PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE

SCHOOL OF ENGINEERING

POLITECNICO DI MILANO

DIPARTIMENTO DI INGEGNERIA CIVILE E AMBIENTALE

COPPER TAILINGS AS SUPPLEMENTARY CEMENTITIOUS MATERIAL: ACTIVATION, LEACHING AND ENVIRONMENTAL BEHAVIOUR

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Thesis submitted to the Office of Graduate Studies in partial fulfilment of the requirements for the Degree of Doctor in Engineering Sciences

Advisors:

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Santiago de Chile, July, 2020

PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
SCHOOL OF ENGINEERING

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A Angela, gracias por acompañarme

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LIST OF ABBREVIATIONS

ACI: American Concrete Institute

BC: Base Case (for comparison of mixtures)

CSH: Calcium Silicate Hydrates

DU: Declared Unit

EBSD: Electron Backscattered Diffraction

FU: Functional Unit

LCA: Life Cycle Assessment

LSX: Studied Tailing, Long-Standing (X: correlative # can be between 1 and 6)

OPC: Ordinary Portland Cement

OPY: Studied Tailing, Ongoing Production (Y: correlative # can be 1 or 2)

PSD: Particle Size Distribution

SCM: Supplementary Cementitious Material

SEM: Scanning Electron Microscope

TGA: Thermogravimetric Analysis

TT: Treated copper Tailing

w/b; water-to-binder ratio (by mass)

w/c: water-to-cement ratio (by mass)

XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence

OUTLINE OF THE THESIS

The present thesis comprises the findings and results of my doctoral work, that have been developed, discussed and showed in three journal articles. Chapters 2, 3 and 4 constitute each one of these articles, and include all the information, results, tables and figures as showed in publications or manuscripts.

The thesis is organized in 5 chapters:

***Chapter 1** – Introduction*

This chapter constitutes the general rationale of this research, including information about Supplementary cementitious materials (SCM), cement and copper industry, entrapment mechanisms and leaching of copper on cementitious mixes, environmental evaluation of concrete mixes with SCM and it presents a current state of the art of these topics. The research gaps found in this review are followed by the statement of the hypotheses, general and specific objectives and a brief explanation of the used methodology. Finally, a brief discussion of the results is presented.

***Chapter 2** – Development of a new supplementary cementitious material from the activation of copper tailings: Mechanical performance and analysis of factors*

This chapter presents the findings and results of the exploration in the use of copper tailings as supplementary cementitious material, and the activation of tailings to improve their cementitious capacity.

***Chapter 3** – Mechanism for copper entrapment in concrete mixtures containing tailings*

This chapter presents the findings and results related with the understanding of the mechanism of entrapment of copper into the cementitious matrix and the leaching of copper compound once tailings are put into a concrete mixture.

Chapter 4 *– Environmental impacts evaluation of treated copper tailings as supplementary cementitious material*

Results of the evaluation of the environmental impacts of the use of tailings (in the form of treated tailings) as supplementary cementitious material are presented in this chapter. The proposal of a methodology to evaluate concrete mixtures with SCM and the results of the performed Life Cycle Assessment of these mixtures is showed.

Chapter 5 *– Conclusions and Perspectives*

This final chapter presents some brief general conclusions and perspectives of this work, including some proposals for future work.

PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
ESCUELA DE INGENIERIA

RELAVES DE COBRE COMO MATERIAL CEMENTICIO SUPLEMENTARIO: ACTIVACION, LIXIVIACION Y COMPORTAMIENTO MEDIOAMBIENTAL

Tesis enviada a la Dirección de Postgrado en cumplimiento parcial de los requisitos para el grado de Doctor en Ciencias de la Ingeniería.

FELIPE VARGAS MUÑOZ

RESUMEN

El impacto de la industria del cemento en la generación de gases de efecto invernadero (5-8 % del total global) hace necesario la búsqueda de alternativas a este material que permitan reducir su impacto, sin afectar las ventajas y propiedades que permiten su amplia utilización en la construcción. Por otro lado, la generación de residuos de la industria del cobre, a tasas crecientes debido a la baja ley de los minerales alcanzando las 200 toneladas de relaves por tonelada producida de cobre, hacen que la búsqueda de formas de uso de estos residuos sea una importante necesidad y ofrezca una oportunidad para la minería. Esto es de alto impacto en países productores de cobre como Chile. En esta tesis se investigó la unión de estas dos necesidades: la utilización de relaves de la industria del cobre como material cementicio suplementario. Para esto, se propuso el uso de tratamientos mecánicos y térmicos para mejorar la capacidad cementicia de los relaves, estudiando también la capacidad de la matriz cementicia de retener la lixiviación de cobre y finalmente el desempeño medioambiental de las mezclas de concreto con relaves tratados.

La activación de relaves de cobre mediante tratamientos de molienda y calcinación se estudió comparando mezclas cementicias sin relaves y con relaves sin tratar versus muestras con relaves tratados, esto últimos elegidos entre muestras que mostraron mayor potencial de activación, mostrando aumentos de hasta un 40% en la resistencia mecánica. La heterogeneidad de las muestras se observó al analizar el aumento de entre un 80% y un 140% en la capacidad puzolánica de los relaves una vez tratados.

La lixiviación de metales pesados de muestras cementicias conteniendo relaves fue analizada, estudiando específicamente el mecanismo de atrapamiento de fases de cobre dentro de la matriz cementicia. Se determinó que la razón agua-cemento es estadísticamente significativa al analizar la lixiviación de cobre, y se observó la migración de fases de cobre durante el proceso de hidratación hacia productos cementicios como silicatos de calcio hidratados, lo cual fue comprobado mediante análisis de SEM y XANES. También se midió los niveles de lixiviación generales, observando que cuando los relaves están incorporados en la matriz cementicia, los niveles de lixiviación son despreciables.

Finalmente, con la información anterior se desarrolló una metodología para la medición del impacto medioambiental del uso de relaves como material cementicio suplementario, usando análisis de ciclo de vida (LCA) para determinar el posible beneficio del uso de estos desechos. Como resultado se determinó que los beneficios del uso de relaves dependen de la capacidad de estos como material cementicio suplementario, y que, a mayor nivel de desempeño, mejores son los indicadores ambientales comparados con mezclas sin relaves. La nueva metodología propuesta permite una comparación certera de mezclas cementicias con materiales cementicios suplementarios, facilitando el estudio medioambiental de estos y otros residuos.

Este estudio demostró la factibilidad del uso de relaves como material cementicio suplementario, con las limitaciones impuestas por la heterogeneidad, la presencia de altas concentraciones de cobre y los impactos medioambientales analizados y discutidos.

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PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
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COPPER TAILINGS AS SUPPLEMENTARY CEMENTITIOUS MATERIAL:
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Thesis submitted to the Office of Graduate Studies in partial fulfilment
of the requirements for the Degree of Doctor in Engineering Sciences by

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ABSTRACT

The impact of the cement industry on the generation of greenhouse gases (5-8% of the total worldwide) makes mandatory the search for more environmentally compatible alternatives, without affecting the advantages that allow for its wide use in the construction industry. Moreover, waste generation from copper industry, at increasing rates due to the progressively lower grade of minerals, reaching 200 tons of tailings per ton of produced copper, makes mandatory the search for new ways of using such a waste and offers an opportunity for mining industry to be environmentally compatible as well. This is especially critical in countries were copper industry is relevant and a high impact activity such as Chile. This research project associated these challenges by using tailings from the copper industry as a supplementary cementitious material (SCM) capable of replacing an important part of the cement. To achieve this, the use of mechanical and thermal treatments was studied to improve the cementitious capacity of the tailings, also analysing the capacity of the cementitious matrix to entrap copper and reduce leaching, and finally assessing and evaluating the environmental performance of concrete mixtures with treated tailings.

Copper tailings activation, through grinding and calcination, was studied comparing cementitious mixtures without tailings, with un-treated tailings, and treated tailings, the latter chosen among cases that showed the highest activation potential. The treatments showed increases of up to 40% in mechanical performance. The heterogeneity of tailing samples was observed analysing the increase of pozzolanic capacity between 80% and 140% of the tailings after treatment.

Leaching of heavy metals from cementitious samples containing tailings was analysed, studying specifically the mechanism of entrapment of copper phases within the cementitious matrix. The water-cement ratio was determined to be statistically significant in controlling copper leaching, and migration of copper phases during the hydration process towards cementitious products such as calcium silicates hydrates (CSH) was observed as verified by SEM and XANES. Leaching concentrations were also measured for other metals, observing that when tailings are incorporated into the cementitious matrix, leaching levels are negligible.

Finally, with the previous information and results, a methodology was developed to measure the environmental impact of the use of tailings as SCM, using life cycle analysis (LCA) to determine the possible benefit of the use of these materials. As a result, it was determined that the benefits of the use of treated tailings vary depending on their cementitious capacity as SCM, and, at a higher level of mechanical performance, environmental indicators show better results compared to mixtures without tailings. The new proposed methodology allows an accurate comparison of cementitious mixtures with SCM, allowing a proper environmental study of these and other residues.

This study demonstrated the feasibility of the use of tailings as supplementary cementitious material, with the limitations imposed by heterogeneity, the presence of high copper concentrations and the environmental impacts analysed and discussed.

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PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
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RESIDUI DALLA PRODUZIONE DI RAME COME MATERIALE CEMENTIZIO SUPLEMENTARE: ATTIVAZIONE, LISCIVIAZIONE E PRESTAZIONI AMBIENTALI

Tesi inviata alla Direzione di Post-Laurea in parziale adempimento dei requisiti per il titolo di Dottore in Ingegneria per

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RIASSUNTO

L'impatto dell'industria del cemento sulla generazione di gas a effetto serra (5-8% del totale globale) rende necessaria la ricerca di alternative a questo materiale che ne riducano l'impatto, senza compromettere i vantaggi e le proprietà che ne consentono un ampio utilizzo nel settore delle costruzioni. D'altra parte, la generazione di rifiuti dell'industria del rame, a tassi crescenti a causa del basso contenuto di minerali, che raggiunge 200 tonnellate di residui per tonnellata prodotta di rame, rende la ricerca di modalità di utilizzo di questi rifiuti un'esigenza e un'opportunità importante per l'industria mineraria. Questo è soprattutto vero per i Paesi produttori di rame come il Cile. In questa tesi, è stata studiata l'unione di queste due esigenze: l'uso di residui dell'industria del rame come materiale cementizio supplementare. Per questo, è stato proposto l'uso di trattamenti meccanici e termici per migliorare la capacità dei residui come materiale cementizio, studiando anche la capacità della matrice cementizia di trattenere la lisciviazione del rame (metallo) e infine le prestazioni ambientali delle miscele cementizie contenenti i residui trattati.

L'attivazione dei residui dalla produzione del rame attraverso trattamenti di macinazione e calcinazione è stata studiata confrontando miscele cementizie senza residui e con residui non trattati rispetto a miscele con residui trattati, questi ultimi scelti tra i residui che mostravano il più alto potenziale di attivazione, mostrando aumenti fino al 40% della resistenza meccanica. L'eterogeneità dei residui è stata osservata analizzando l'aumento tra l'80% e il 140% della capacità pozzolanica dei residui trattati.

È stata analizzata la lisciviazione di metalli da miscele cementizie contenenti i residui, studiando in particolare il meccanismo di intrappolamento delle fasi del rame (metallo) all'interno della matrice cementizia. È stato determinato che il rapporto acqua-cemento è statisticamente significativo quando si analizza la lisciviazione del rame e si è osservata la migrazione delle fasi del rame durante il processo di idratazione verso prodotti cementizi come i silicati di calcio idratati (CSH), attraverso l'analisi SEM e XANES. Sono stati inoltre misurati i livelli generali di lisciviazione, osservando che quando i residui sono incorporati nella matrice cementizia, i livelli di lisciviazione sono trascurabili.

Infine, con le informazioni di cui sopra, è stata sviluppata una metodologia per misurare l'impatto ambientale dell'uso dei residui come materiale cementizio supplementare, utilizzando l'analisi del ciclo di vita (LCA) per determinare il possibile beneficio dell'uso di questi rifiuti. I risultati mostrano che i benefici dell'uso dei residui dipendono dalla loro capacità di materiale cementizio supplementare e che, a un livello più elevato di prestazioni, gli indicatori ambientali sono migliori di quelli delle miscele senza residui. La nuova metodologia proposta consente un confronto corretto e accurato di miscele cementizie con materiali cementizi supplementari, facilitando lo studio ambientale di questi e altri residui.

Questo studio ha dimostrato la fattibilità dell'uso dei residui dalla produzione del rame come materiale cementizio supplementare, analizzando i limiti imposti dall'eterogeneità, la presenza di elevate concentrazioni di rame e l'impatto ambientale.

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Chapter 3. Vargas, F., Alsina, M., Gaillard, J., Pasten, P., López, M. Copper entrapment in concrete mixtures containing tailings as partial replacement of cement. Submitted: April 2020, Journal of Cleaner Production

Chapter 4. Vargas, F., Lopez, M., & Rigamonti, L. (2020). Environmental impacts evaluation of treated copper tailings as Supplementary cementitious materials. Resources, Conservation and Recycling, 160. https://doi.org/10.1016/j.resconrec.2020.104890

1. INTRODUCTION

In recent years, construction industry has developed a growing interest in the reduction of environmental impacts. Concrete, despite being one of the most used materials in the world (A. M. Ramezanianpour et al., 2014), is a highly polluting material. In 2019 cement production reached 4100 million metric tons worldwide (United States Geological Survey, 2020), mainly in Middle East, Africa and East Asia (China and India). In Chile, cement consumption in 2019 was 4.1 million metric tons (ICH, 2019), considering production and imports. Those levels of production make important to analyse the life cycle of the manufacturing of concrete, from the cement production (including the extraction processes of its constituent materials) to the use of concrete until the disposal as a demolition waste product (Turk et al., 2015).

The impact of the cement production into the environment is one of the main reasons for the search of new materials and construction methods in recent years. Calcium silicates are the major constituent of the clinker, obtained by calcining natural carbonates as limestone or chalk, in the presence of clays and subsequently heated to temperatures above 1400 °C, where the carbonates decompose, releasing CO_2 and forming hydraulic phases together with other present materials (Moretti & Caro, 2017). The production of 1 metric ton of Portland cement involves the emission of approx. 1 ton of CO_2 to the atmosphere: about 50% comes from the decomposition of carbonates (Schneider et al., 2011). Globally, clinker production accounts for between 5% and 8% of total CO_2 emissions (Miller, 2018). The clinker represents 95% by mass of Portland cement (Mehta & Monteiro, 2014) and so the capacity to reduce costs and minimize the negative effects of its production will have an important impact on future technology development in concrete construction and industry. Research has been carried out in different ways to reduce the impact of the cement production, some examples are the reduction of clinkerisation temperatures by adding new components in the kiln, new methods of mixing, carbon capture and the use of Supplementary cementitious materials to replace part of the cement to fill in concrete (Schneider et al., 2011).

1.1 Supplementary cementitious materials

A Supplementary Cementitious Material (SCM) can be defined, according to Thomas, as "a large group of materials that are widely used in concrete in addition to Portland cement" (M. Thomas, 2013). Studies on the use of SCM have been carried out on different materials, such as natural pozzolans (Ercikdi et al., 2010), fly ash (Matos et al., 2019), blast furnace slag (Shi et al., 2008), silica fume (Rossen et al., 2015), metakaolin (Adjoudj et al., 2014), rice husk ash (Habeeb & Mahmud, 2010) and other by-products of different industries (Lothenbach et al., 2011). The effect of the use of SCM in concrete can be divided into two contributions occurring simultaneously:

a) **Chemical Contribution**: it refers to the contribution to the pozzolanic and hydraulic reactions in the process of cement hydration. Mainly, SCM contribute to the pozzolanic reaction, because most of them does not have cementitious properties (Lothenbach et al., 2011). This contribution is related to the chemical composition and particle size distribution present in the SCM. In general, SCM used in replacement of cement have lower calcium concentrations than Portland cement, but higher siliceous material concentrations allowing for the formation of calcium silicate hydrates (CSH) during cement hydration.

b) **Physical Contribution**: SCM particles act during the hydration process as a nucleating point, related with the space between particles and the surface where the hydration products aggregate (Zunino & Lopez, 2017). Given this physical contribution, even inert materials can work as SCM without the need for specific chemical compositions, validating their use from a view of durability, strength, workability, etc.

In addition, it has been investigated the use of mixtures that consider the use of various types of SCM, combining both effects efficiently, such as ternary or quaternary blends

(Bentz et al., 2015; Celik et al., 2015; Khodabakhshian et al., 2018; Schöler et al., 2015). This approach can help to further reduce the use of Portland cement, with replacement levels that can reach 60% (Bentz et al., 2012), and adequately balance the physical and chemical contribution to cement hydration process.

In recent developments, it has been studied the use of tailings as a SCM. It has been researched the use of tungsten tailings (Choi et al., 2009), sulphates tailings (Zheng et al., 2015), iron tailings (Zhao et al., 2014) as a SCM and as a fine aggregate, and copper tailings (Onuaguluchi & Eren, 2012). In this context, due to the volumes involved, research on the use of copper tailings has taken great relevance. Nevertheless, to improve their cementitious capacity, this kind of by-products need to be activated.

1.2 Supplementary cementitious materials activation

The improvement of performance of SCM in concrete has been investigated since mid-20th century, with the use of thermal treatments. Optimal temperatures to observe chemical and mineralogical changes with potential to improve the effect of these SCM are 800°C for andesite (Souri et al., 2015), 650°C-700°C for kaolinite and kaolinite-bentonite (Taylor-Lange et al., 2015). However, other SCM show lower improvements with calcination: zeolites has been researched with temperatures above 300°C without showing great pozzolanic capacity after the treatment, and changes are more related due to morphological and particles size than chemical contribution (Küçükyıldırım & Uzal, 2014; Seraj et al., 2016). Nonetheless, these treatments can affect other performance variables such as workability.

Changes in particles size also has been researched for SCM as an effective method to improve the performance of cement blends. Recent researchers (Jain, 2012; Souri et al., 2015; Tironi et al., 2013) have shown that the combined effect of thermal and milling treatments have an increased effectiveness, with particles size above 45 µm. Treatments without high temperatures processes also show improvements in reactivity of zeolites (Burris & Juenger, 2016) and kaolin (Ilić et al., 2016).

Other activation strategies include using additions of calcium oxides and calcium hydroxides. This has been investigated to enhance the hydraulic and pozzolanic activity; an example is the activation of fly ashes after the mixing process proposed by Bui, Ogawa, Nakarai, & Kawai (2015). Other SCM as metakaolin and rice husk ashes activation have been investigated. Mechanical properties (Grist et al., 2013) and durability have been studied also (Hossain et al., 2015). It has been reported improvements in early age strength when adding calcium oxide with fly ash in ternary blends, with replacement levels above 5% of the primary SCM (Antiohos & Tsimas, 2004). Pozzolan blend with calcium hydroxides have similar hydration products than Portland cement hydration products, such as calcium silicate hydrates and calcium aluminates hydrates (A. A. Ramezanianpour, 2014).

1.3 Copper mining industry environmental impact

The copper mining industry is one of the most important extractive industries worldwide, with productions levels of 20 million of metric tons (tons thereafter) estimated for 2019 (United States Geological Survey, 2020). Of this production, 28% was extracted in Chile. Since 2013, copper industry has increased by 10%. Each ton of refined copper generate 196.5 tons of tailing (Onuaguluchi & Eren, 2012) and, depending on the metallurgical process associated with the type of rock, between 2.2 and 3 tons of copper slag (Shi et al., 2008). Whereas in Chile in 2018 were produced 5.87 million cubic meters of copper, the by-products such as copper slag was 16 million tons and tailings were almost 580 million tons (SERNAGEOMIN, 2019a). The tailings are produced when the crushed rock enters the separation process performed by floating of the “copper concentrate”, where the fraction without high copper concentrations (with concentrations less than 30% by mass) is discarded as tailing. Typical concentrations that can be found in copper tailings are 0.06 % by mass of copper oxides and sulphates. The copper slag is produced by applying a silica oxide flow to the “copper concentrate” fraction, where the iron oxides and silica oxides are separated and discarded (Schlesinger et al., 2011).

Tailings, as a by-product of a mineralogical process, have high concentrations of toxic elements, as copper, arsenic, tungsten, lead, strontium (Argane et al., 2015; Moya et al., 2019). It has been measured concentrations of 6900 mg/kg of copper compounds in Chilean copper tailings (Carkovic et al., 2016) which is one of the most common toxic elements found in copper tailings (SERNAGEOMIN, 2019b).

The range considered harmful for human health in soil for copper compounds is typically bellow 400 mg/kg for residential soils. Regulations indicate that maximum allowable concentration is 600 mg/kg of copper for soils used for an industrial activity, according to Brazilian regulations (Carkovic et al., 2016). Therefore, concentrations of copper in tailing can reach 38 times the maximum allowable concentrations for human health.

1.4 Copper tailings in concrete

Research on new SCM has led to the study of the use of tailings as a substitute of cement or as a substitute of aggregates in concrete. The use of copper tailings has been researched as SCM (Onuaguluchi & Eren, 2012; B. S. Thomas et al., 2013a) and as fine aggregate replacement (Zou et al., 2015). Copper tailings have also been investigated as principal element in the production of bricks trough geopolymerization process (Ahmari & Zhang, 2012).

In blends with Portland cement and tailings, Onuagulachi & Eren (2012) have indicated that at replacement levels of 10% by mass, concrete strength exceeds the normal performance. It has been demonstrated that with major replacement levels (until 20%) there is no major impacts in compressive strength at 28 days. In durability, it has been demonstrated that properties such as sulphate attack resistance and chloride penetration also have better performance at replacement levels of 10% (Onuaguluchi & Eren, 2012). Similar conclusions have been obtained with higher concentration of copper tailings in concrete durability when is used as a fine aggregate (B. S. Thomas et al., 2013a).

The use of tailing for geopolymer bricks production also has been studied. The geopolymerization processes is based on mineral polymers formation in alkaline environment with normal to high pressure (below 35 MPa), from ambient temperatures of from ambient to 120°C, the use of alkaline activators (sodium hydroxide, potassium hydroxide and calcium hydroxide), and silicates (Masi et al., 2014). The chemical composition of these geopolymers, with –Si-O-Al-O- molecular arrangements, allows the use of silicates and alumina in highly compact arrangements in high pH environments (Ahmari & Zhang, 2012). Research carried out for the production of geopolymers blocks have had promising results, with 28 MPa of unconfined compressive strength with 16% of water, 15 M of concentration of NaOH in water, 90° and 0.5 MPa forming pressure (Ahmari & Zhang, 2012). Durability also has been investigated: due to the nature of the geopolymerization process, these blocks are affected in acidic environments, nonetheless, with no significant differences between them and Portland cement geopolymers blocks.

1.5 Leaching of cementitious mixtures with tailings

Cement chemistry during hydration process has been widely studied in the past (Taylor, 1997), however the particular cement chemistry of hydration processes with the presence of SCM has not been fully determined for the entire spectrum of them (Lothenbach et al., 2011). This can be related with the entrapment mechanism of metals present in tailings, such as copper.

