKAINEN, M. 2020. Assessment of mine tailings as precursors for alkali-activated materials for on-site applications. *Construction and Building Materials*, 246, 118470.
- PEREIRA, J. A., SCHWAAB, M., DELL'ORO, E., PINTO, J. C., MONTEIRO, J. L. & HENRIQUES, C. A. J. H. 2009. The kinetics of gibbsite dissolution in NaOH. 96, 6-13.
- SIMONSEN, A. M. T., SOLISMAA, S., HANSEN, H. K. & JENSEN, P. E. 2020a. Evaluation of mine tailings' potential as supplementary cementitious materials based on chemical, mineralogical and physical characteristics. *Waste Management*, 102, 710-721.
- SIMONSEN, A. M. T., SOLISMAA, S., HANSEN, H. K. & JENSEN, P. E. J. W. M. 2020b. Evaluation of mine tailings' potential as supplementary cementitious materials based on chemical, mineralogical and physical characteristics. 102, 710-721.
- SNELLINGS, R., LI, X., AVET, F. & SCRIVENER, K. 2019. Rapid, Robust, and Relevant (R3) Reactivity Test for Supplementary Cementitious Materials. *ACI Materials Journal*, 116.
- YE, J., ZHANG, W., SHI, D. J. C. & RESEARCH, C. 2017. Properties of an aged geopolymer synthesized from calcined ore-dressing tailing of bauxite and slag. 100, 23-31.