For different metals and other elements present in tailings, it has been proposed trapping mechanisms within the structure of the cement hydration products: chemically (the inclusion of these elements in a new compound produced during the hydration process) or physically (adsorbed or encapsulated) (Guo et al., 2017), which has also been researched in polymerization processes (F.-H. Wang et al., 2015).

One problem with the presence of these toxic elements is leaching, generating loss of mass and risk for the human health. Concrete leaching (leaching of concrete hydration compounds) is produced by the hydrolysis of calcium hydrated compounds in the cementitious matrix (Mehta & Monteiro, 2014). Calcium hydroxides have high solubility in water (1230 mg/L). When calcium hydroxides are lost, cementitious matrix can be attacked by chemical compounds. In the presence of toxic elements, some of them will be lost because of the loss of calcium compound (some of them can be chemically related with calcium). Others will be exposed once the cement matrix is damaged by loss of mass.

In the case of copper tailings, copper compounds are an important source of possible leaching, due to their concentrations. Copper is a transition metal with atomic number 29. It is found in nature as a pure metal, but in most of the exploited minerals is found in combination with Molybdenum and other metals like Gold or Silver. In tailings, copper can be found normally in Cu^{+2} oxidation state, in the form of oxides (CuO), sulphates ($CuSO_4$) and Chalcopyrite ($CuFeS_2$). The presence of copper in the hydration of cement generates strength losses at high replacement levels (Ma et al., 2010).

The mechanism of incorporation or entrapment of copper into the cementitious matrix has not been validated. Some researchers have studied about the incorporation of copper into the hydrated cement and believe that would come closer to a model of encapsulation or adsorption (Huang et al., 2014). In this case, the encapsulation or adsorption mechanism is not clear and if it is related with the packing and density of the hydration products (F.-H. Wang et al., 2015).

Packing can be defined as the way that the hydration products, such as CSH, in cement are produced and how these products are ordered into the cementitious matrix. The density of CSH is related with the water content (Taylor, 1997), related also with porosity of the paste. With lower porosity, it is more difficult for the ions to migrate and leachate into the cementitious matrix.

1.6 Environmental studies on the use of Supplementary cementitious materials

The effect of the addition of SCM into cementitious mixtures has been studied widely and for a long time, focused on mechanical performance and effects on durability (Juenger & Siddique, 2015). Nevertheless, the environmental impact of the use of those materials has been only recently incorporated into the analysis and decision-making of their use. Most of the studies have focused on the most commons SCM, such as fly ash (Celik et al., 2015; De Schepper et al., 2014; Petek Gursel et al., 2014) and slags (Chen et al., 2010; K. H. Yang et al., 2015), with few studies on other less common SCM as Sewage Sludge Ashes (Nakic, 2018), Diatomaceous earths (Li et al., 2019), Rice Husk Ash (Gursel et al., 2016) or combinations of SCM with recycled aggregates (Kurda et al., 2018). Due to novel use of tailings as SCM, there are no studies about their environmental performance when used as SCM.

Studies show the benefit of the use of SCM into a concrete mixture: when fly ash is incorporated into a concrete mixture, reductions of over 60% can be seen on kg of CO2-eq per cubic meter of concrete (Celik et al., 2015; Kurda et al., 2018) for replacement levels up to 50% by mass. Nevertheless, some issues arise when comparisons are made between studies and results, specifically inside studies comparing mixtures with and without SCM.

A well-known and standardise methodology to analyse and compare the environmental performance of products or processes is the Life Cycle Analysis (LCA), and cradle-to-gate focus is widely used because of the lack of information on the use of concrete after production. Nevertheless, a majority of studies consider those SCM as waste, with no consensus on allocation of the production impact (Saade et al., 2019) and with lack of information about the avoided disposal of those materials, that instead need to be considered in the analysis (Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on Waste and Repealing Certain Directives, 2008). Moreover, the most common problem found is the comparison of concrete mixtures with different performances, at different concrete mixture designs, changing the boundaries and the base comparison on each study.

1.7 Comparison of concrete mixtures from an environmental point of view

A consistent comparison of any product with their proposed alternative to evaluate the increase or decrease of any environmental performance is fundamental in order to obtain a true picture of the use of that material (Klopffer & Grahl, 2015). In the case of concrete mixtures with SCM, comparison based on a common basis is important due to high environmental impacts of concrete mixtures and huge amounts of concrete used worldwide (De Schepper et al., 2014). So it is really important to choose a proper Functional Unit (FU) in the LCA.

A Functional Unit is defined in the ISO 14040 standard as a *"quantified performance of a product system for use as a reference unit"*. In most of the studies about the use of concrete as SCM, a declared unit (simpler to define, a unit without an associate performance) is used, commonly defined as a cubic meter of concrete. This can lead to error in the estimation of the impacts. Some studies propose the use of factors or ex-post analyses to normalize the results by mechanical performance (Damineli et al., 2010), or the use of factors that can include compressive strength, durability measured as permeability (Sagastume Gutiérrez et al., 2017) and/or binder content or a combination of those factors (Panesar et al., 2017). Moreover, concrete design not always is considered, and the type of mixtures is changed without consideration on rheology, water content, aggregates content, plasticizers or other factors. Also, when comparing concrete mixures at equal performances, provisions need to be made in order to avoid changes into mixture design.

1.8 Statement of the problem

The increasing interest in the use of SCM in recent years has the potential to reduce the environmental impacts of concrete and cement production, relevant for impact categories such as global warming or ozone depletion. According to the information provided in the previous section, improving and understanding the benefits of the use of those SCM imposes significant challenges. The ideal use of any SCM must combine the use of alternative materials, such as by-products, with three properties: first, a positive impact on the environment, second, high impact into the concrete properties and third, at low cost. With the use of tailings as a SCM, the following difficulties can be identified:

- Tailings heterogeneity
- Lack of information about tailings properties, chemically and physically
- The presence of toxic elements, such as copper, into tailings
- Lack of a proper way to evaluate and compare concrete mixtures with SCM, including tailings, from an environmental point of view

1.9 Hypotheses

As result of the previous bibliographical research, focused on the use of tailings as SCM, the improvement of the mechanical properties, the study of leaching risks and the environmental performance of concrete made with this SCM, the following hypotheses were proposed:

Regarding the performance improvement of mixtures containing tailings as supplementary cementitious material:

H.Ia *Tailings cementitious capacity is improved by a combination of heat treatment under 900 °C and decreasing particle size of 15%, which improve performance in mechanical strength of concrete.*

H.Ib *There is an environmental performance benefit on the use of concrete mixtures containing copper tailings as supplementary cementitious material* *compared with concrete mixtures without copper tailings as supplementary cementitious material up to 10% measured as* CO_2 *release*

Regarding the form copper is incorporated into the cement hydration products:

H.IIa *The contribution of free lime and alkali at the beginning of the hydration process, in larger proportions than those in Portland cement, improves chemical entrapment of copper present in tailings*.

H.IIb *Changes in hydration products packing due to higher concentrations of CSH due to changes on water-to-binder ratio, improves the physical entrapment of copper present in tailings.*

1.10 General Objective

The aim of this research is to contribute to the understanding of the chemistry and hydration of cement in the presence of tailing from the copper industry, to the study of the risk of the use of this material as SCM with presence of copper, and the environmental performance of this concrete mixtures. To achieve this, for the consecution of this research, the following main objectives were used as a guide through the development of the research work:

To provide mechanical, safety and environmental information in order to increase the use of copper tailings as supplementary cementitious material

1.11 Specific Objectives

For this research, specific objectives where proposed to achieve the main objective. Related with the two groups of hypotheses stated, three groups of specific objectives were used through the development of the research.

Related with improvement of cementitious properties of tailings as SCM:

O1.a *Quantify the benefits of physical and chemical treatments on cementitious properties of tailings*

O1.b *Maximize the use of tailings as a supplementary cementitious material*

Related with the leaching and entrapment of copper into de cementitious matrix:

O2.a *Quantify the effect on mechanical strength of the hydration products generated in the presence copper*.

O2.b *Trap copper to cementitious mixtures to reduce or eliminate the risk of leaching*

Related with the environmental performance of concrete mixtures containing copper tailings as supplementary cementitious material:

O3.a *Quantify the environmental impacts of physical and chemical treatments*

O3.b *Quantify the environmental benefits of the use of copper tailings as supplementary cementitious material in concrete mixtures*

1.12 Research Scope

The scope of this research is related to the tailings used in the investigation. Two types of tailings were considered:

- The use of tailings collected from Chilean copper mining sites (the world largest copper producer) to work with actual residues conditions. One type of tailing is from long standing sites, thus, abandoned mining sites. The other type is from ongoing production sites, thus, from mining facilities still on work.

Also, related with the development of the research:

- The use of ordinary Portland cement for all the concrete mixtures, despite the extended use of pozzolanic cement in the Chilean context.

- The use of data and statistics based on the Chilean context or adapted to the Chilean context (the last, due to the lack of information in most cases).

The most relevant generated volume of tailings in Chile is that from copper mining industry. Specific problems for their incorporation as a SCM are to be considered like the presence of heavy metals and heterogeneity. However, these wastes have great potential for use as cement replacement material from social, environmental and economic point of view.

1.13 Research Methodology

For research development, a 5-stage methodology was proposed and used. Each one of these main stages had its own methodology for collecting data and sampling (if necessary) and for statistical data analysis. A scheme of the used methodology can be seen in figure 1.1. The characterization proposed tests were carried out at the age of 28 days for mechanical properties, with additional measurements at 7 and 90 days. For leaching measurements, 28 days age concrete and mortar mixtures were used. For hydration products and copper entrapment measurements, samples between 24 and 7 days were used. Pastes and mortar mixtures were used in most of the research.

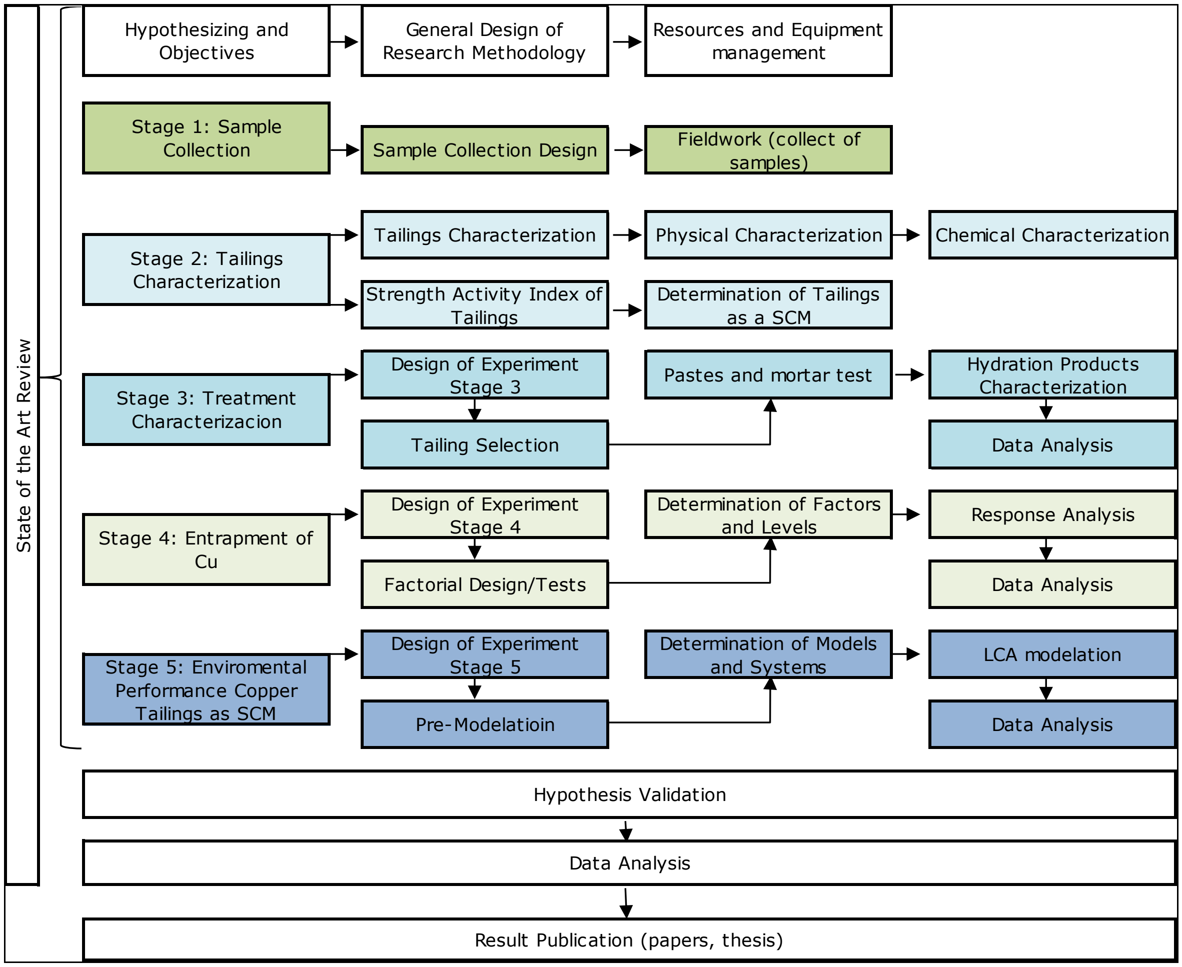

Figure 1.1 Scheme of research methodology used during the development of this research.

Stage 1: Samples Collection

Samples collection consisted in the preparation, design of the methodology and properly the collection of samples. For this study, 10 tailings were selected, of whom 8 tailings finally were used in the study: 6 from abandoned mining sites (designed from LS1 to LS6) and 2 from ongoing mining operations (OP1 and OP2).

Stage 2: Tailings characterization and effect as supplementary cementitious material

Chemical and physical characterization of the tailings were made in this stage. Also, characterization of the effect of the tailings as SCM, without any treatment, was made in this stage. PSD (Particle Size Distribution), TGA (Thermogravimetric analysis), calorimetry, SEM (Scanning Electron Microscope), XRD (X-Ray Diffraction) and XRF (X-Ray Fluorescence) were among the test used to characterize tailings, pastes and mortars. The data collected in this stage was used in all the following stages, for comparison purposes.

Stage 3: Treatments effect on tailings

In this stage, three of the most promissory tailings obtained from the previous stage were used. In this stage, the effect at different levels of the treatments under study was analysed. SEM, XRD, calorimetry, TGA were among the test used.
A second-order model of response surface called central composite design (CCD) was used, which allowed high levels of rotatability of factors, to determine a direction of maximum response. Levels were chosen based on results of stage 2.

Stage 4: Copper entrapment

Three factors influencing copper entrapment were considered and their statistical significance was determined. Factors were chosen according to literature and a tailing was chosen due to higher concentration of copper compared with other samples. This stage was divided in the study of factors to determine statistical significance, where a factorial design $n=2^3$ was used at different hypothetical situations (changes on pH on the cementitious mix); and determination of the phases or special position of copper compound during hydration of cementitious mixtures. For this, XRD, SEM, EBSD, and leaching measurements were made.

Stage 5: Environmental performance of concrete mixtures

This stage was divided in two sub-phases. First, a methodology was developed and proposed for the proper comparison of mixtures with treated tailings; secondly, different scenarios were proposed to compare the environmental performance of concrete mixtures with and without SCM. This was made by applying the Life Cycle Assessment methodology, and sensitivity analyses were made for transportation and the consideration of the avoided impacts associated with the final disposal of tailings. Data from previous stages was used to determine concrete mixture design and behaviour of the mixtures.

1.14 Preview of Results

Findings from this research are presented as follow related with each stage and analysis of the consecution of hypotheses and objectives. Detailed results, in the form of three papers, can be seen in chapters 2, 3 and 4.

1.14.1 Related with activation of copper tailings for use a SCM

Eight tailings were collected from six abandoned mines and two ongoing production copper mines. With these 8 tailings, physical and chemical analysis were performed to characterize the properties of each of them. Figure 1.2 shows a comparison between tailings and other SCM in a ternary diagram. Particle size showed that tailings are coarser than cement. On average, mixtures at 20% replacement level show a decrease of 35% (range 20-55% decrease) compared with mixtures without tailings on mechanical performance. Based on TGA analysis, 3 tailings were chosen and were calcined (between 550 and 950°C) and milled (measured as time, between 0 and 60 minutes), to determine the improvement on cementitious capacity. To analyse response, a central composite design of 2 factors was used. Responses analysed were mechanical performance, calorimetry and pozzolanic activity, measured with the novel R3 method.

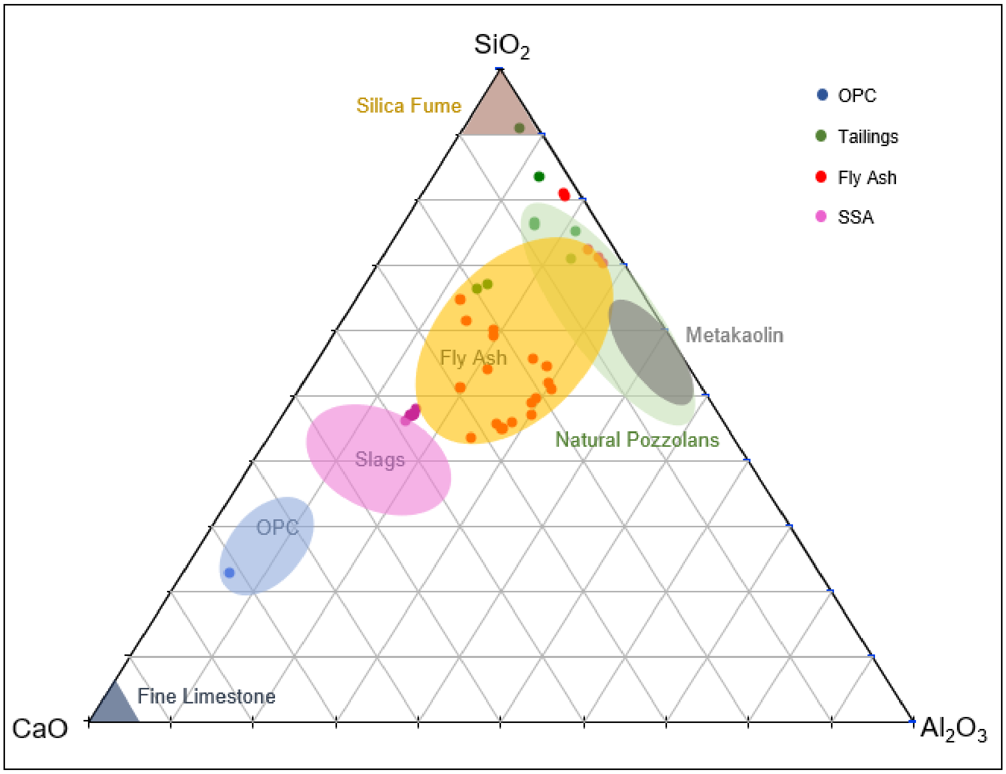

Figure 1.2 Ternary diagram of SCM. OPC (blue): Ordinary portland cement use for this research. Tailings (green): samples used on this research. Fly Ash (red): collected samples of chilean fly ash. SSA (purple): samples from (Oliva et al., 2019).

Compressive strength results showed that in mixtures at 20% replacement levels, at optimum treatment levels (different for each tailing), an average increase of 34% was observed. At 40% replacement levels, 40% increases on mechanical performance was observed as average. Measurements on pozzolanic activity tested through calorimetry showed an increase between 50% and 130%, that was related with a loss of mass at certain ranges of temperature.

1.14.2 **Related with mechanism of entrapment of copper on cementitious mixtures**

Two tailings obtained from the previous stage, with high concentrations of copper (above 2000 mg/Kg), were chosen to understand the way copper is entrapped into the cementitious matrix. Leaching measurements using EPA method 1313 (U.S. EPA, 2012) were performed and low levels of concentration of toxic elements were detected in the leachate. This is equal for other metals also (Figure 1.3), showing that most of these elements remain trapped into the cementitious matrix. In the case of copper, one tailing was analysed on a factorial design for 3 factors (2^3): calcium oxide addition, sodium hydroxide addition and water-to-binder ratio, to determine whether of those factors affect the leaching of copper. Leaching measurements using the same EPA 1313 were used to determine statistical significance at different pH, showing that mostly water-to-binder ratio is relevant from a statistical point of view on leaching of copper, that can be related with permeability and quality of hydration products.

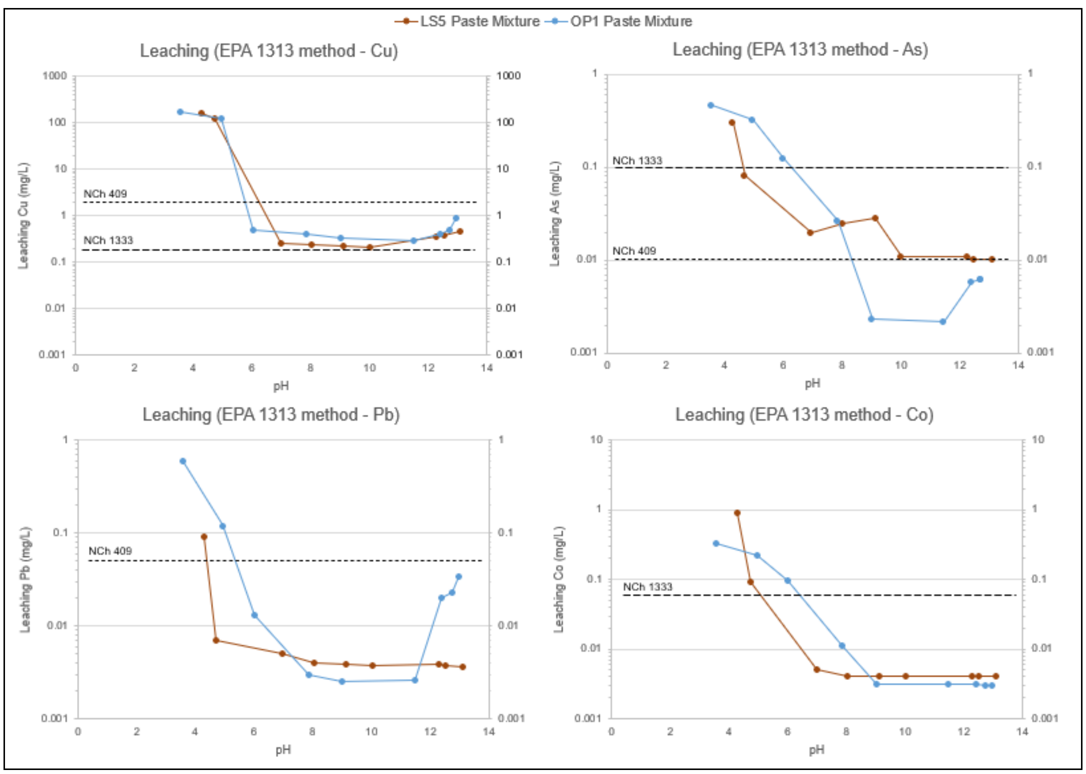

Figure 1.3 Leaching measurements for 2 tailings. Method EPA 1313. Comparison with chilean standards for quality of water.

With SEM- EBSD analysis at different ages of hydration (24h, 48h, 3 days and 7 days were carried out) the physical position of copper compound in the cementitious mixture was determined, showing that after few days, copper compounds can be found associated with hydration products such as CSH and calcium hydroxides. Through XANES analysis, this was confirmed, showing that copper compounds form migrates and precipitates on calcium hydrates phases.

1.14.3 Related with environmental performance of concrete mixtures with treated tailings

Two treated tailings from the first part of this research were selected to analyse their environmental impact as SCM, considering their performance from a mechanical point of view. Because of the absence of a production system for treated tailings, this was proposed based on laboratory data for the mechanical performance as concrete mixtures, their requirements of energy for treatments and release of water and CO_2 due to decarboxylation during this process. A Life Cycle Assessment (LCA) was carried out to estimate the environmental performance of mixtures with treated tailings compared to concrete mixtures without treated tailings.

Methodological issues related with the proper comparison of concrete mixtures with SCM in existing literature led to the formulation during this research of a new methodology to work with this type of concrete mixtures. A comparison between samples with the same mechanical performance, fixing water content and binder content in mixtures with SCM, and changing cement content in mixtures without SCM, allowed to quantify the effect of treated tailings as SCM.

Considering this, results showed that increasing the mechanical performance of treated tailings improves the environmental performance of the concrete mixture, while if there is a low performance of concrete mixtures with treated tailings, due to higher replacement levels, concrete mixtures without SCM have better environmental performance. Nevertheless, and considering results from the previous stages, for all concrete mixtures with SCM, due to the avoided disposal of tailings, there is an important benefit in the impact categories related with leaching of toxic elements to the environment, showing reduction from 0.1 to 12 times on those related impacts (eutrophication and ecotoxicity).

2. DEVELOPMENT OF A NEW SUPPLEMENTARY CEMENTITIOUS MATERIAL FROM THE ACTIVATION OF COPPER TAILINGS: MECHANICAL PERFORMANCE AND ANALYSIS OF FACTORS

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Abstract

The use of tailings as aggregate and Supplementary cementitious materials has been studied previously. Nevertheless, tailings are generally used as collected, without treatment, showing low cementitious capacity allowing low replacement levels of cement (below 15%). This research studies eight copper tailings to determine which tailings are likely to improve their cementitious capacity as supplementary cementitious material by using thermal and mechanical treatments. In the first stage, using TGA and PSD, the capacity of the tailings to undergo chemical transformations through a thermal treatment of up to 1000°C and physical transformation through low-energy milling for up to 180 min, were explored. Relevant chemical modifications were observed over the range of 500°C to 900°C, with peaks between 600°C and 800°C. It was also observed that due to the nature of rock processing prior to mineral extraction, the particle size was able to be reduced by 50% after 60 min of milling or less. With these results, a central composite design was proposed using thermal treatment temperatures between 600°C and 800°C (central point at 700°C) and milling with a central point at 30 min. The results show that the mechanical performance of the mixtures can be improved by up to 40% at 90 days compared to untreated tailings at a 40% replacement level.

Keywords: Tailing, heat treatments, mechanical treatments

2.1 Introduction

The impact of cement production on the environment is one of the main factors in the search for new materials and construction methods. The production of 1 metric ton of Portland cement involves the emission of nearly 1 t of CO_2 to the atmosphere: approximately 50% comes from the decomposition of carbonates (Schneider et al., 2011). Globally, clinker production accounts for 5% of total CO_2 emissions (Ludwig & Zhang, 2015). Supplementary cementitious materials (SCM) have been used to replace part of the cement (Schneider et al., 2011) to reduce the impact of the production of cement. In recent developments, the use of tailings as SCM has been studied: the use of tungsten tailings (Choi et al., 2009), phosphates (Zheng et al., 2015), iron (Zhao et al., 2014), and copper (Onuaguluchi & Eren, 2012) both as SCM and as a fine aggregate.

The copper mining industry is one of the most important extractive industries worldwide, with production levels of approximately 19.4 million t in 2016 (Apodaca, 2016). Each ton of refined copper generates 196.5 tons of tailings (Onuaguluchi & Eren, 2012) and—depending on the technique applied, which is associated with the type of rock—between 2.2 and 3 t of copper slag (Shi et al., 2008). The tailings are a mixture of by-products generated from the extraction process from the ores using mineral and hydrometallurgical processes (C. Wang et al., 2014), specifically when the crushed rock enters the separation process performed by floating of the “copper concentrate”, in which the fraction of high copper concentrations (30% by mass) is further processed, and the rest is discarded as tailings (Davenport et al., 2002).

The use of copper tailings has been researched both as SCM with Portland cement (Deng et al., 2014; Onuaguluchi & Eren, 2012, 2013b, 2015; B. S. Thomas et al., 2013b) and as a fine aggregate replacement (Zhang et al., 2014). Copper tailings have also been investigated as a principal element in the production of bricks through a geopolymerization process (Ahmari & Zhang, 2012). In blends with Portland cement and tailings, one study (Onuaguluchi & Eren, 2012) indicated that at replacement levels of 10% by mass, concrete strength exceeds the normal performance by 16.2% over 28 days. However, it has been demonstrated that with higher replacement levels (until 20%), there is no sizable impact or even loss in compressive strength over 28 days up to 15% (Zhang et al., 2014).

The effect of the use of any SCM in concrete can be divided into two contributions occurring simultaneously (Juenger & Siddique, 2015; M. Thomas, 2013):

a. Chemical contribution: also called the pozzolanic effect, related to the reaction and hydration products of portlandite and aluminosilicate phases present in the SCM´s (Lothenbach et al., 2011).

b. Physical contribution: also called the *filler effect*, related to the space between particles and the surface in the hydration products (Lothenbach et al., 2011) which can be separated from the chemical effect (Zunino & Lopez, 2016).

Considering both effects and the poor performance shown by copper tailings as SCM at higher replacement levels (B. S. Thomas et al., 2013a; Zhang et al., 2014), activation stands as an alternative to transformation into a more attractive cementing material (Peng et al., 2015). The improvement of performance in Supplementary cementitious materials has been researched since the mid-20th century, with the use of thermal treatments. Optimal temperatures for chemical and mineralogical changes with the potential to improve the chemical effect of SCM are 800° for andesite (Hamidi et al., 2013) and 650–700° for kaolinite and kaolinite-bentonite (Souri et al., 2015; Taylor-Lange et al., 2015). However, other SCM show lower improvements with calcination: zeolites have been researched with temperatures above 300° without showing great pozzolanic capacity after the treatment, and changes are more closely related due to morphology and particle size than chemical contribution (Küçükyıldırım & Uzal, 2014; Seraj et al., 2016).

Changes in particle size also have been researched for SCM as an effective method to improve performance, generally with high-energy methods (Burgos et al., 2014; Fuentes et al., 2014). The combined effect of thermal and milling treatments has increased effectiveness, with particle size above 45 μm (Hamidi et al., 2013; Tironi et al., 2013).

Treatments without high-temperature processes also show improvements in the reactivity of zeolites (Burris & Juenger, 2016) and kaolin (Ilić et al., 2016) when combined with milling. The combined effect of different treatments has also been documented for some pozzolanic and non-pozzolanic materials (Jain, 2012).

The aim of this research was to scientifically define promising treatments to maximize the cementitious activity of copper tailings to enable their feasible use as SCM in concrete. Therefore, a first stage was developed on tailings to observe their performance as SCM as found without any treatment. The optimal temperatures and the appropriate grinding time needed to obtain changes in particle size were then determined. Finally, a central composite factorial design was used to observe the effect of each treatment separately and in combination on selected tailings.

2.2 Materials and methods

Eight samples of tailings were collected from different sources in Chile and used in this study in a first exploratory stage. Six of the tailings came from long-standing tailings (LS) in Copiapo, Chile and two from ongoing production (OP) mines in Salamanca and Til-Til, Chile. Among the eight original tailings, three were selected to assess the effect of the treatments in their performance as Supplementary cementitious materials. The tailings were collected by means of sampling in at least three locations of the deposit and then homogenized by mixing them in one representative sample of 40 kg. For this research, only the fraction of tailings passing through a No. 30 sieve (600 μm) was considered, i.e., the larger particles (approximately 15%) were discarded. For the experimental program conducted, type I OPC was used.

2.2.1 Chemical characterization

The chemical composition of the tailings was determined by X-ray fluorescence (XRF), using a Bruker S8 Tiger spectrometer, and the results are shown on Table 1. The specific gravity (SG) of the raw materials is included in the table.

The mineralogy composition of the tailings was determined by qualitative X-ray diffraction (XRD), using a Miniflex diffractometer of 30 kV, 10 Maq; Rigaku with a Cu Kα source. The diffractograms were recorded between angles 2θ = 5°and 40°with a scan rate of 2°/min at room temperature.

Table 2.1 Chemical composition of OPC and tailings. Chemical composition data are presented as oxide percentage by weight.

Percentage of Oxides (%)	OPC	OP1	OP2	LS1	LS2	LS3	LS4	LS5	LS6
SiO_2	20.3%	62.90%	59.90%	49.40%	60.20%	51.90%	73.70%	42.60%	31.8%
Al_2O_3	4.9%	9.50%	16.90%	10.30%	12.20%	16.70%	5.40%	8.80%	6.9%
Fe_2O	3.1%	12.60%	2.80%	18.70%	7.00%	10.60%	12.50%	11.00%	37.9%
CaO	63.0%	2.80%	2.70%	5.10%	5.90%	4.40%	1.80%	12.70%	8.6%
MgO	0.3%	1.10%	1.90%	2.70%	1.70%	3.80%	0.50%	2.50%	2.4%
SO_3	2.5%	0.70%	1.30%	2.60%	1.40%	0.40%	0.40%	1.80%	0.1%
Na_2O	0.2%	1.30%	3.20%	1.30%	2.30%	3.80%	0.50%	1.60%	2.7%
K_2O	0.8%	3.30%	4.10%	2.60%	2.60%	2.90%	1.30%	1.80%	1.8%
TiO_2	0.4%	0.20%	0.70%	0.50%	0.70%	1.10%	0.40%	0.40%	0.5%
P_2O_5	0.1%	0.10%	0.30%	0.20%	0.30%	0.40%	0.10%	0.10%	0.1%
MnO	0.1%	0.10%	<LOD	0.20%	0.10%	0.30%	0.10%	0.70%	0.20%
CuO	<LOD	0.70%	1.00%	0.30%	0.80%	0.70%	0.40%	0.20%	0.30%
LOI	2.3%	4.40%	5.30%	5.80%	4.20%	2.80%	3.00%	14.50%	6.4%
Specific Gravity	3.124	3.01	2.992	2.925	2.79	2.778	2.887	2.864	3.211

2.2.1.1 Thermogravimetric analysis (TGA)

Simultaneous thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on the eight untreated tailings to understand how thermal treatment affects phase decomposition and to determine the best treatment temperature. The

TGA/DSC tests were performed on crushed samples, passed through a No. 200 sieve (75 µm opening), using a TA Instruments TGA/DSC Q600. During the test, the chamber gas used was nitrogen at a 50 mL/min flow. The samples were stabilized in alumina crucibles at 30°C for 10 min and then heated from 30°C to 1000°C at a rate of 20°C/min.

2.2.2 Physical characterization

Particle size distributions (PSD) of the eight tailings and OPC were measured using a Malvern Mastersizer 2000 laser diffractometer. Isopropanol (refractive index 1.378) was used as a dispersant, and the PSD was measured for 12 s five times while stirring at 2000 rpm to obtain an average measurement. The PSD results for the untreated tailings are shown on Figure 1. For the SEM images, samples were dried and gold coated. Magnifications between 300× and 5000× with an accelerating voltage of 15 kV were used.

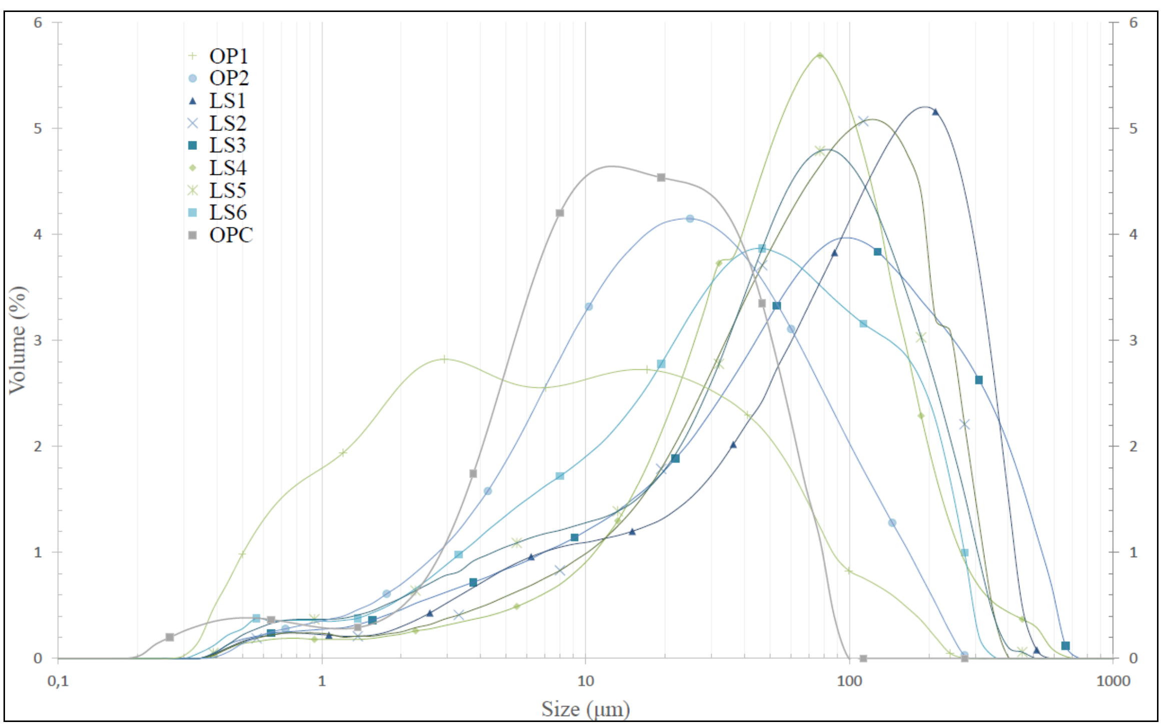

Figure 2.1 Particles size distributions (PSD) of OPC and 8 tailings.

2.2.3 Tailing strength development

Mixture proportioning was designed by mass to avoid the effect of volume changes due to thermal and mechanical treatments. The water-to-cementitious (w/c) materials ratio of the pastes was fixed at 0.5 by mass. Three 100 % OPC mixtures were selected as references, with w/c ratios of 0.5, 0.55 and 0.6. The samples were tested at 7, 28 and 90 days.

2.2.4 Treatment on tailings

The treatments in tailings were performed according to the following procedure: first, the tailings in batches of 200 g were introduced in the mill. For the milling procedure, a rotational mill was chosen, similar to the conditions present in mills currently used to grind other SCMs, since this type of milling would be more feasible to implement in an industrial environment. The thermal treatment on the tailings was then performed in the same batch of 200 g using a programmable Nabertherm HT 40/16 electric muffle oven. The heating cycle started at room temperature and proceeded at 10°C/min to the maximum temperature indicated by the experimental program. The maximum temperature was stabilized for 20 min, and then the oven was left to cool to room temperature at a free rate. The resulting calcined tailings were stored in sealed plastic containers until the date of mixture.

2.2.5 Isothermal calorimetry

Isothermal calorimetry tests were conducted to assess the effect of the treatments at the central point and compare it with the untreated tailings, analysing only the pozzolanic capacity of the tailings. The measurements were taken using a TAM Air isothermal calorimeter using the procedure proposed previously (Avet et al., 2016; Snellings & Scrivener, 2015) at 20°C, in mixes with portlandite and calcium sulphate (LC^3-50 system), with single replication.

2.3 Exploration of Factors: Results and Discussion

In this stage, an exploratory procedure was developed to obtain a relevant experimental region of interest for the activation stage and the experimental design.

The first step was a review of the compressive strength of paste mixes of untreated tailing at 7, 28 and 90 days, at a replacement levels of 20%, 40% and 50% by mass.

The second analysis was related to the use of TGA/DSC curves to obtain a range of temperatures in which chemical changes on tailings could be observed. With these results, and the analysis of the XRD patterns, the potential of the tailings as a supplementary cementing material could be assessed. With the result of this step, three tailings were selected considering the potential capacity of tailings as supplementary cementitious material and their origin, so recent and long-standing tailings were evaluated. The final three tailings were used in a third analysis, which was related to the particle size changes due to different milling times. The mill was operated at 40 rpm, with samples milled for 15, 30, 60, 90, 120, 150 and 180 min.

2.3.1 Compressive strength

The results of the untreated tailings pastes are shown in Figure 2. It can be seen that depending on the tailing, the results vary widely. All tailings exhibit lower strength ratios than the OPC paste at the same w/c ratio, the expected result considering the replacement (Onuaguluchi & Eren, 2013a, 2012; B. S. Thomas et al., 2013a). Specifically, reductions in compressive strength between 20% and 80% were obtained depending on the tailing and replacement level.

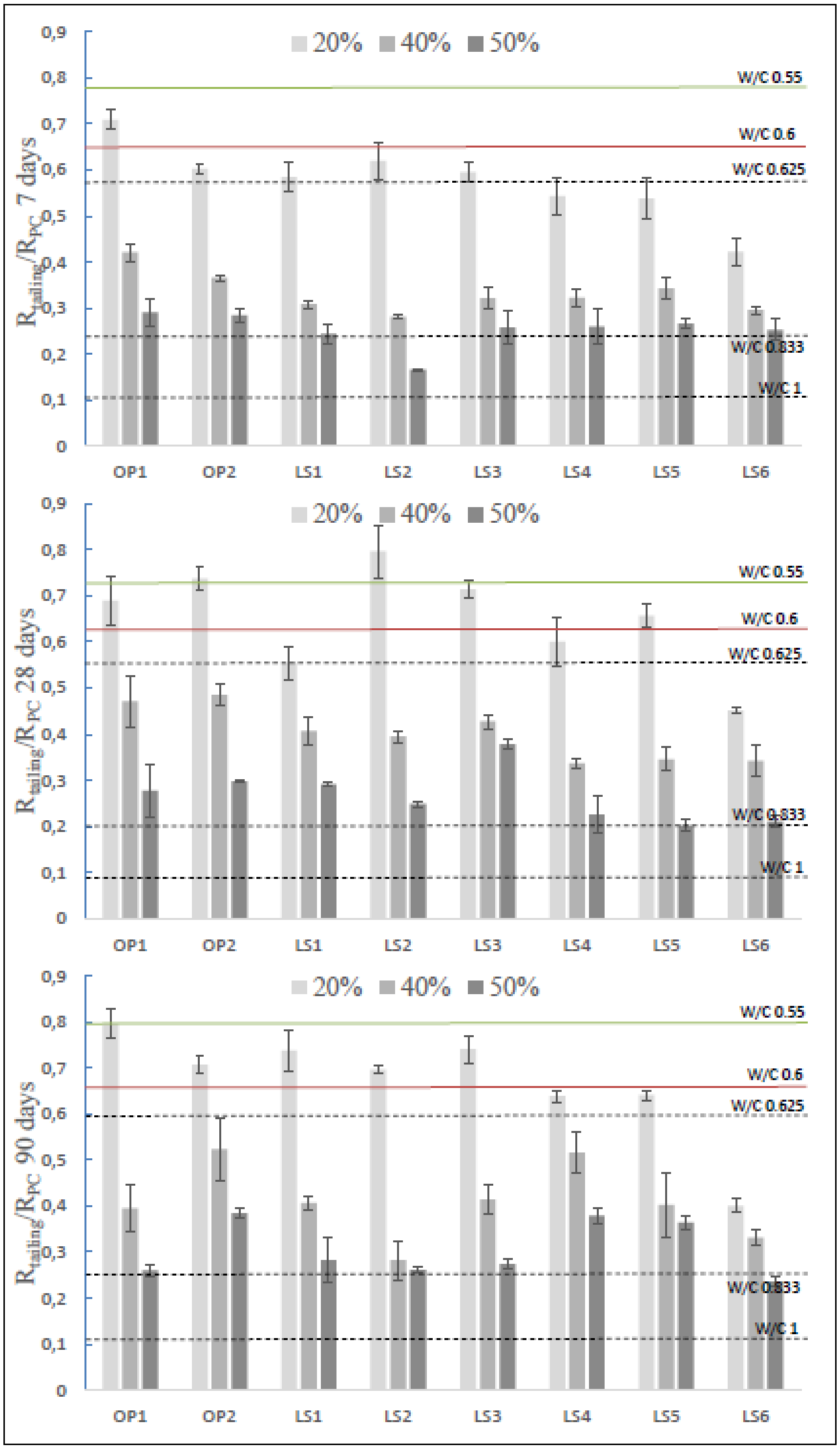

Figure 2.2 Compressive strength ratios (referenced to the 100% OPC mixture) versus tailing mixtures at 7, 28 and 90 days for 20%, 40% and 50% replacement levels.

This shows that the base cementitious capacity of the tailings can vary importantly. At later ages, the gap in compressive strength between OPC paste at w/c of 0.4 and the pastes with tailings tend to decrease, which is attributable to the presence of phases capable of generating pozzolanic reactions in the tailings (Aïtcin, 2016; Lothenbach et al., 2011).

If the comparison is made against OPC pastes considering only the cement reduction—i.e., an increase to a new w/c ratio (dashed lines)—the improvement in compressive strength is important. This means that the use of raw tailings in addition to the cement, instead of replacing cement, improves compressive strength significantly. For example, tailings OP1, OP2, LS2 and LS3 show important increases in compressive strengths in the analysis compared to their respective dash lines.

For the next stage, mixtures with a 40% replacement level will be used to assess the improvements due to the treatments more precisely. In addition, tailings OP1 and LS1 were selected due to their performance and their difference in precedence (one is from an ongoing production mine, and the other is from a long-standing tailing).

2.3.2 Temperature: TGA-DSC and XRD pattern

TGA-DSC results obtained for all tailing samples are shown in Figure 3. The results show the differences between the tailings regardless of the similarities in chemical composition. Nevertheless, there are some common peaks in mass loss and endothermic peaks. After the mass loss due to water content below 150°C, the first mass loss and endothermic peak, between 400°C and 640°C, is related to the transformations of kaolinic phases present in the tailings, due to dehydroxylation and the loss of hydroxyl groups (Cao et al., 2016; Hamidi et al., 2013; Taylor-Lange et al., 2015). Due to the low amount on the mass loss (below 3%), it is expected that the pozzolanic activity of the tailings will be low (Teklay et al., 2014). The second endothermic peak and mass loss is centered at 750°C. This temperature is related to the decarbonation of carbonate minerals such as calcite and dolomite (Cao et al., 2016; Hamidi et al., 2013). In the case of tailings LS1, LS2 and LS5, this mass loss is between 2% and 6%. With these results, the chosen tailings were OP1, LS1 (from the previous step) and LS5. As the results show major mass loss at temperatures between 500°C and 800°C, the experimental space of interest was chosen between 600°C and 800°C, centred at 700°C. At these temperatures, major improvement is expected in the performance of the tailings as SCM.

The XRD patterns (Figures 4, 5 and 6) show similar results to TGA, with the previous selected temperatures of thermal treatment. First, the high crystallinity of the minerals of the tailings was reported previously, with the presence of kaolin, calcite and dolomites, due to the nature of the rock from which copper is extracted in Chile (Smuda et al., 2008, 2014). Second, it can be seen that at 600°C, the kaolin phase peaks disappear due to the change into amorphous phases (Hamidi et al., 2013; Taylor-Lange et al., 2015). At 800°C, finally, the calcite and dolomite peaks disappear due to dehydroxylation of these phases (Hamidi et al., 2013). The presence of another clay mineral, montmorillonite, is also noted, whose structure also changes between 600°C and 800°C (Taylor-Lange et al., 2015). Even with this change, the total amount of this phase by weight (measured in TGA) is not expected to exceed 8%, which is consistent with previous tailing measurements in Chile (Smuda et al., 2008, 2014).

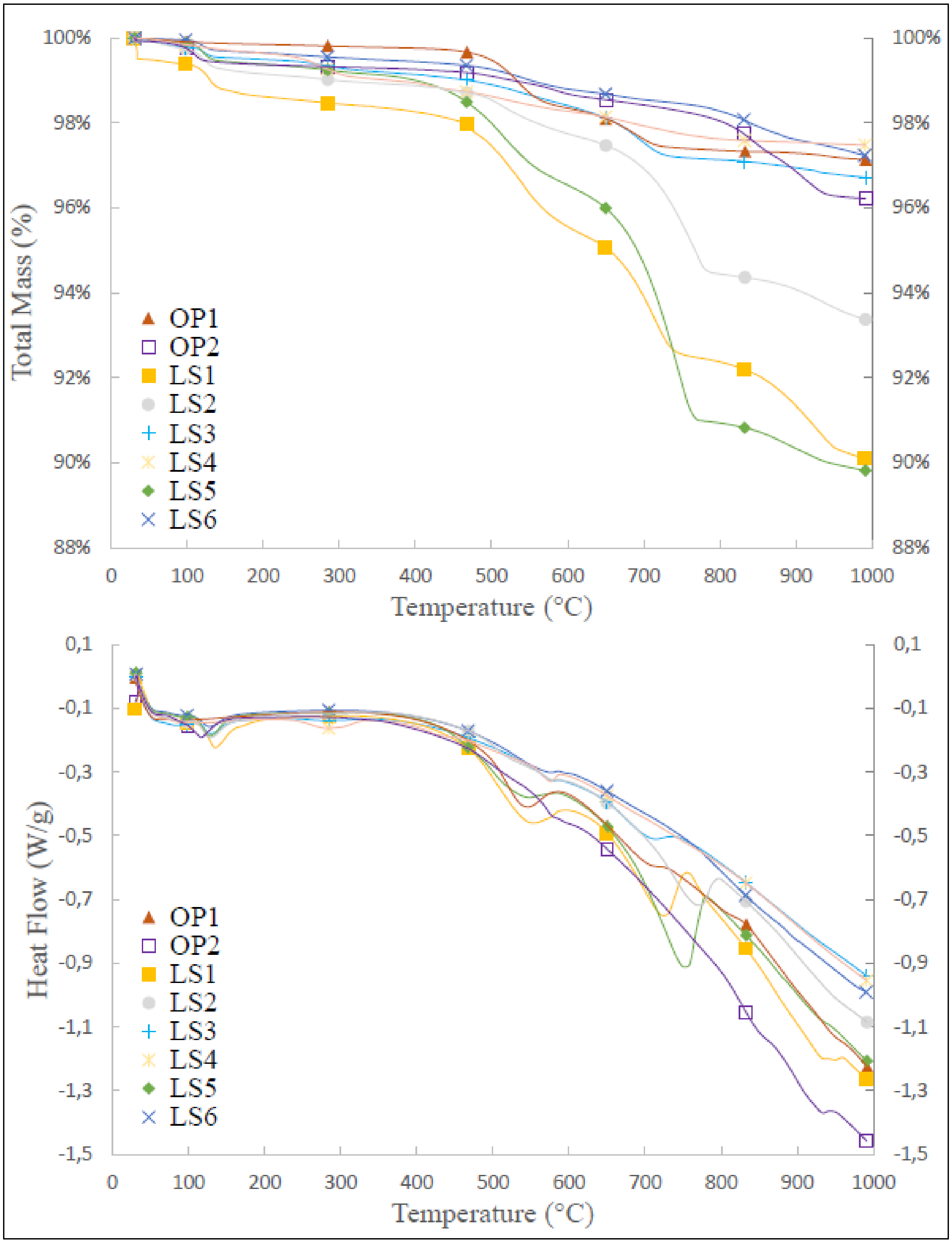

Figure 2.3 Thermogravimetric curve (TGA) and differential scanning calorimetry (DSC) curves of 8 tailings.

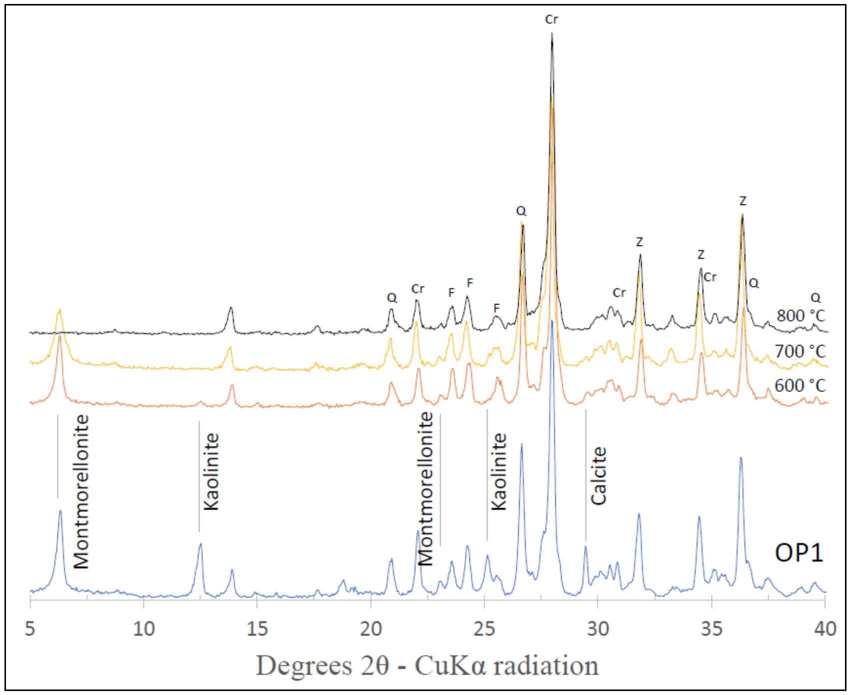

Figure 2.4 XRD Pattern of OP1 tailing, untreated and calcined at 600, 700 and 800°C (Q: quartz; Cr: cristobalite; Z: zinc oxide (i.s.); F: feldspar).

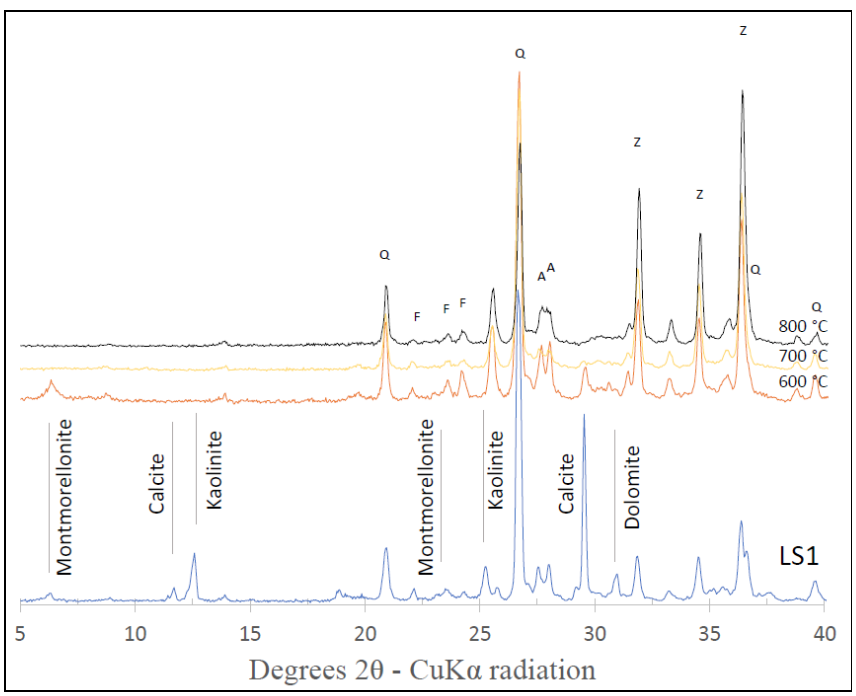

Figure 2.5 XRD pattern of LS1 tailing, untreated and calcined at 600, 700 and 800°C (Q: quartz; Cr: cristobalite; A: anorthite; Z: zinc oxide (i.s.); F: feldspar).

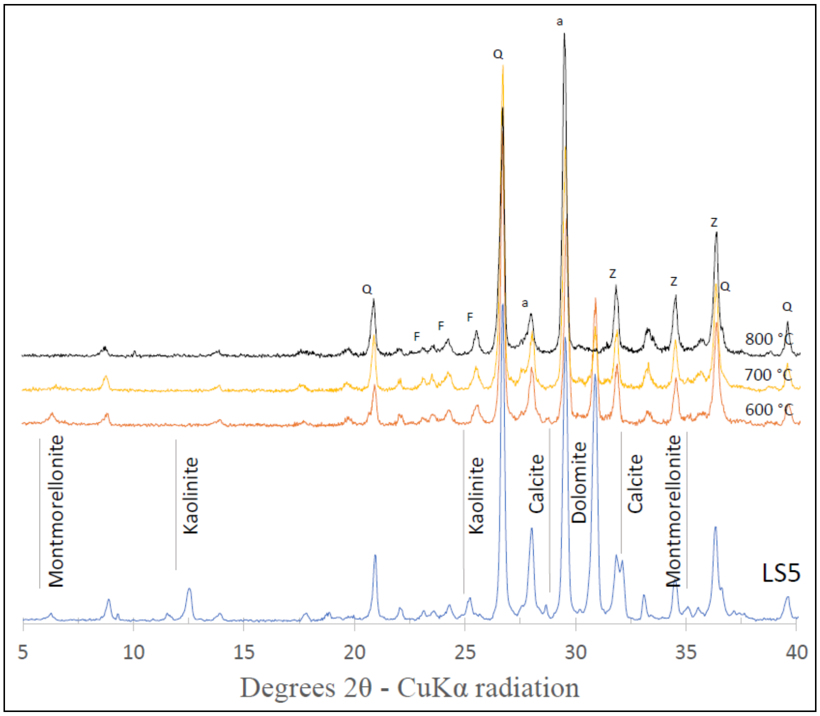

Figure 2.6 XRD pattern of LS5 tailing, untreated and calcined at 600, 700 and 800°C (Q: quartz; a: albite; Z: zinc oxide (i.s) ; F: feldspar).

2.3.3 Grinding time: Particle size distribution (PSD) and SEM images

In Figure 1, it is observed that the PSD of untreated tailings has values comparable to those of other Supplementary cementitious materials (M. Thomas, 2013). The results of the exploratory milling process of 3 tailings can be seen in Figure 7. There is a significant decrease in particle size in the first 60 min of milling for the old tailings. In the case of mine tailings in production, the reduction is smaller because the particle size is already small when the process is started. Due to the differences in the rock process and the development of the mine production, the particle size of the tailings has been reduced to optimize the extraction of copper from the ores for newer productions (Davenport et al., 2002). The results show that with 60 min max. milling, the particle size decrease is important. The times chosen for the next step were centred at 30 min.

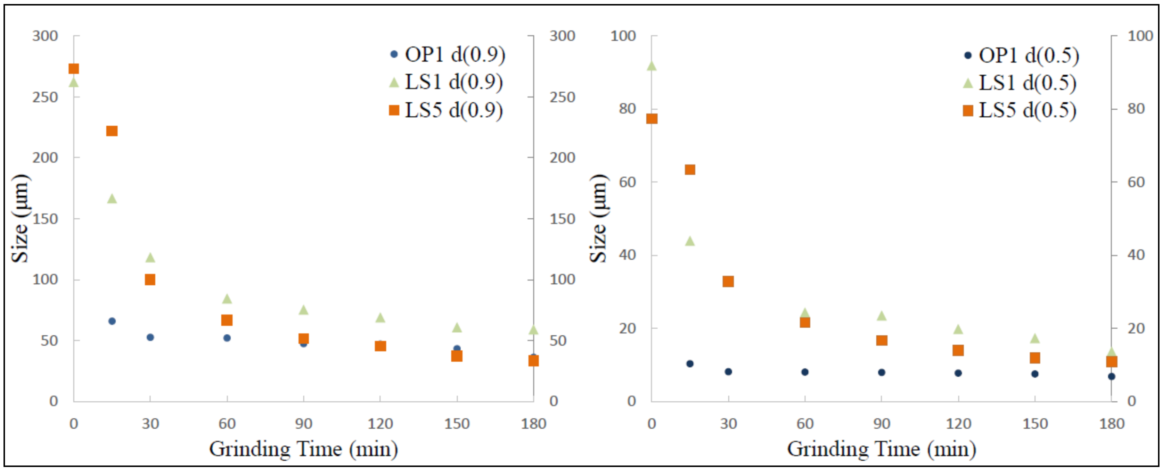

Figure 2.7 Particle size fraction d(0.9) and d(0.5) of 3 tailings after grinding.

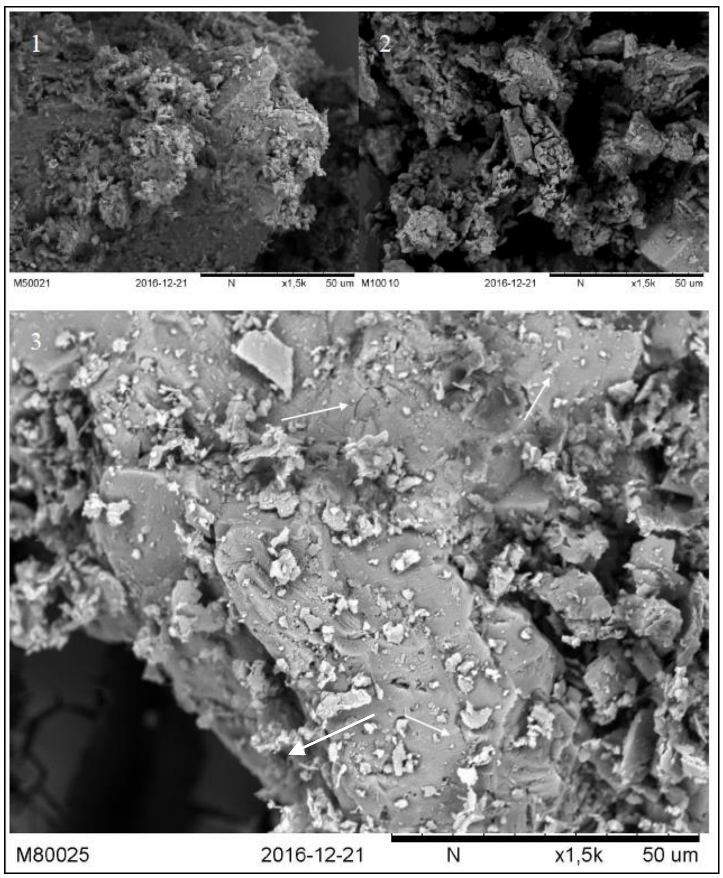

Figure 2.8 SEM microphotographs of tailings (1: OP1; 2: LS1; 3: LS5). Particle microfractures are observed in the LS5 image, some of them denoted by arrows.

In Figure 8, the SEM images shows the morphology of the tailing particles, which follow the characteristic pattern of particles from milling treatments such as those subjected to the mineralogical process. In image number 3 (LS5 tailing), the presence of microfractures that facilitate the milling process of the tailings has been emphasized.

2.3.4 Experimental design for treated tailing pastes

For the next stage, the results of the exploration of factors were considered to obtain an experimental region of interest. The chosen replacement level was 40% by mass. The range of temperature considered for the thermal treatment was centred at 700° ± 100°. The base range of time for the milling treatment was centred at 30 min ± 21.22 min. A second-order model of response surface called central composite design for two factors is proposed, which allows high levels of rotatability of factors. The model considers a significance level of 95%. Another advantage of the chosen experimental design is that it allows better mapping of the chosen experimental area and determines a direction of maximum response (Figure 9) (Montgomery, 2017). In the case of the grinding time, the factorial points were chosen to allow the use of the star points (axial points) at 0 and 60 min. This is due to the mathematical formulation of the model, which requires α values of 1.414 times the distance to the factor points of the design. The design factor levels and runs for the studied experimental region of interest are given in Table 2. Three replications were made for each point of the design.

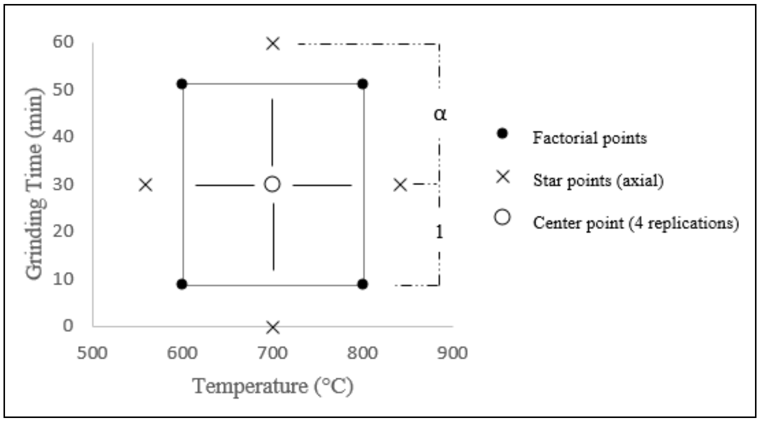

Figure 2.9 Central composite design and experimental region covered.

Table 2.2 Design factor levels and runs at 40% replacement level.

Run	**Experimental Coded Factors**		**Factors**	
			Temperature	Grinding Time
	A	B	C°	min
1	-	-	600	8.78
2	+	-	800	8.78
3	-	+	600	51.21
4	+	+	800	51.21
5	- α	0	558.6	30
6	α	0	841.2	30
7	0	- α	700	0
8	0	α	700	60
9 - 12	0	0	700	30

2.4 Treatment on tailing: Results and discussion

2.4.1 Experimental design for treated tailing pastes

The individual compressive strength obtained for each tailing at 7 and 90 days can be seen in Table 3. The results are expressed as ratios between the compressive strength of a treated tailing and that obtained with the same tailing, but untreated; thus, the improvements due to treatments can be easily observed. As expected, the results vary widely among tailings. Table 4 presents the regression-coded estimates for each tailing and the statically significant estimates.

No correlation was found between the thermal treatment and the grinding time for the three tailings due to the small amount of material that effectively undergoes transformations due to the high crystallinity and presence of crystalline phases of silicon oxide in the tailings (Figure 4, 5 and 6). In addition, the changes in particle size before and after the thermal treatment were measured, but no statistically significant differences in particle size were found.

Table 2.3 Compressive strength ratios (referenced to the same tailing without treatment) versus mixtures at 7 and 90 days of age, 40% replacement level.

Tailing	Factor Levels		40% Replacement Level					
			OP1		LS1		LS5	
Run	Temperature C°	Grinding Time min	7 days	90 days	7 days	90 days	7 days	90 days
1	600	8.78	1.32	0.99	0.67	1.04	1.27	1.04
2	800	8.78	0.57	1.19	0.73	1.20	1.44	1.25
3	600	51.21	1.45	1.61	1.03	1.04	1.47	1.14
4	800	51.21	1.41	1.33	1.02	1.16	1.53	1.56
5	558.6	30	1.44	1.07	0.64	1.08	1.17	1.20
6	841.4	30	1.31	1.12	0.27	1.17	1.46	1.36
7	700	0	1.09	1.04	0.82	1.06	1.35	1.38
8	700	60	1.23	1.30	1.13	1.01	1.58	1.36
9	700	30	1.33	1.26	0.91	0.99	1.66	1.43
10	700	30	1.33	1.23	0.85	1.08	1.57	1.47
11	700	30	1.32	1.22	0.65	1.08	1.62	1.41
12	700	30	1.31	1.23	0.69	1.08	1.71	1.49

For the OP1 tailing, there is a general decrease in the ratios between 7 and 90 days, and the significant estimates are in both ages and grinding times. With the TGA analysis (Figure 3), the OP1 test shows a loss mass less than 2%, without any endothermic peak showing a chemical transformation of phases between 600°C and 800°C. The endothermic peak observed was at 550°C, indicating that in the experimental space selected, the thermal effect may be hidden in the average value obtained by the regression. Although this tailing showed a smaller particle size decrease when analysing the grinding times (Figure 7), the statistical analysis suggests that it may have been acted on by more reactive particles, which allow the increase and the positive effect on the result by increasing the milling times.

In the case of LS5 tailing, the estimates of the regression show that at early ages, the grinding time and temperature are statistically significant, which agrees with the previous observation in the TGA and XRD test (Figures 3 and 5). Those figures show important mass losses in the experimental region of interest, related to changes in crystalline structures present in the tailings and changes in particle size due to the milling procedure. At 90 days, the grinding time loss relevance becomes statistically insignificant. This agrees with what has been reported on the chemical and physical effects of Supplementary cementitious materials (Lothenbach et al., 2011; Zunino & Lopez, 2016), where it has been observed that the physical effect has a greater impact at early ages, while the chemical effect has a greater impact at later ages. The estimates for temperature also show a maximum in the experimental region of interest, indicating that thermal treatment above 750°C decreases compressive strength. At that temperature, the decarbonation of dolomite and calcite contributes to the formation of the calcium and magnesium oxides, and the effect of these oxides at later ages is less relevant for the pozzolanic activity.

Finally, the LS1 tailing shows a similar behaviour to the LS5 tailings, explained partially by their similarities in TGA and particle size reduction. However, the differences between statistically significant factors in each case and the differences between the estimates are related to the different chemical compositions between LS1 and LS5. In the case of the LS1 tailing, the untreated tailing had a higher compressive strength than the LS5 tailing, so it is possible to assume that with this tailing, there is no severe impact on the resistance because we can already be at the limit of its capacity as supplementary cementitious material for the chosen experimental region. In this case, also, the tailing does not have a maximum in the experimental region of interest, which indicates that for this case, there are temperatures higher than those of the conducted test that allow its increased capacity as SCM.

Table 2.4 Estimates and significance of coded estimates on regression models for treatments on tailings, at 95% significance level, for 7 and 90 days. Boldface indicates estimates that are statistically significant.

	Estimate (Compressive Strength Ratio)					
Source	OP1-7d	OP1-90	LS1-7d	LS1-90	LS5-7d	LS5-90
Average	**1.3213**	**1.2354**	**0.7777**	**1.0544**	**1.6435**	**1.4503**
A: Temperature	-0.2417	-0.0040	**-0.1186**	**0.0999**	0.1614	**0.2150**
B: Grinding Time	**0.2896**	**0.2813**	**0.2738**	-0.0240	**0.1561**	0.0969
A*A	0.0124	-0.0632	**-0.2490**	**0.0853**	-0.3114	**-0.2090**
A*B	0.3546	-0.2394	-0.0333	-0.0224	-0.0517	0.1058
B*B	-0.1995	0.0092	**0.2742**	-0.0034	-0.1593	-0.1198

By analysing the obtained resistances (Figure 10), it can be seen that the final resistance can increase by up to 40% at 7 days and up to 35% related to the resistance of the untreated tailings. Mixtures such as these with high replacement levels and low relative strengths show a significant improvement when using treated tailings.

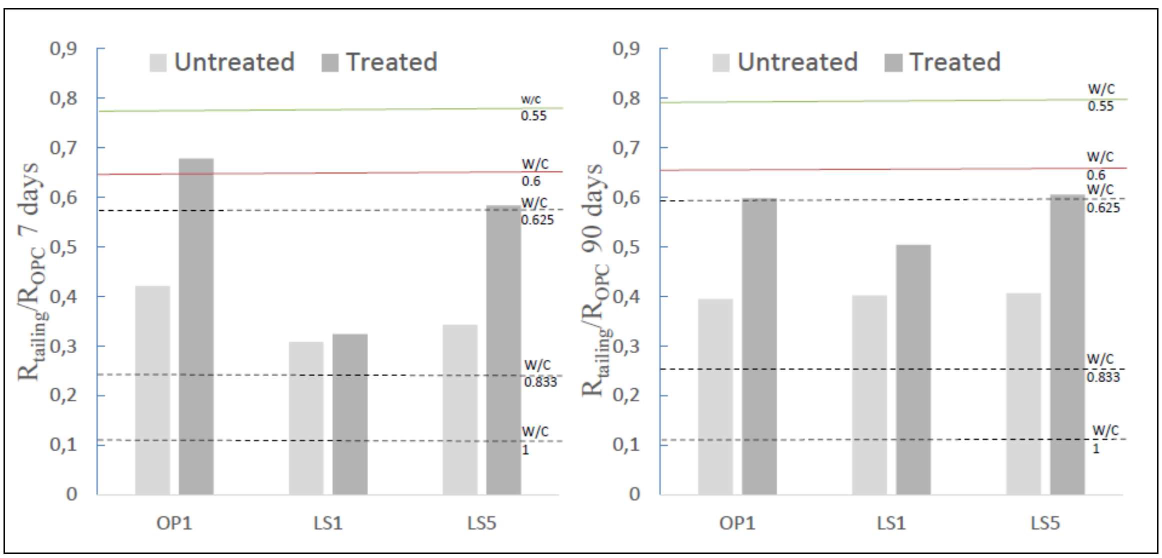

Figure 2.10 Compressive strength ratios (referenced to the 100% OPC mixture) versus tailing mixtures at 7 and 90 days for 40% replacement level for untreated and treated tailings, maximum value for each regression model.

2.4.2 Isothermal calorimetry

The increase in the pozzolanic activity related to the activation of the tailings can be seen in Figure 11a. Although the tailings show a low pozzolanic capacity, mainly due to the absence of reactive phases and the high crystallinity of the compounds present in them, an improvement in the pozzolanic capacity of the tailings can be observed due the proposed treatments. When comparing the results for the 3 tailings, those with greater increases in their pozzolanic capacity (LS1 and LS5) are the same as those with greater losses of mass measurable by TGA (Figure 3) until the analysed temperature of 700°C (central point of the experimental region of interest).

Chemical transformations are considered to occur at temperatures up to 650° C for the kaolinitic phases, which indicates a greater contribution to the pozzolanic activity (Taylor-Lange et al., 2015). A strong relation between the mass loss and the heat release results obtained for these 3 tailings can be seen. The mass loss, considered between 150°C and 650°C, coincides with the temperatures where the most important chemical transformations are observed from the pozzolanic point of view, especially between 400°C and 650°C (Souri et al., 2015; Taylor-Lange et al., 2015; Teklay et al., 2014). Even though the mass loss in the 150-650°C range may contain the decomposition of phases that promote hydraulic reactions, it is still a promising way to quantify the pozzolanic potential of a treated tailing

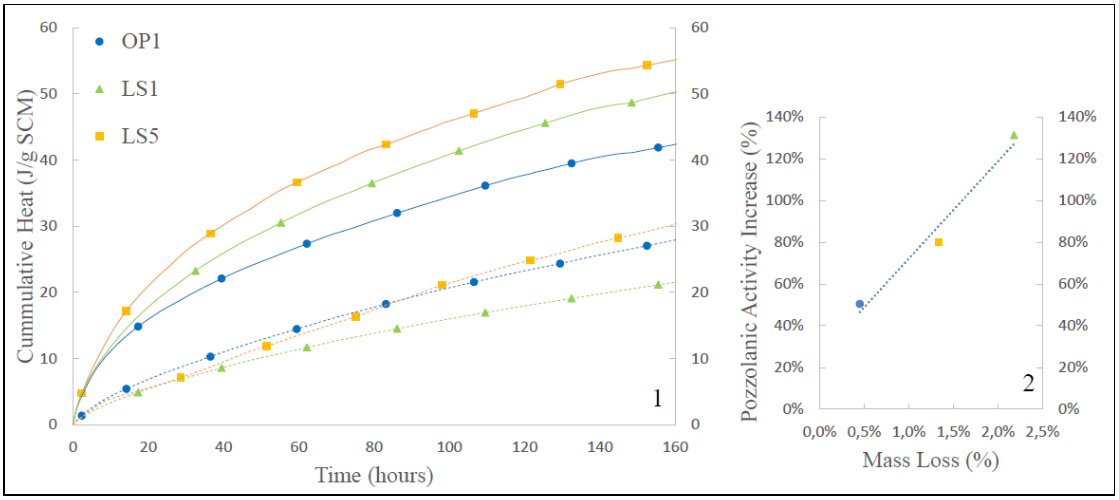

Figure 2.11 1. Cumulative heat (J/g of SCM) of untreated (dashed line) and treated (700°C, 30 min grinding) tailings. 2. Relation between mass loss under 650°C and increase in pozzolanic capacity, measured as cumulative heat release at 7 days.

2.5 Conclusions

Sustainability in the construction and cement industry may have points in common with waste disposal of other industries at important levels, such as the copper mining industry. The use of tailings as a cement replacement is one alternative to reduce the impact of the production of cement and management of the disposal of tailings into the environment.

The present study conducted a chemical and physical characterization of eight tailing samples. The samples were used as collected, and the treatments and procedures could be scaled to industrial levels.

Based on the findings presented in this study, the following conclusions can be stated:

1. Each tailing has a different behaviour under compressive strength, according to its chemical composition and physical characteristics. With the tailings and tests carried out herein, it is impossible to conclude that there are quantifiable factors in common to explain this behaviour, being necessary a case-by-case analysis to

determine potential use as supplementary cementing material and the levels, experimental space and effect of treatments on each tailing.

2. At replacement levels over 20%, the decrease in compressive strength is important. Nevertheless, the decrease is less than the lower bound case, which is to extract the portion of cement without replacing it with tailings. This suggests an important potential use of the untreated tailings in addition to cement—for example, as fine aggregate—and of the treated tailings as fine aggregate with low contribution as SCM.

3. With TGA analysis, it is possible to estimate the potential benefits in cementitious activity of applying the thermal treatments. Moreover, it was possible to link these benefits with the analysis of the DSC curves and with XRD patterns. In the case of the tailings analysed in this study, the mass losses observed at 550°C and 740°C were related with chemical transformations of calcium and kaolinitic phases, which improve the behaviour of the tailings as SCM.

4. Due to the nature of the mechanical processing of the rock in the extraction of the copper minerals, the grinding of tailings demands relatively low energy to reduce the size of the particles in the long-standing tailings. Although the relevance of the grinding process is less effective in new tailings, the time of grinding is statistically significant to increase the reactivity of those tailings.

5. No statistically significant correlation was found between thermal and mechanical treatments. This might be explained by the low percentage of material that undergoes chemical transformations due to thermal treatments, so the correlation loses relevance.

6. The impact of the thermal treatments is statistically significant at later ages when there are changes in the chemical phases present in the tailings due to thermal treatments. On the other hand, the impact of the mechanical treatment is statistically significant at early ages.

7. Proper use of different analytical techniques such as TGA, XRD, XRF, PSD and calorimetry can predict the SCM performance of the tailings and improve the cementing capacity as SCM by changing the heating and grinding conditions of the treatments.

8. Different treatments may impact the behaviour of tailings as SCM differently. However, it is feasible to improve the use of tailings as SCM by searching for optimal levels for both thermal and mechanical treatments, and the impact of these treatments can improve the mechanical performance of tailings up to 40% at 90 days.

Future research needs to explore alternatives to (i) further improve the cementitious and pozzolanic such as chemical compounds, alkaline activators, different heating and cooling rates, total time of treatments, (ii) advanced characterization of the tailing for identifying chemical or physical markers that could predict the potential capacity of a tailing as a SCM; and (iii) study of other relevant properties at the mortar and concrete scale, such as, rheology, workability, compressive strength, effect of free CaO and MgO and other possible phases generated by the treatments, durability among other.

2.6 Acknowledgements

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2.7 References

Ahmari, S., Zhang, L., 2012. Production of eco-friendly bricks from copper mine tailings through geopolymerization. Constr. Build. Mater. 29, 323–331. doi:10.1016/j.conbuildmat.2011.10.048

Aïtcin, P.-C., 2016. Supplementary cementitious materials and blended cements, Science and Technology of Concrete Admixtures. doi:10.1016/B978-0-08-100693-1.00004-7

Avet, F., Snellings, R., Alujas Diaz, A., Ben Haha, M., Scrivener, K., 2016. Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. Cem. Concr. Res. 85, 1–11. doi:10.1016/j.cemconres.2016.02.015

Burgos, D.M., Cardona, L.M., Delvasto, S., 2014. Estudio de dos materiales volcánicos y efecto del tipo de molienda en su reactividad. Rev. Ing. construcción 29, 159–174. doi:10.4067/S0718-50732014000200003

Burris, L.E., Juenger, M.C.G., 2016. Milling as a pretreatment method for increasing the reactivity of natural zeolites for use as Supplementary cementitious materials. Cem. Concr. Compos. 65, 163–170. doi:10.1016/j.cemconcomp.2015.09.008

Cao, Z., Cao, Y., Dong, H., Zhang, J., Sun, C., 2016. Effect of calcination condition on the microstructure and pozzolanic activity of calcined coal gangue. Int. J. Miner. Process. 146, 23–28. doi:10.1016/j.minpro.2015.11.008

Chancey, R.T., Stutzman, P., Juenger, M.C.G., Fowler, D.W., 2010. Comprehensive phase characterization of crystalline and amorphous phases of a Class F fly ash. Cem. Concr. Res. 40, 146–156. doi:https://doi.org/10.1016/j.cemconres.2009.08.029

Choi, Y.W., Kim, Y.J., Choi, O., Lee, K.M., Lachemi, M., 2009. Utilization of tailings from tungsten mine waste as a substitution material for cement. Constr. Build. Mater. 23, 2481–2486. doi:10.1016/j.conbuildmat.2009.02.006

Davenport, W.G., King, M., Schlesinger, M., Biswas, A.K., 2002. Overview. Extr. Metall.

Copp. 1–16. doi:10.1016/B978-008044029-3/50004-6

Deng, Y., Zhang, C., Wei, X., 2014. Influence of lithium sulfate addition on the properties of Portland cement paste. Constr. Build. Mater. 50, 457–462. doi:10.1016/j.conbuildmat.2013.09.058

Fuentes, M., Zúñiga, A., Díaz, M., Rocha, E., Díaz, S., 2014. Molienda mecánica por alta energía de minerales mexicanos para producir concreto de alto desempeño (CAD). Rev. Ing. construcción 29, 256–269. doi:10.4067/S0718-50732014000300003

Hamidi, M., Kacimi, L., Cyr, M., Clastres, P., 2013. Evaluation and improvement of pozzolanic activity of andesite for its use in eco-efficient cement. Constr. Build. Mater. 47, 1268–1277. doi:10.1016/j.conbuildmat.2013.06.013

Ilić, B., Radonjanin, V., Malešev, M., Zdujić, M., Mitrović, A., 2016. Effects of mechanical and thermal activation on pozzolanic activity of kaolin containing mica. Appl. Clay Sci. 123, 173–181. doi:10.1016/j.clay.2016.01.029

Jain, N., 2012. Effect of nonpozzolanic and pozzolanic mineral admixtures on the hydration behavior of ordinary Portland cement. Constr. Build. Mater. 27, 39–44. doi:10.1016/j.conbuildmat.2011.08.006

Juenger, M.C.G., Siddique, R., 2015. Recent advances in understanding the role of Supplementary cementitious materials in concrete. Cem. Concr. Res. 78, 71–80. doi:10.1016/j.cemconres.2015.03.018

Küçükyıldırım, E., Uzal, B., 2014. Characteristics of calcined natural zeolites for use in high-performance pozzolan blended cements. Constr. Build. Mater. 73, 229–234. doi:10.1016/j.conbuildmat.2014.09.081

Lothenbach, B., Scrivener, K., Hooton, R.D., 2011. Supplementary cementitious materials. Cem. Concr. Res. 41, 1244–1256. doi:10.1016/j.cemconres.2010.12.001

Ludwig, H.-M., Zhang, W., 2015. Research review of cement clinker chemistry. Cem. Concr. Res. doi:10.1016/j.cemconres.2015.05.018

Montgomery, D.C., 2012. Design and Analysis of Experiments, Design. doi:10.1198/tech.2006.s372

Onuaguluchi, O., Eren, O., 2013a. Rheology, strength and durability properties of mortars containing copper tailings as a cement replacement material. Eur. J. Environ. Civ. Eng. 17, 19–31. doi:10.1080/19648189.2012.699708

Onuaguluchi, O., Eren, Ö., 2015. Reusing copper tailings in concrete: corrosion performance and socioeconomic implications for the Lefke-Xeros area of Cyprus. J. Clean. Prod. doi:10.1016/j.jclepro.2015.09.036

Onuaguluchi, O., Eren, Ö., 2013b. Rheology, strength and durability properties of mortars containing copper tailings as a cement replacement material. Eur. J. Environ. Civ. Eng. 17, 19–31. doi:10.1080/19648189.2012.699708

Onuaguluchi, O., Eren, Ö., 2012. Cement mixtures containing copper tailings as an additive: durability properties. Mater. Res. 15, 1029–1036. doi:10.1590/S1516-14392012005000129

Peng, K., Yang, H., Ouyang, J., 2015. Tungsten tailing powders activated for use as cementitious material. Powder Technol. 286, 678–683. doi:10.1016/j.powtec.2015.09.012

Schneider, M., Romer, M., Tschudin, M., Bolio, H., 2011. Sustainable cement production—present and future. Cem. Concr. Res. 41, 642–650. doi:10.1016/j.cemconres.2011.03.019

Seraj, S., Ferron, R.D., Juenger, M.C.G., 2016. Calcining natural zeolites to improve their effect on cementitious mixture workability. Cem. Concr. Res. 85, 102–110. doi:10.1016/j.cemconres.2016.04.002

Shi, C., Meyer, C., Behnood, A., 2008. Utilization of copper slag in cement and concrete. Resour. Conserv. Recycl. 52, 1115–1120. doi:10.1016/j.resconrec.2008.06.008

Smuda, J., Dold, B., Spangenberg, J.E., Friese, K., Kobek, M.R., Bustos, C.A., Pfeifer, H.-R., 2014. Element cycling during the transition from alkaline to acidic environment in an active porphyry copper tailings impoundment, Chuquicamata, Chile. J. Geochemical Explor. 140, 23–40. doi:10.1016/j.gexplo.2014.01.013

Smuda, J., Dold, B., Spangenberg, J.E., Pfeifer, H.-R., 2008. Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: Implications on sources and mobility of elements during transport and early stages of deposition. Chem. Geol. 256, 62–76. doi:10.1016/j.chemgeo.2008.08.001

Snellings, R., Scrivener, K.L., 2015. Rapid screening tests for Supplementary cementitious materials: past and future. Mater. Struct. 49, 1–15. doi:10.1617/s11527-015-0718-z

Souri, A., Kazemi-Kamyab, H., Snellings, R., Naghizadeh, R., Golestani-Fard, F., Scrivener, K., 2015. Pozzolanic activity of mechanochemically and thermally activated kaolins in cement. Cem. Concr. Res. 77, 47–59. doi:10.1016/j.cemconres.2015.04.017

Taylor-Lange, S.C., Lamon, E.L., Riding, K.A., Juenger, M.C.G., 2015. Calcined kaolinite–bentonite clay blends as Supplementary cementitious materials. Appl. Clay Sci. 108, 84–93. doi:10.1016/j.clay.2015.01.025

Teklay, A., Yin, C., Rosendahl, L., Bøjer, M., 2014. Calcination of kaolinite clay particles for cement production: A modeling study. Cem. Concr. Res. 61–62, 11–19. doi:10.1016/j.cemconres.2014.04.002

Thomas, B.S., Damare, A., Gupta, R.C., 2013a. Strength and durability characteristics of copper tailing concrete. Constr. Build. Mater. 48, 894–900. doi:10.1016/j.conbuildmat.2013.07.075

Thomas, B.S., Damare, A., Gupta, R.C., 2013b. Strength and durability characteristics of copper tailing concrete. Constr. Build. Mater. 48, 894–900. doi:10.1016/j.conbuildmat.2013.07.075

Thomas, M., 2013. Supplementary Cementing Materials in Concrete. CRC Press, Boca Raton.

Tironi, A., Trezza, M.A., Scian, A.N., Irassar, E.F., 2013. Assessment of pozzolanic activity of different calcined clays. Cem. Concr. Compos. 37, 319–327. doi:10.1016/j.cemconcomp.2013.01.002

U.S. Geological Survey, 2017. Mineral Commodity Summaries 2017, U.S. Geological Survey. doi:http://dx.doi.org/10.3133/70140094.

Wang, C., Harbottle, D., Liu, Q., Xu, Z., 2014. Current state of fine mineral tailings treatment: A critical review on theory and practice. Miner. Eng. 58, 113–131. doi:10.1016/j.mineng.2014.01.018

Zhang, C., Zhou, T., Wu, Q., Zhu, H., Xu, P., 2014. Mechanical Performances and Microstructures of Cement Containing Copper Tailings. ASIAN J. Chem. 26, 1371–1375.

Zhao, S., Fan, J., Sun, W., 2014. Utilization of iron ore tailings as fine aggregate in ultra-high performance concrete. Constr. Build. Mater. 50, 540–548. doi:10.1016/j.conbuildmat.2013.10.019

Zheng, K., Zhou, J., Gbozee, M., 2015. Influences of phosphate tailings on hydration and properties of Portland cement. Constr. Build. Mater. 98, 593–601. doi:10.1016/j.conbuildmat.2015.08.115

Zunino, F., Lopez, M., 2016. Decoupling the physical and chemical effects of Supplementary cementitious materials on strength and permeability: A multi-level approach. Cem. Concr. Compos. 65, 19–28. doi:10.1016/j.cemconcomp.2015.10.003

3. MECHANISM FOR COPPER ENTRAPMENT IN CONCRETE MIXTURES CONTAINING TAILINGS

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Abstract

The use of copper tailings as supplementary cementitious material can reduce the environmental impact of concrete production. One concern about the use of tailings is that their content of toxic metals, including copper, can lead to potentially toxic leachates from the cementitious matrix. By combining microscopic and spectroscopic approaches we investigate the mechanisms by which copper from a supplementary cementitious material is entrapped in the cementitious matrix. We show that the most significant factor associated with copper leaching was the water-to-binder ratio (w/b): a decrease in the water-to-binder ratio reduces copper leaching. SEM-EDS micrographs allows us to spatially localize enriched copper clusters within the cementitious paste hydration products. In early stages of the cementitious paste formation (i.e., 24 h), no spatial correlation between copper and hydration products was found. After seven days, copper was spatially associated with calcium silicate hydroxides. Finally, Cu K-edge XANES spectroscopy provides insights into the chemical speciation of copper in the cementitious paste. It shows that copper sulfide phases remain invariant, whereas the sulfate phases are subjected to dissolution and reprecipitation influenced by the relatively high pH from calcium hydroxides formed during hydration. Despite the low level of copper leaching on cementitious mixtures, improving factors such as w/b and promoting the formation of hydration products such as calcium hydroxides can effectively reduce the risk of copper leaching. Further understanding of metal entrapment mechanisms could lead to strategies that reduce the mobility of toxic elements when using mining residues as Supplementary cementitious materials for concrete production.

Keywords: Leaching, chemical entrapment, physical entrapment, cementitious mixtures, copper tailings.

3.1 Introduction

CO_2 is the primary greenhouse gas emitted to the atmosphere by human activity (EPA and Change Division, 2019). The production of 1 metric ton of Portland cement emits between 0.85 and 1 ton of CO_2 to the atmosphere (Monteiro et al., 2017). To reduce the impact of greenhouse emissions from concrete production, Supplementary cementitious materials (SCM) have been used to partially replace the required cement (Schneider et al., 2011). SCM may act in two ways during hydration: chemically by replacing or generating new hydration products on the cementitious matrix, and physically as nucleation points where hydration products can aggregate. Mining residues have been reported as possible SCM, including copper debris (Aguilar et al., 2005), copper tailings (Onuaguluchi and Eren, 2012) and treated copper tailings (Vargas and Lopez, 2018) which are copper tailings mechanically processed to reduce their particle size and/or thermally processed to reduce their crystallinity. One drawback of using tailings as SCM is their content of toxic elements that may affect human and ecosystem health (e.g., arsenic, lead, copper), as they can be released from the cementitious matrix during the early stages of cementation.

Copper is a common toxic element found in tailings from mining operations (Smuda et al., 2008), because of the current technological unfeasibility of completely extracting the metal from the ore. Copper is found in most economic ores as an oxide, sulfate or sulfide, in combination with molybdenum and other metals such as gold or silver (Davenport et al., 2002). In tailings, copper is commonly found in the Cu^{+2} oxidation state, in the form of oxides (CuO), sulfates ($CuSO_4$), sulfides such as chalcopyrite ($CuFeS_2$), and other minor phases. The presence of copper oxides in hydrated cement causes strength loss at replacement levels over 1% (Ma et al., 2010). On the other hand, concrete mixtures with 10% replacement level of copper tailing (% by mass of cement replaced by tailing), have shown higher resistance to acid attack, and lower resistance to sulfate attack with respect to concrete mixtures with no replacement (Onuaguluchi and Eren, 2012). In addition, concrete mixtures with 40% replacement level of treated copper tailings have shown minimum loss of mechanical strength, depending on the nature of the tailing (Vargas and Lopez, 2018).

Several trapping mechanisms of copper in the cement hydration products have been proposed (Conner and Hoeffner, 1998; Shi and Spence, 2004). One of such mechanisms is physical encapsulation (Huang et al., 2014; Li et al., 2001), although the nature of encapsulation has not been clearly identified yet. Other proposed mechanism is chemical entrapment: the inclusion of copper in a new compound produced during the hydration process). The formation of double hydroxide precipitates (Ca2(OH)4·4Cu(OH)2*2H2O) in the presence of pure calcium silicates solutions is a prime example of chemical entrapment mechanism (Chen et al., 2007). Nevertheless, there is no agreement on the exact mechanism of entrapment of copper in cement hydration products (Guo et al., 2017). The aim of this research is to elucidate the trapping mechanism of copper in the cement hydration products, through locating the copper phases in the microstructure of the cementitious matrix and its phases.

3.2 Materials and methods

A composite copper tailing sample (40 kg) was collected from a source deposit in Copiapo, Chile, by sampling at three different points on the surface of the deposit. The chosen source deposit was a long-standing tailing (LS1) with a high concentration of copper, above most of recommended standards (range 63-400 mg/Kg for residential soils) (Carkovic et al., 2016).

Only the fraction of tailings passing the sieve N° 30 (600 μm) was considered, i.e., the larger particles (approximately 15% by mass) were discarded, as proposed previously (Vargas and Lopez, 2018). This study used type I Ordinary Portland Cement (OPC) to produce the cementitious mixtures.

3.2.1 Chemical characterization

The chemical composition of the LS1 tailing and OPC was determined by X-ray fluorescence (XRF) using a Bruker S8 Tiger spectrometer.

Additionally, samples were digested to determine trace metal contents according to procedure EPA3050b (US Environmental Protection Agency, 1996) and then analyzed by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) (Agilent 7500ce instrument).

The mineralogical composition of the tailing was determined by X-ray diffraction (XRD) using a Siemens D500 X-ray diffractometer. The diffractometer was operated at 40 kV and 30 mA, with scans taken from 5–70° 2θ with a step size of 0.2° 2θ and a 2 s dwell time.

3.2.2 Physical characterization (PSD)

Particle size distributions (PSD) of the tailings and OPC were measured using a Malvern Mastersizer 2000 laser diffractometer. Isopropanol (refractive index 1.378) was used as a dispersant, and the PSD was measured for 12 s five times while stirring at 2000 rpm to obtain an average measurement, using the Mie Scattering principle.

3.2.3 Tailing strength development

Mixture proportioning was performed by mass. Three 100% OPC mixtures were selected as references. The samples were prepared and tested at 28 days of age according to ASTM C109, and the same samples were then milled down for performing the leaching experiments.

3.2.4 Environmental leaching experiments

Leaching tests were carried out using EPA Method 1313 (U.S. EPA, 2012). This protocol is a parallel batch extract test consisting of nine parallel batch extractions at pH values from 2 to 13 and a liquid-to-solid ratio of 10. Nitric acid (Fisher Chemical, 70% w/w) was used to adjust pH given the basic nature of the samples. After 28 days of curing at 23°C, the samples of cementitious matrices with tailings were pretreated by hand milling in an agate mortar and pestle, to reduce their particle size below 2 mm.

The rotation speed was set at 28 ± 2 rpm according to the leaching protocol. Agitation was maintained for 48 hours. Leaching tests were conducted in duplicate for all materials.

Statistical analysis was carried out on leaching results of samples at pH over 11 to analyze simulated behavior at the same conditions as on the cementitious matrix. This procedure aims to increase the specific surface of the sample by grinding, limiting the effect of changes in porosity due to changes in chemical composition and water-to-binder ratio.

3.2.5 Leaching Experimental Design

Three factors were chosen to analyze an experimental region of interest. First, the chemical composition was purposely changed to analyze the copper phases generation in the cementitious matrix. That is, the concentration of calcium was modified by adding up to 10% by mass of dried calcium hydroxide to promote the formation of calcium precipitates or copper hydroxide. Second, the concentration of sodium was modified by dissolving up to 2% by mass of sodium hydroxide into the water. Sodium promotes the formation of geopolymers in the cementitious matrix by replacing aluminum and calcium by metals such as copper (Hossain et al., 2015). Third, the water-to-binder ratio was varied between 0.45 and 0.5, to change physical entrapment properties by purposely promoting changes in the microstructure, porosity and compaction of the cement hydration products, such as calcium silicate hydrate (C-S-H).
A fixed replacement level of 20% by mass was chosen for all mixtures. A single factorial model for three factors (23 = 8 runs) was used to assess and compare the factors affecting copper entrapment. The advantages of this experimental design are its simplicity and the possibility of detecting interactions between factors (Montgomery, 2017). The design

factor levels and runs for the experimental region of interest are shown in Table 1. Two replications were made for each design point.

Table 3.1 Design factor levels and runs at 20% replacement level.

Run	Experimental Coded Factors			Factors		
	$Ca(OH)_2$	Na(OH)	Water-to-binder ratio	$Ca(OH)_2$ % by mass	Na(OH) % by mass	Water-to-binder ratio
1	-	-	-	0%	0%	0.45
2	+	-	-	10%	0%	0.45
3	-	+	-	0%	2%	0.45
4	+	+	-	10%	2%	0.45
5	-	-	+	0%	0%	0.5
6	+	-	+	10%	0%	0.5
7	-	+	+	0%	2%	0.5
8	+	+	+	10%	2%	0.5

3.2.6 SEM-EDS Mapping

For EDS processing and mapping, cementitious matrix samples were manufactured and then hydration was stopped in cementitious matrix samples at either 24 h or 7 days. The samples had a 0.5 water-to-binder ratio with 40% paste and 60% inert filler by mass. The cementitious materials of this test are composed of 50% OPC and 50% tailings by mass.

The sample preparation consists of drying with isopropanol, impregnation with a hydrophilic acrylic resin of low viscosity (LR White), polishing and carbon-coating. For EDS mapping, EBSD (electron backscatter diffraction) was used on a Quanta FEG 250 instrument, with magnification between 800x and 4000x. Tests were carried out in duplicate.

3.2.7 X-ray absorption near edge structure

The identity of copper phases in the tailing and hydrated cement samples were determined by X-ray absorption near edge structure (XANES) spectroscopy. Cu K-edge XANES spectra were recorded at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) bending magnet beamline, located in Sector 5 of the Advanced Photon Source, Argonne National Lab (APS-ANL, Argonne, IL, USA). The incident X-ray energy was modulated with a Si (111) monochromator, with an intrinsic energy resolution of 1.2 eV at the Cu K-edge (8979 eV). XANES spectra of samples were acquired in fluorescence mode with a four-element silicon-drift detector (Vortex-ME4). Between 4 and 6 scans were collected per sample. XANES spectra were normalized by fixing the absorption threshold energy to the nominal energy of the Cu K-edge (8979 eV), to perform phase identification via linear combination fitting (LCF) with known reference standards (Gaillard et al., 2001; Manceau et al., 1996; Newville, 2013; Tong et al., 2015). XANES spectra of standards were acquired in transmission mode through ionization chambers (Oxford Danfysik). Standards were obtained as either chemical reagents (Sigma-Aldrich) or as minerals (Excalibur Minerals Corp.). The mineralogy of the latter standards was confirmed through X-ray diffraction. Samples and standards were mechanically pulverized and sieved to less than 150 mm of particle size and sealed between Kapton or Scotch tape before measurement. The LCF procedure considered a fit window of -30 to 90 eV above the threshold energy, with fractions of identified standards forced to sum to 1. The normalized sum of squared residuals (i.e., chi-square) was used as the parameter for goodness of fit.

3.3 Results and Discussion

3.3.1 Chemical Characterization

XRF and ICP-MS results are shown in Table 2. The XRD pattern in Figure 1 shows quartz as a crystalline phase in LS1 tailings, as it has been reported for other copper tailings (Ahmari and Zhang, 2012; Vargas and Lopez, 2018), with minor phases such as cristobalite, calcite, muscovite, feldspar, magnetite and anorthite. Copper phases were not detected due to either low concentration or absence of crystallinity.

Table 3.2 Chemical composition of OPC and tailings. Chemical composition data are presented as oxide percentage by weight. Trace element concentrations are presented as mg/kg.

XRF			**ICP-MS (Digestion)**		
Percentage of Oxides (%)	OPC	Tailing LS1	Element (mg/kg)	OPC	Tailing LS1
SiO_2	20.36	49.40	As	16.68	114.8
Al_2O_3	5.82	10.30	Cd	0.36	1.64
Fe_2O	2.3	18.70	Co	6.38	59.65
CaO	62.49	5.10	Cu	33.01	2939.5
MgO	3.3	2.70	Cr	90.46	15.74
SO_3	3.3	2.60	Ni	27.92	39.19
Na_2O	0.89	1.30	Pb	20.03	116.55
K_2O	0.15	2.60	Se	0.86	2.08
TiO_2	0.28	0.50	Sr	688.7	38.62
P_2O_5	0.16	0.20	V	86.72	58.74
Mn_2O_3	0.04	0.20	Zn	131.3	480.6
Los on Ignition (LOI)	2.1	5.80	**Specific Gravity**	3.142	2.925

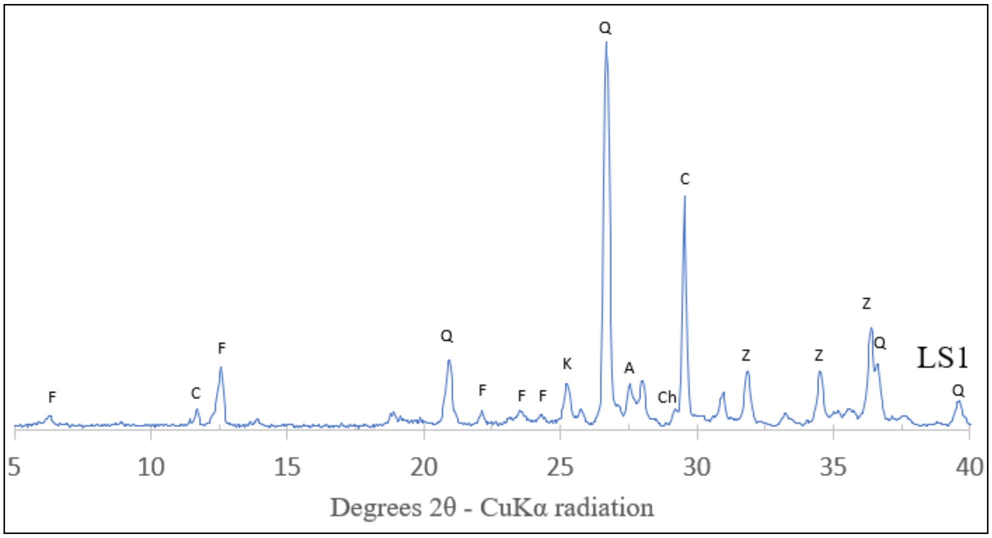

Figure 3.1 XRD pattern of LS1 tailings (Q: quartz; C: Calcite; K: kaolinite; A: anorthite; Z: zinc oxide added as standard; F: other phases such as cristobalite, muscovite, feldspar, magnetite).

3.3.2 Particle Size Distribution (PSD)

The OPC showed a finer particle size distribution than that of the LS1 tailing (See Fig. 2). OPC had a D50 value of 19.3 □m, typical in OPC where the size ranges between 1 and 100 □m, which is also common in this material. The tailings had a D50 value of 87.8 □m with a maximum size of 600 □m due to the sieving process.

Tailings were coarser than the OPC, which was expected since the long standing tailings were produced with less effective milling technology. Despite the coarser particle size of the tailing with respect of OPC, with a D25 of 28.2 □m, and a D10 value of 7.04 □m, part of the tailings can chemically react with cement during the hydration process and part of the tailings can act as nucleation points.

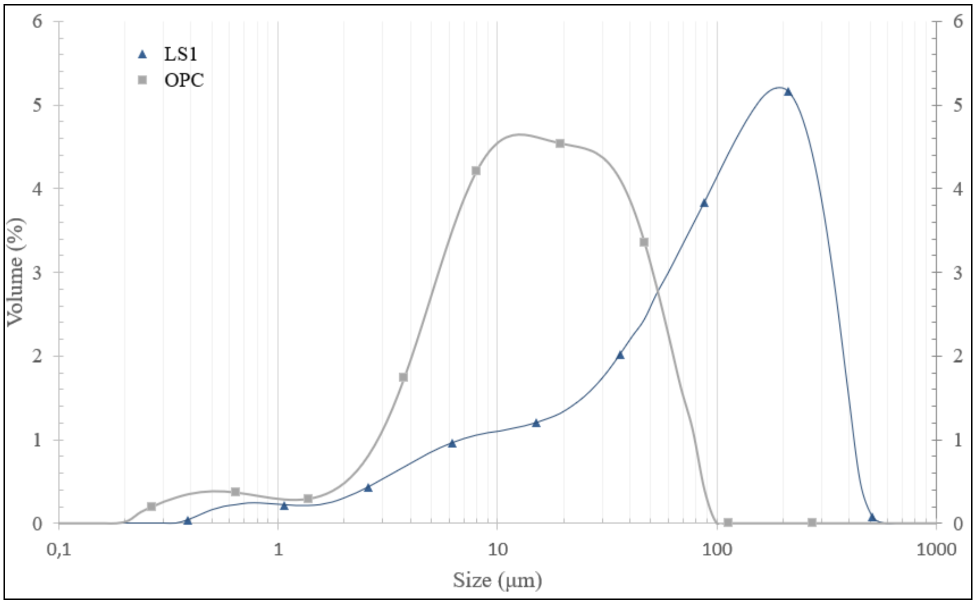

Figure 3.2 Particle size distributions (PSD) of OPC and LS1 tailings.

3.3.3 Compressive Strength and Porosity

The results for the tailings pastes are shown in Table 3. Porosity according to the formulae proposed by Powers, Ryshkevich and Balshin's (Erniati et al., 2015) was calculated with compressive strength data.

Table 3.3 Compressive strength of pastes at 28 days, 20% replacement level.

				20% replacement level			
	Factor Levels			MPa	%	%	%
Run	% Addition $Ca(OH)_2$	% Addition NaOH	W/C ratio	28 days	Porosity (Powers)	Porosity (Ryshkevich)	Porosity (Balshin's)
1	0%	0%	0,45	36,4	46%	8.0%	7.5%
2	10%	0%	0,45	37,9	45%	7.5%	7.0%
3	0%	2%	0,45	28,6	50%	10.7%	10.2%
4	10%	2%	0,45	21,6	54%	13.8%	13.3%
5	0%	0%	0,5	23,1	54%	13.1%	12.5%
6	10%	0%	0,5	25,6	52%	11.9%	11.4%
7	0%	2%	0,5	23,9	53%	12.7%	12.2%
8	10%	2%	0,5	20,4	55%	14.5%	13.9%

For compressive strength, the water-to-binder ratio and the percentage of sodium hydroxide added, and the interaction between them were statistically significant. Conversely, the percentage of $Ca(OH)_2$ added had no statistically significant effect on the strength; this could be attributed to polymerization processes and alkalinity in the cementitious matrices, volume changes and water availability (Sant et al., 2012). In the case of porosity, results have the same trends and can be seen as in relation with the statistically significant factors showed for mechanical performance.

3.3.4 Leaching

Results showed that leaching of copper was low when tailings were embedded into the cementitious matrix (see Fig.3). The copper concentration in the leachates were below national and international drinking water standards (e.g., NCh 409 (INN, 2005) and EC 98/83 (European Parliament and Council, 1998)) for all runs on an alkaline environment, typical of a cementitious mix. Copper oxides have typical amphoteric behavior (Conner and Hoeffner, 1998), while copper hydroxides are mildly amphoteric, showing less solubility when moving from neutral pH to either direction.

The alkaline nature of the cementitious mixtures, due to the presence of Ca(OH)2 as a hydration product, suggests lower leaching when tailings are used in concrete production.

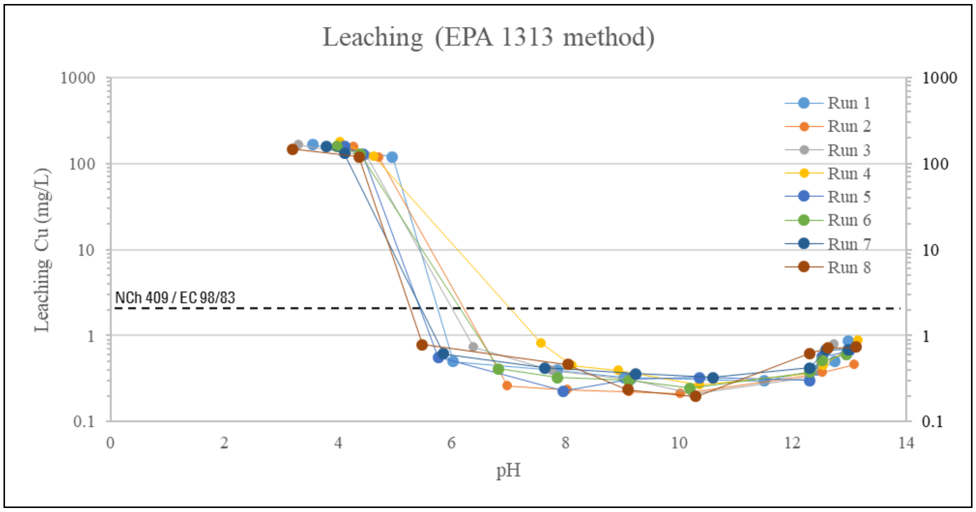

Figure 3.3 Leaching curves for each experimental design point (8 run according to Table 1) for Cu in cement paste according to EPA method 1313.

To analyze the leaching curves and the statistical relevance of selected factors, Half-Normal Probability Plots (Montgomery, 2017) were constructed using 95% confidence intervals (see Figs. 4 and 5). Each data point represents a factor or a combination of factors (up to second order), including: calcium hydroxide addition, sodium hydroxide addition, water-to-binder ratio, and the combination of those factors. The central line in these plots represents a normal distribution and each factor deviating from the central line is statistically significant. That is, factors (data points on the plot) falling on the central line cannot be discriminated from the statistical error of the experiment and are not statistically significant.

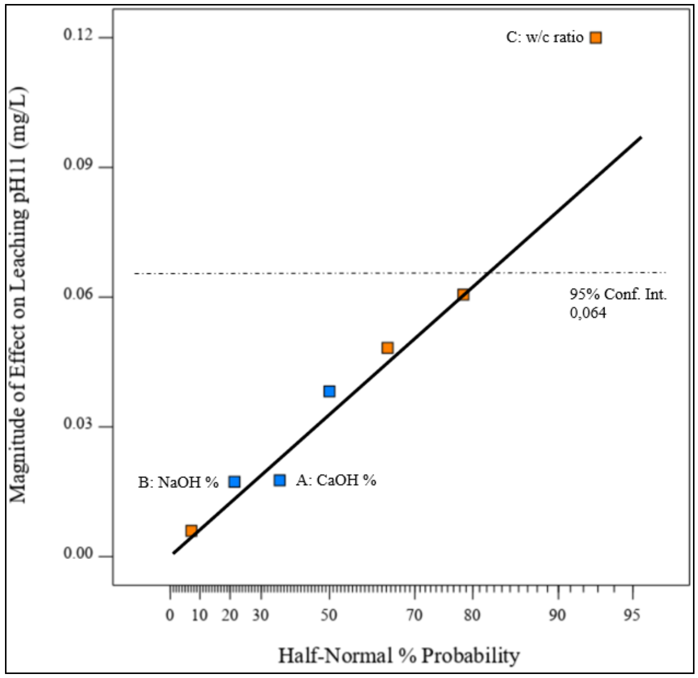

Figure 3.4 Half normal probability plot of estimated copper leaching effects at pH 11. The *water-to-binder ratio* factor is statistically significant.

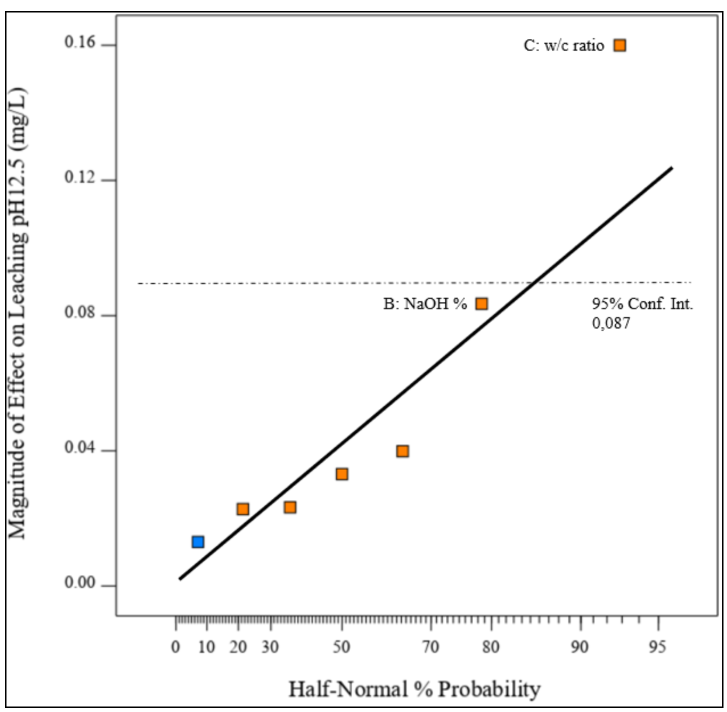

Figure 3.5 Half normal probability plot of estimated copper leaching effects at pH 12.5. The *water-to-binder ratio* factor is statistically significant.

The only factor than can be stated as statistically significant to the copper leaching is the water-to-binder ratio (at pH 11 and pH 12.5). The alkaline range was chosen for the analysis, since it better represents the natural cementitious matrix environment. For instance, pH 11 (Figure 4) and pH 12.5 (Figure 5), are typical lower limits for cementitious matrices with SCMs (Mehta and Monteiro, 2014).

The fact that water-to-binder ratio is statistically significant, can be explained by two effects that are influenced by the change in this factor: first, a high water-to-binder ratio, increases porosity and ultimately permeability making copper phases more prone to leaching. Second, a lower water-to-binder ratio promotes calcium silicate hydrate formation making the microstructure more compact (Hou et al., 2018; Vandamme et al., 2010), and increasing the probability of copper getting trapped in the cementitious matrix. This suggest a physical entrapment mechanism of copper phases in the cementitious matrix.

3.3.5 EDS Mapping

For each analysis, scatter plots were used to determine phases in the cementitious matrix (Scrivener et al., 2016). Figure 6 shows the EDS-mapping of a cementitious matrix after 24 hours of hydration where elemental composition was run to obtain a map of typical hydration products. Scatter plots were used to determine specific hydration products and the concentration of copper in those zones.

The higher concentration of copper was found at the tailings and aggregate edges when mapping was done at 24 hours of hydration (Phase mapping E in Figure 6). A two-sample t-test showed that there was no significant difference in copper concentration between calcium silicate hydrates and calcium hydroxides, with α=0.05. A copper concentration of 0.39 ± 0.22% was measured for the calcium silicate hydrate phase (Phase mapping C in Figure 6), while a copper concentration of 0.22 ± 0.13% was measured for calcium hydroxide (Phase mapping D in Figure 6), and dehydrated phases.

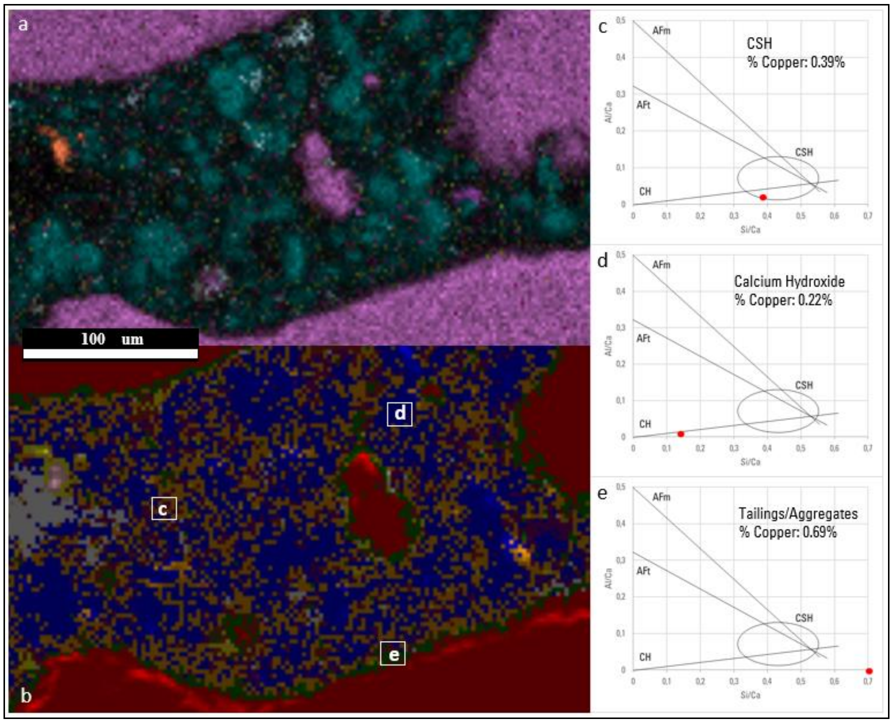

Figure 3.6 EDS Mapping and results for 24-h paste mixture. a. Elemental mapping b. Phase mapping c. Calcium Silicate Hydrate plot d. Calcium Hydroxide and nonhydrated phases plot. e. Aggregates and tailings edge hydration products.

Figure 7 shows the EDS-mapping of a cementitious matrix after 7 days of hydration. In this case, the copper concentration was significantly different (two-sample t-test, $\alpha=0.05$) between calcium silicate hydrates (1.01 ± 0.38%) and other phases measured, notably calcium hydroxides (0.35 ± 0.2%), the other key hydration product on cementitious matrices.

Copper in the calcium silicate hydrate phase has been proposed by some authors as a mechanism for entrapment of metal phases in the cementitious matrix (Guo et al., 2017; Li et al., 2001) and may explain the correlation between the cementitious matrix compaction (related with calcium silicate hydrates and the water-to-binder ratio) observed in the section 3.4. The difference in copper concentration between calcium silicate hydrate phases and calcium hydroxide phases can be explained by physical entrapment. That is, copper phases may replace some part of the crystalline microstructure of calcium silicate hydrates. An alternate explanation is that a chemical entrapment, in which Cu is sorbed or forms a solid-solution within these hydration products ($Ca_2(OH)_4 4Cu(OH)_2 \cdot 2H_2O$ as one possible precipitate). These results show that copper phases migrate toward these hydration products as they form and take up more space.

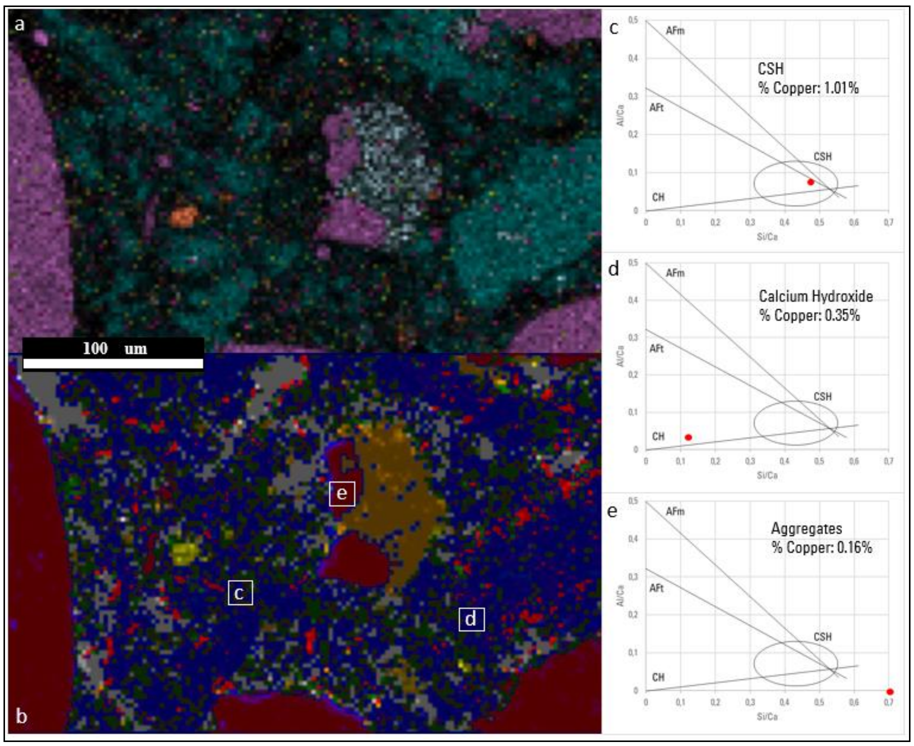

Figure 3.7 EDS Mapping and results for 7-days paste mix. a. Elemental mapping b. Phase mapping c. Calcium Silicate Hydrate plot d. Calcium Hydroxide and nonhydrated phases plot. e. Aggregates.

3.3.6 Cu K-edge XANES spectroscopy

Following the geology of the Atacama Region (SEGERSTROM, 1967), the copper reference phases used to interpret the composition of the tailing and the cementitious mixtures by XANES spectroscopy consisted of (1) sulfide minerals, i.e., chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covellite (CuS) and chalcocite (Cu_2S); (2) silicates such as chrysocolla and dioptase ($CuSiO_3 \cdot H_2O$), (3) sulfates, i.e., brochantite ($Cu_4SO_4(OH)_6$), (4) oxides/hydroxides: tenorite (CuO) and cupric hydroxide ($Cu(OH)_2$) and (5) metallic copper. The Cu K-edge XANES spectra of these references are presented in Figure 8A. Characteristic Cu K-edge XANES absorption features of the reference standards were considered in this analysis. For the case of Cu(II) compounds, a $1s \rightarrow 3d$ electric quadrupole transition produces a very weak pre-edge absorption at 8977-8979 eV, whose intensity depends on the dihedral angle of the coordination metal complex (Kau et al., 1987; Sano et al., 1992). This transition is stronger for tetrahedral complexes, as seen for the case of chalcopyrite (Figure 8A).

Cu(II) compounds also show an absorption feature approximately at 8986 eV, which is formally assigned as an 1s→4p electric dipole transition, whose intensity depends on the degree of ligand-to-metal charge transfer excitation (Pattrick et al., 1997). On the other hand, Cu(I) compounds such as bornite and covellite exhibit an absorption peak below 8985 eV that likely corresponds to a 1s→4p electric dipole transition (Kau et al., 1987).

Figure 8B presents the XANES spectra of the LS1 tailing and the cementitious paste samples. Both samples exhibit absorption pre-edges at 8979 eV and 8986 eV, which are consistent with presence of chalcopyrite. Assessment of additional references to interpret the XANES spectra was performed by constructing a reduced domain of the previously listed reference phases through principal component analysis (PCA)(Da Silva-Cadoux et al., 2012). Projection of the samples into the first 2 principal components suggests spectral similarity of the samples with tenorite and cupric hydroxide. Consequently, chalcopyrite, brochantite, tenorite and cupric hydroxide were selected as references for the LCF analysis. Results from the LCF analyses are presented in Figures 8B and 8C. The LS1 tailing and the cementitious paste samples share similar absorption features, which reflects predominant concentrations of chalcopyrite (42 ± 1% and 32 ± 1%, respectively) and similar concentrations of tenorite (20 ± 2% and 26 ± 3%, respectively). Notably, the cementitious paste sample shows presence of cupric hydroxide (28 ± 2%), a phase which is absent in the LS1 tailings sample. In addition, there is a significant decrease in the brochantite concentration from the tailing (38 ± 2%) to the hydrated cement sample (14 ± 3%).

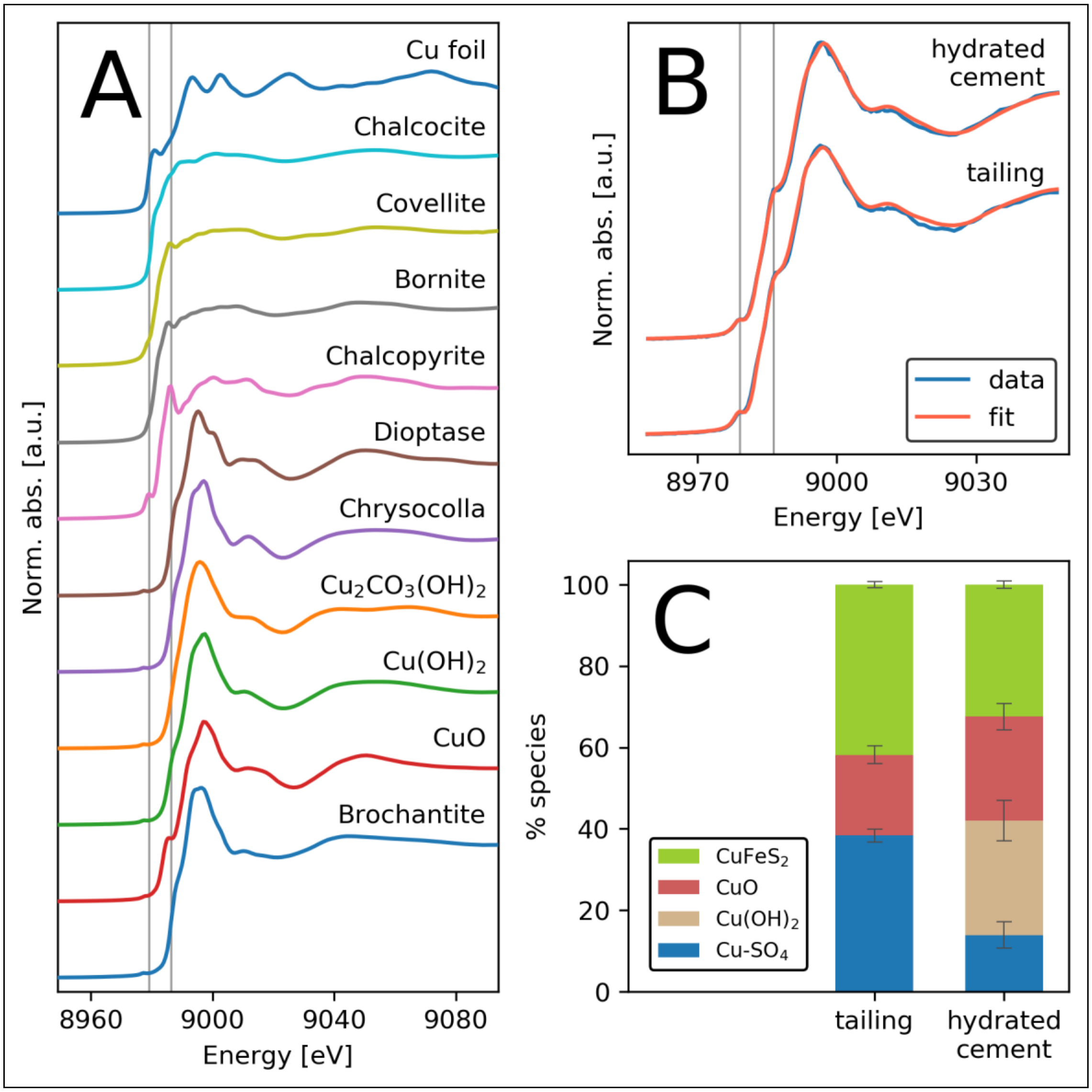

Figure 3.8 Cu K-edge XANES spectra of reference standards and samples: (A) XANES spectra of references considered for the LCF analysis; (B) XANES spectra of tailing and cementitious paste samples, including their corresponding linear combination fit. Gray lines indicate the location of characteristic absorption peaks of chalcopyrite (8979 and 8986 eV); (C) Summary of LCF results for the samples, including the estimated standard deviations.

SEM and XANES spectroscopy indicate that copper sulfides remain a relatively recalcitrant fraction during hydration of the cementitious matrix. On the other hand, copper sulfates dissolve upon hydration, with copper selectively migrating to the alkaline hydrated fraction (i.e., spatially associated with calcium hydrates) and precipitating as copper hydroxide.

The proposed partitioning mechanism for copper is consistent with previous observations of metal leaching from cement-based materials containing copper waste materials, which suggested that copper precipitates as either a hydrate or hydroxide species on the surface of calcium silicate hydrates (Li et al., 2001). In addition, leachability tests of copper from cement-based stabilized steel processing sludge (Malviya and Chaudhary, 2006) also showed a pH dependence that was interpreted as solubilization from hydroxide phases. Finally, sequential extraction tests from 17-year-old cement-based stabilized soil sludge (Wang et al., 2014) indicated that most of Cu was present in the oxide fraction, likely as tenorite or cupric hydroxide. Such findings support the proposed partition mechanism for copper in cement-based materials from this research.

3.4 Conclusions

The use of copper tailings as a supplementary cementitious material is an alternative that reduces the impact of cement and concrete production while also reducing the impact of storage and disposal of this leftover product from the mining industry. Although, heavy metals in copper tailings entails environmental and health concerns, the mobility of copper may be constrained when tailings are used in concrete production. This study conducted a series of tests to assess the mechanisms for copper entrapment in the cementitious matrix and to identify key factors controlling such mechanisms.

The following can be concluded based on the findings of this research:

1. Water-to-binder ratio was found to be statistically significant in affecting copper leaching from the cementitious matrix, while the other two factors under investigation (concentration of calcium hydroxide and sodium hydroxide) were found to be not statistically significant. In concrete

mixtures with water-to-binder ratios below 0.5, leaching could be neglected or treated as a minor problem.

2. While copper cannot be associated to any specific hydration product of the cementitious matrix after 24 hours of hydration, SEM- EDS mapping reveals a higher copper concentration in the calcium silicate hydrates (C-S-H) compared to other hydrated phases, after 7 days of hydration. This suggests that copper migration is controlled by the physical fate of hydration products.

3. Cu K-edge XANES results show that for the case of the LS1 tailing, dissolution of copper sulfate and precipitation of cupric hydroxide results from hydration of the cementitious matrix. Notably, copper sulfide and oxide phases remain mostly invariant from the tailing to the cementitious matrix. Association of copper associated with aluminosilicate phases was not detected.

4. Changes in copper solubility during leaching tests can be explained by changes in permeability and compaction of hydration products, specifically, calcium silicate hydrates (C-S-H). This finding is supported by EDS mapping, where copper migrates to alkaline phases and aggregates mostly as cupric hydroxide.

5. Copper entrapment can be explained by a combination of chemical and physical mechanisms, by which copper sulfate phases dissolve and reprecipitate along with calcium silicate hydrates mostly as cupric hydroxide. Improving the quality of this hydration product improves the entrapment of copper and reduces the copper leaching in cementitious mixtures.

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3.6 References

Aguilar, L., Roldán, W., Zetola, V., Urrutia, C., 2005. Uso de ripios provenientes de procesos de lixiviación del cobre en la fabricación de hormigones The usage of originating debris of copper leaching processes in cement concretes. Rev. Ing. construcción 20, 223–232.

Ahmari, S., Zhang, L., 2012. Production of eco-friendly bricks from copper mine tailings through geopolymerization. Constr. Build. Mater. 29, 323–331. doi:10.1016/j.conbuildmat.2011.10.048

Carkovic, A.B., Calcagni, M.S., Vega, A.S., Coquery, M., Moya, P.M., Bonilla, C.A., Pastén, P.A., 2016. Active and legacy mining in an arid urban environment:

challenges and perspectives for Copiapó, Northern Chile. Environ. Geochem. Health 38, 1001–1014. doi:10.1007/s10653-016-9793-5

Chen, Q.Y., Hills, C.D., Tyrer, M., Slipper, I., Shen, H.G., Brough, A., 2007. Characterisation of products of tricalcium silicate hydration in the presence of heavy metals. J. Hazard. Mater. 147, 817–825. doi:10.1016/J.JHAZMAT.2007.01.136

Conner, J.R., Hoeffner, S.L., 1998. A critical review of stabilization/solidification technology. Crit. Rev. Environ. Sci. Technol. 28, 397–462. doi:10.1080/10643389891254250

Da Silva-Cadoux, C., Zanella, L., Gaillard, J.F., 2012. Selecting reference compounds for determining chemical speciation by X-ray absorption spectroscopy. J. Anal. At. Spectrom. 27, 957–965. doi:10.1039/c2ja10318d

Davenport, W.G., King, M., Schlesinger, M., Biswas, A.K., 2002. Overview. Extr. Metall. Copp. 1–16. doi:10.1016/B978-008044029-3/50004-6

Epa, U., Change Division, C., 2019. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2017 – Main Text.

Erniati, Tjaronge, M.W., Zulharnah, Irfan, U.R., 2015. Porosity, pore size and compressive strength of self compacting concrete using sea water, in: Procedia Engineering. Elsevier Ltd, pp. 832–837. doi:10.1016/j.proeng.2015.11.045

European Parliament and Council, 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official Journal of the European Union. doi:10.1017/cbo9780511610851.055

Gaillard, J.-F., Webb, S.M., Quintana, J.P.G., 2001. Quick X-ray absorption spectroscopy for determining metal speciation in environmental samples. J. Synchrotron Radiat. 8, 928–930. doi:10.1107/S0909049500020963

Guo, B., Liu, B., Yang, J., Zhang, S., 2017. The mechanisms of heavy metal immobilization by cementitious material treatments and thermal treatments: A review. J. Environ. Manage. 193, 410–422. doi:10.1016/J.JENVMAN.2017.02.026

Hossain, M.M., Karim, M.R., Hossain, M.K., Islam, M.N., Zain, M.F.M., 2015. Durability of mortar and concrete containing alkali-activated binder with pozzolans: A review. Constr. Build. Mater. 93, 95–109. doi:10.1016/j.conbuildmat.2015.05.094

Hou, D., Li, H., Zhang, L., Zhang, J., 2018. Nano-scale mechanical properties investigation of C-S-H from hydrated tri-calcium silicate by nano-indentation and molecular dynamics simulation. Constr. Build. Mater. 189, 265–275. doi:10.1016/J.CONBUILDMAT.2018.08.215

Huang, X.Q., Hou, H.B., Zhou, M., Wang, W.X., 2014. Mechanical Properties and Microstructure Analysis of Copper Tailings Solidifying with Different Cementitious Materials. Adv. Mater. Res. 878, 171–176. doi:10.4028/www.scientific.net/AMR.878.171

INN, 2005. NCh 409/1.Of2005 - Agua potable - Parte 1: Requisitos.

Kau, L.S., Spira-Solomon, D.J., Penner-Hahn, J.E., Hodgson, K.O., Solomon, E.I., 1987. X-ray absorption edge determination of the oxidation state and coordination number of copper. Application to the type 3 site in Rhus vernicifera laccase and its reaction with oxygen. J. Am. Chem. Soc. 109, 6433–6442. doi:10.1021/ja00255a032

Li, X.., Poon, C.., Sun, H., Lo, I.M.., Kirk, D.., 2001. Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. J. Hazard. Mater. 82, 215–230. doi:10.1016/S0304-3894(00)00360-5

Ma, X.-W., Chen, H.-X., Wang, P.-M., 2010. Effect of CuO on the formation of clinker minerals and the hydration properties. Cem. Concr. Res. 40, 1681–1687. doi:10.1016/j.cemconres.2010.08.009

Malviya, R., Chaudhary, R., 2006. Leaching behavior and immobilization of heavy metals in solidified/stabilized products. J. Hazard. Mater. 137, 207–217. doi:10.1016/j.jhazmat.2006.01.056

Manceau, A., Boisset, M.C., Sarret, G., Hazemann, J.L., Mench, M., Cambier, P., Prost, R., 1996. Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. Environ. Sci. Technol. 30, 1540–1552. doi:10.1021/es9505154

Mehta, P.K., Monteiro, P.J.M., 2014. Concrete: Microstructure, Properties, and Materials, Fourth Edition, 4th Editio. ed. McGraw-Hill Education: New York, Chicago, San Francisco, Athens, London, Madrid, Mexico City, Milan, New Delhi, Singapore, Sydney, Toronto, New York.

Monteiro, P.J.M., Miller, S.A., Horvath, A., 2017. Towards sustainable concrete. Nat. Mater. 16, 698–699. doi:10.1038/nmat4930

Montgomery, D.C., 2017. Design and Analysis of Experiments, Design.

doi:10.1198/tech.2006.s372

Newville, M., 2013. Larch: An Analysis Package for XAFS and Related Spectroscopies. J. Phys. Conf. Ser. 430, 012007. doi:10.1088/1742-6596/430/1/012007

Onuaguluchi, O., Eren, Ö., 2012. Cement mixtures containing copper tailings as an additive: durability properties. Mater. Res. 15, 1029–1036. doi:10.1590/S1516-14392012005000129

Pattrick, R.A.D., Mosselmans, J.F.W., Charnock, J.M., England, K.E.R., Helz, G.R., Garner, C.D., Vaughan, D.J., 1997. The structure of amorphous copper sulfide precipitates: An X-ray absorption study. Geochim. Cosmochim. Acta 61, 2023–2036. doi:10.1016/S0016-7037(97)00061-6

Sano, M., Komorita, S., Yamatera, H., 1992. XANES spectra of copper(II) complexes: correlation of the intensity of the 1s .fwdarw. 3d transition and the shape of the complex. Inorg. Chem. 31, 459–463. doi:10.1021/ic00029a022

Sant, G., Kumar, A., Patapy, C., Le Saout, G., Scrivener, K., 2012. The influence of sodium and potassium hydroxide on volume changes in cementitious materials. Cem. Concr. Res. 42, 1447–1455. doi:10.1016/J.CEMCONRES.2012.08.012

Schneider, M., Romer, M., Tschudin, M., Bolio, H., 2011. Sustainable cement production—present and future. Cem. Concr. Res. 41, 642–650. doi:10.1016/j.cemconres.2011.03.019

Scrivener, K., Snellings, R., Lothenbach, B., 2016. A Practical Guide to Microstructural Analysis of Cementitious Materials, A Practical Guide to Microstructural Analysis of Cementitious Materials. doi:10.1201/b19074

SEGERSTROM, K., 1967. Geology and Ore Deposits of Central Atacama Province, Chile. GSA Bull. 78, 305–318. doi:10.1130/0016-7606(1967)78[305:GAODOC]2.0.CO;2

Shi, C., Spence, R., 2004. Designing of cement-based formula for solidification/stabilization of hazardous, radioactive, and mixed wastes. Crit. Rev. Environ. Sci. Technol. 34, 391–417. doi:10.1080/10643380490443281

Smuda, J., Dold, B., Spangenberg, J.E., Pfeifer, H.-R., 2008. Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: Implications on sources and mobility of elements during transport and early stages of deposition. Chem. Geol. 256, 62–76. doi:10.1016/j.chemgeo.2008.08.001

Tong, T., Hill, A.N., Alsina, M.A., Wu, J., Shang, K.Y., Kelly, J.J., Gray, K.A., Gaillard, J.F., 2015. Spectroscopic characterization of TiO2 polymorphs in wastewater treatment and sediment samples. Environ. Sci. Technol. Lett. 2, 12–18. doi:10.1021/ez5004023

U.S. EPA, 2012. Method SW-846 - 1313 : LIQUID-SOLID PARTITIONING AS A FUNCTION OF EXTRACT pH USING A PARALLEL BATCH EXTRACTION PROCEDURE SW-846. Us. Epa 14429.

US Environmental Protection Agency, 1996. Method 3050B: Acid Digestion of Sediments, Sludges, and Soils.

Vandamme, M., Ulm, F.-J., Fonollosa, P., 2010. Nanogranular packing of C–S–H at substochiometric conditions. Cem. Concr. Res. 40, 14–26. doi:10.1016/J.CEMCONRES.2009.09.017

Vargas, F., Lopez, M., 2018. Development of a new supplementary cementitious material from the activation of copper tailings: Mechanical performance and analysis of factors. J. Clean. Prod. 182, 427–436. doi:10.1016/J.JCLEPRO.2018.01.223

Wang, F., Wang, H., Al-Tabbaa, A., 2014. Leachability and heavy metal speciation of 17-year old stabilised/solidified contaminated site soils. J. Hazard. Mater. 278, 144–151. doi:10.1016/j.jhazmat.2014.05.102

4. ENVIRONMENTAL IMPACTS EVALUATION OF TREATED COPPER TAILINGS AS SUPPLEMENTARY CEMENTITIOUS MATERIAL

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Abstract

Supplementary cementitious materials (SCMs) have been researched to improve properties of concrete, including environmental indicators. Copper Treated Tailings (TT) have shown a promissory use as SCM but need of mechanical and thermal treatment has an impact on their environmental performance. The impact of the use of SCMs on the mechanical properties mixtures and environmental indicators needs to be considered into the calculations, such as the mechanical performance decrease and the leaching of some potentially harmful elements from the mixture. This study calculates the environmental impacts of the use of TT as SCM. Three scenarios are evaluated: equivalent mechanical performance at the same water-to-cementitious (w/c) ratio, maximum mechanical performance, and maximum allowable replacement level (i.e. minimum allowable mechanical performance). To achieve each level of mechanical performance, different replacement levels were tested for mixtures with TT, and different w/c ratios were tested for mixtures without TT, at a constant water level to vary only the binder content. Results show that at higher mechanical performance TT mixtures show better environmental indicators than mixtures without TT. In the case of TT mixtures with lower mechanical performance, environmental benefits of the use of TT shows a decrease in environmental indicators of concrete with TT. It is concluded that considerations need to be made on the properties of the SCM for a proper comparison of concrete mixes. Avoided impacts and the relative contribution of cement depending on the performance and level of replacement are also important considerations to be made for a proper environmental comparison.

Keywords: Copper Treated Tailings, Environmental Impact, Cementitious Mixtures, Supplementary cementitious materials, Life Cycle Assessment

4.1 Introduction

Cement production represents between 8-10% of anthropogenic emissions of carbon dioxide in the world (Robayo-Salazar et al., 2018): the manufacturing of 1 tonne of cement is roughly equivalent to the release of 1 tonne of CO_2 (Mehta & Monteiro, 2014). Because of the impact of the production of this material, the use of Supplementary cementitious materials (SCMs) has been widely explored in the last years (Fan & Miller, 2018; Lothenbach et al., 2011). The focus is on the use of low carbon materials to replace cement or to make more efficient the use of cement into mixtures, reducing the amount of cement used for each cubic meter of concrete (Juenger et al., 2019), and as consequence, decreasing their environmental impact (Van den Heede & De Belie, 2012). Natural pozzolans (Fan & Miller, 2018), zeolites (Küçükyıldırım & Uzal, 2014), calcined clays (Taylor-Lange et al., 2015; Yanguatin et al., 2017) and sewage sludge (Oliva et al., 2019) have gained interest in the last years as new SCMs as well as slags (D. Yang et al., 2017) and tailings (Choi et al., 2009). Copper slags and copper tailings are relevant due to their levels of production.

Production of copper reached 21 million tonnes worldwide in 2018 (U.S. Geological Survey, 2019), with China, Peru and Chile as the main producers. For each 1 tonne of refined copper, between 2 and 3 tonnes of copper slag and 196.5 tonnes of tailing are released to the environment and stored mostly on tailing dams or subterranean (Davenport et al., 2002). Tailings are placed in big dams at a rate of approximately 540 millions of tonnes each year in Chile alone (SERNAGEOMIN, 2019b).

Copper tailing has been studied as SCM with generally poor performance (Onuaguluchi & Eren, 2015; B. S. Thomas et al., 2013a) due to high crystallinity and particle size not compatible with hydration of cement. Mechanical and thermal treatments have been applied to improve performance of tailings from different sources in Chile as SCM, allowing the use of more material as replacement of cement (Vargas & Lopez, 2018). A reduction in particle size due to grinding treatment and a change into crystallinity of some interest phases at certain temperatures of calcination have improved cementitious capacity of tailings up to 40%.

Life Cycle Assessment (LCA) has been used as methodology to calculate the potential environmental impacts of mixtures with SCMs, such as fly ash (Celik et al., 2015), Ground Blast Furnace slag (GBFS) (Lee & Park, 2005; Robayo-Salazar et al., 2018), rice husk ash (Gursel et al., 2016) or sewage sludge (Nakic, 2018). LCA is considered the best method to assess the environmental impacts, but contradictory data between different studies and huge differences in the scope of research made can be found (Damineli et al., 2010; K. H. Yang et al., 2015). Moreover, previous studies consider the impact of the inclusion of SCMs to be negligible due to the consideration that most of those materials are wastes (Petek Gursel et al., 2014), with only a few studies considering allocation of those materials considering them as by-products (Chen et al., 2010; Seto et al., 2017), mainly focusing on the most common and studied SCMs (i.e. fly ash, GBFS). In the case of treated tailings, Extractive Waste Directive 2006/21/EC (*Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the Management of Waste from Extractive Industries and Amending Directive 2004/35/EC*, 2006) and ISO 14044 standard recommend considering it as a waste, because of its nature as an unintended residue. Due to no further use of treated tailing is certain, and no direct use of the material is possible, no allocation is advised (Di Maria et al., 2018). Nevertheless, the use of energy, involved in the treatments of tailings such as milling and calcination to produce TT and transportation needs to be considered to estimate the environmental impact of the use of this material as a replacement of cement.

The aim of this research is to evaluate the potential environmental impact of the use of treated tailings (TT) as SCMs, at different replacement levels according to specific performance levels in a concrete made for the Chilean context. Moreover, this research wants to determine whether the use of TT improves the environmental indicators of concrete or, due to the requirement of mechanical and thermal treatments, generates an additional environmental problem.

4.2 Methodology

4.2.1 Goal and scope definition

The aim of this LCA is to evaluate the environmental benefits of the use of TT as SCM into concrete mixtures, based on tailings and concrete production in Chile. The Functional Unit (FU) is the cubic meter (m^3) of concrete with a specific mechanical performance (see section 2.1.2), within three proposed scenarios (see section 4.2.1.3).

The system boundaries include all the processes from the production of aggregates, cement, water, extraction of tailing from the tailing dam, production of the TT and until the concrete leaves the concrete mixture facility, in a cradle-to-gate model system. The use and end-of-life of the concrete were excluded from the analysis due to lack of information and uncertainty on the future use of each concrete mixture. Figure A.1 shows the process flow of the concrete production system chosen for the modelling to the LCA.

As for modelling, the SimaPro 8.3 software was used to perform the LCA analysis. ReCiPe v1.12 (H) was the characterization method chosen to assess the environmental impacts due to its global scope and the fact that there is no specific method for the Chilean context. The midpoint impact categories analysed were climate change, ozone depletion, ozone formation, freshwater ecotoxicity, marine water ecotoxicity, terrestrial acidification, freshwater eutrophication, marine eutrophication, particle matter formation, water consumption and mineral resource depletion.

4.2.1.1 Characteristics of tailings and treated tailings production

For this study, two tailings were collected from different sources: one from an ongoing production mine (OP1) and the other one from an abandoned tailing deposit (LS5). Both tailings were used on a previous study (Vargas and Lopez, 2018). Table A.1 shows chemical composition and trace element concentrations for tailings and Ordinary Portland Cement (OPC) used during the study.

In the LCA, 30 minutes of grinding were considered for the mechanical treatment for both tailings. Temperature of calcination was selected as 600 °C for OP1 tailing and 700 °C for LS5 tailing, according to the results shown in Vargas and Lopez (2018). Energy requirements for calcination and grinding as well as mass losses due to water and carbon dioxide emissions were considered in the modelling (see section 2.2), according to data collected from laboratory measurements.

Concerns about the use of tailing and other materials as cement replacement include the presence of heavy metals and other toxic elements that can leach from the mixtures to the environment and be a risk for human health. Several authors show that leaching of toxic elements from tailings is reduced by the entrapment of those elements into the cementitious matrix, for example, for arsenic-rich tailings (Kim et al., 2016), lead-zinc tailings (Wang et al., 2018), tailings as aggregate replacement (Argane et al., 2015), or in geopolymeric mixtures (Ahmari and Zhang, 2013).

4.2.1.2 Modelling approach

One of the first steps on the development of an LCA is the definition of the functional unit (FU), according to standard ISO 14040. Nevertheless, there is no specific recommendation on the selection of a proper FU for studies like this one. FU is defined in ISO 14040 (2006) as the “quantified performance of a product system for use as a reference unit” (p. 4), while a declared unit only considers a unit of measurement (e.g. 1 m3 of concrete or 1 kg of cement, for example) without considering any performance (e.g. MPa or years of durability). For concrete mixtures, one main issue related with the proper comparison on different mixtures is the selection of the FU (Sagastume Gutiérrez et al., 2017). In the case of mixtures with SCMs, many studies use cubic meter (m3) as FU despite of being actually a declared unit with no performance associated. This happens in studies on mixtures with fly ash (Kurda et al., 2018), rice husk ash (Gursel et al., 2016), natural volcanic pozzolan

(Robayo-Salazar et al., 2018), and sewage sludge (Nakic, 2018). This can lead to misinterpretation and error on the estimation of the impacts of the use of SCM.

Damineli et al. (2010) proposed the binder index (bi) as FU that considers the amount of cement and the mechanical performance at a certain age of the concrete. Also, they proposed a global warming indicator for the comparison of concrete mixtures: the CO2 intensity index (cics) that considers the release of carbon dioxide per unit of performance. Nevertheless, to calculate this the emissions related with the production of SCMs are considered to be zero, which is true only if transportation is neglected for materials as fly ash or GBFS, regardless the recommendations of including transportation of those wastes as by-products (Di Maria et al., 2018). Besides this, many SCMs like TT require different processes such as sieving, heating, and milling, to be fully functional and more suitable for replacing cement, and these processed require energy.

Sagastume Gutiérrez et al. (2017) proposed the Cement Functional Performance (CFP) based on the binder index (bi) by Damineli. CFP considers the ratio between the mass of binder and the mechanical performance plus the durability in years with the use of a specific cement. This work compares mixtures with cement and zeolites, considering the emissions of the production of the clinker replacement materials. In this case, the ACI (American Concrete Institute) method was used for the mixture design (ACI 211.1, 2009). The SCM used (zeolite) was added to the cement as clinker replacement producing a blended cement, which is different from other SCM typical applications.

Panesar et al. (2017) proposed the use of 6 factors that comprise combinations of volume, binder content, mechanical performance and rapid chloride permeability to compare properly mixtures with different performances at a same base line. Those factors vary from a simple FU that is the cubic meter of concrete (declared unit) to ratio between binder index of a sample with a base case without SCM, to a complex FU that consists in a cubic meter of concrete considering binder index, mechanical performance and durability. This study used slag and silica fume as SCMs for comparison, showing that the proper selection of the FU can show big differences on the LCA impact category results, with results varying from 52% to 89% for the same type of mixture.

Considering all of this, environmental impact characterization results can vary widely changing the FU when comparisons are made between mixtures with or without SCMs where performance change. To avoid any bias on the consideration of the proper comparison properties, the proposed FU in this study is a cubic meter of concrete with a certain specified mechanical performance level, measured as compressive strength. This aims to obtain robust and simple comparisons of the use of TT as a SCM where the performance does not vary. For the mixture design, the ACI method was used, as proposed by Sagastume Gutiérrez et al. (2017). Nevertheless, to make comparison more accurate, some considerations need to be stated:

1. To compare only the effect of the use of the TT, water content will remain the same for all the mixtures. To maintain a minimum workability, the water-to-binder ratio by mass is fixed at 0.5 on TT mixtures.

2. There is a lack of information on the interaction between the TT and additives, such as plasticizers or water reducers. Because of this, use of additives into the mixture can depend on the amount of TT and could be different for each mixture. Considering this, no additives are considered into the mixtures.

3. The binder content by mass is the same for the mixtures with TT. To adjust volume (due to lower density of tailings compared to cement) total aggregate content is reduced in the TT mixtures but maintaining the coarse-to-fine aggregate ratio.

4. To compare mixtures with the same mechanical performance, cement content was changed in concrete mixtures without TT, increasing or reducing the water-to-binder ratio but maintaining the water content. This approach allows for valid comparison between the mixtures with and without TT.

The goal of this approach is to make comparisons using the mixture design and the properties of the materials as an input, considering the mechanical performance of the mixtures with TT.

4.2.1.3 Concrete mixture design

Since the cementitious capacity of the OPC and TT are not identical, the comparisons for the LCA need to be performed under alternative scenarios. Three scenarios were proposed and applied to each of the tailings as shown in **Figure 4.1**.

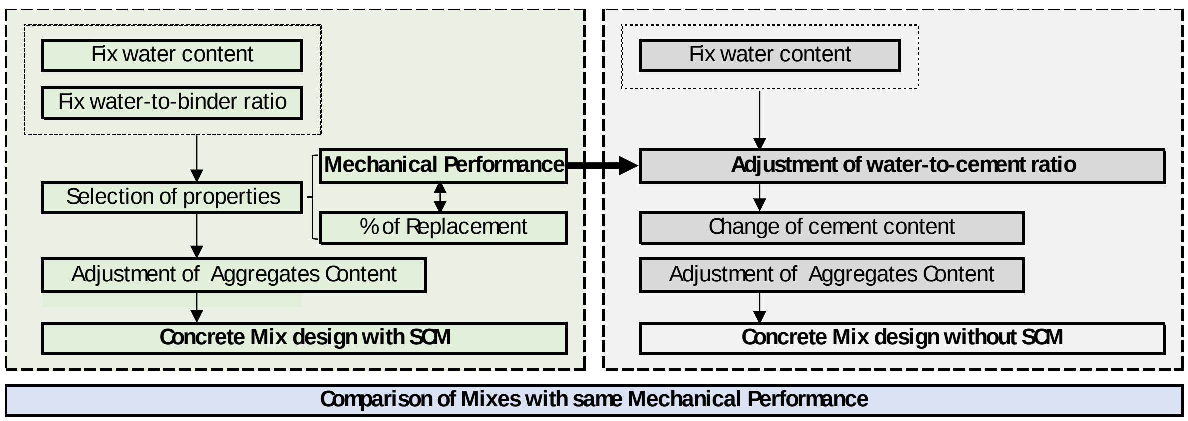

Figure 4.1 Scheme of the design of the comparison scenarios for LCA.

The experimental program, was an extension of a previous work (Vargas & Lopez, 2018), where 15 new data points were included with specimens made with TT at different replacement levels (10, 15, 20, 30 and 50%) and other made without TT at different water-to-binder ratio (0.4, 0.44, 0.45, 0.48, 0.50, and 0.65). The proposed scenarios are (**Figure 4.2**, **Table 4.1**):

1. Equivalent Mechanical Performance: concrete without TT at 0.5 water-to-binder ratio and mechanical performance of 34 MPa (dotted line in **Figure 4.2**) is compared with a mixture with TT at the same water-to-binder ratio (circle and square series in **Figure 4.2.a**) and the same mechanical performance achieved with

a certain replacement level of OPC by TT (intersection between dotted line and circle and square series in **Figure 4.2.a**).

2. Maximum Mechanical Performance: concrete with TT at 0.5 water-to-binder ratio and maximum mechanical performance with certain replacement level of OPC by TT (peak points triangles in **Figure 4.2.a**) is compared with a mixture without TT at a lower water-to-binder ratio and the same mechanical performance (triangles in **Figure 4.2.b**).

3. Minimum Allowable Mechanical Performance (**Figure 4.2** solid line): concrete with TT at 0.5 water-to-binder ratio, and 40% replacement level of OPC by TT or more and 20 MPa (intersection between solid line and circle and square series in **Figure 4.2.a**) is compared with a mixture without TT at a higher water-to-binder ratio and the same mechanical strength (intersection between solid line and square series in **Figure 4.2.b**). Twenty MPa is the minimal mechanical performance for structural purposes with a minimum resistance to chemical attacks (chloride and carbonation) as defined by European and Chilean standards, i.e. 20 MPa (*EN 206 Concrete - Specification, Performance, Production and Conformity*, 2013; *NCh170.Of2016 - Hormigón - Requisitos Generales*, 2016). This represents also the maximum replacement level for these mixtures.

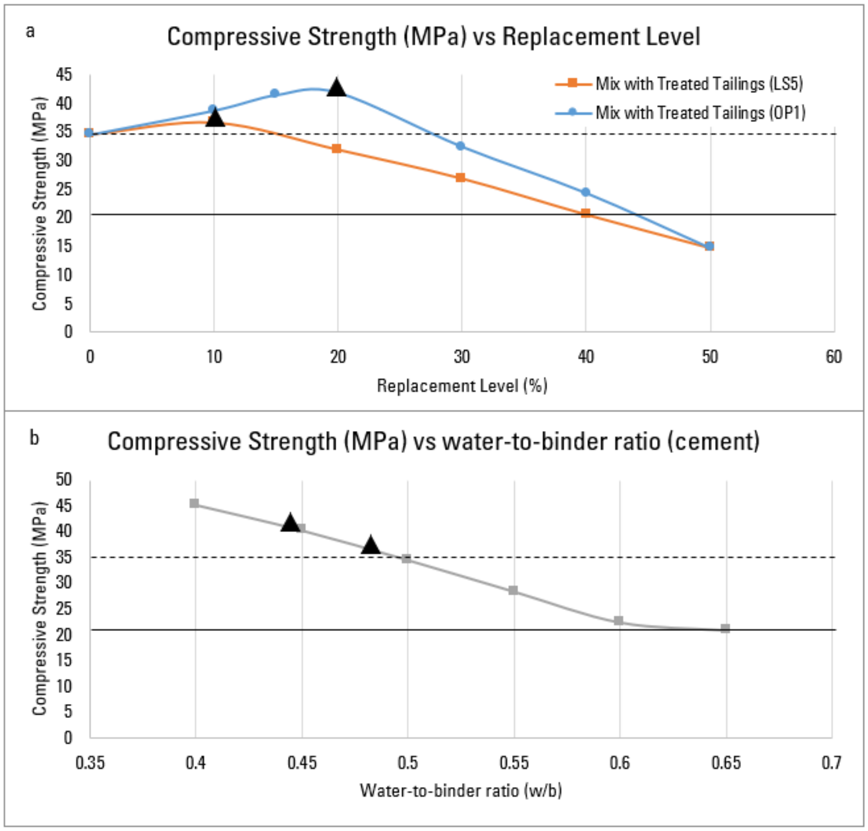

Figure 4.2 (a): Mechanical performance vs Replacement Level for mixtures with Treated Tailing at the same water-to-binder ratio. (b): Mechanical performance vs water-to-cementitious ratio for mixtures without Treated Tailing.

The changes in mechanical performance on the mixtures without TT to match mechanical performance with mixes with TT in scenarios 2 and 3, was performed by changing the amount of cement, maintaining the amount of water (changing water-to-binder ratio at a fixed water content). Table 2 shows the mixture design for each case selected for the LCA. The equivalent mechanical performance (scenario 1) mixtures consider a mechanical performance of 34 MPa, obtained at a replacement level of 27.8% for the OP1 tailing and 14.4% for the LS5 tailing.

For scenario 2, maximum mechanical performance was 41.5 and 36.6 MPa for OP1 and LS5 tailings respectively. Those strengths were obtained at a replacement level of 20% for the OP1 tailing and 10% for the LS5 tailing.

Finally, for scenario 3, the minimum allowable mechanical performance (20 MPa) is obtained at a replacement level of 43% for the OP1 tailing and 40% for the LS5 tailing.

Table 4.1 Mixture design for LCA, mechanical performance, replacement level for each concrete case (BC: base case for each scenario made with concrete without TT; OP: concrete mixture with OP1 tailing; LS: concrete mixture with LS5 tailing; number represent the mechanical performance).

	Equivalent Mechanical performance			Maximum Mechanical performance				Minimum Allowable Mechanical performance		
Quantity (kg)	BC-34	OP-34	LS-34	BC-41	OP-41	BC-37	LS-37	BC-20	OP-20	LS-20
Cement	356	257	305	420	285	378	320	261	199.7	214
Treated Tailing	0	99	51	0	71	0	36	0	156.3	142
Coarse Aggregate	958	957	957	958	994	958	966	958	915.7	958
Fine Aggregate	930	928	928	858	892	911	920	1011	966.2	919
Water	178	178	178	178	178	178	178	178	178.0	178
Water-to-binder ratio	0.50	0.50	0.50	0.42	0.50	0.47	0.50	0.68	0.50	0.50
Replacement Level (% by mass)		27.8	14.4		20.0		10.0		43.9	40.0
Mechanical Performance (MPa)	34.5	34.5	34.5	41.5	41.5	36.6	36.6	20.6	20.6	20.6

4.2.2 Inventory data

LS5 tailing was collected in Copiapo and OP1 tailing was collected in Til Til, respectively at 700 km and 100 km approximately from the city of Santiago, the main consumption point of concrete in the country. This is considered as the baseline scenario.

Primary data, based on a previous work (Vargas and Lopez, 2018), was used for the energy requirements and emissions of the production of the TT (Figure 4). In particular, the energy required to produce TT is equivalent to 0.836 kWh per kg of treated OP1 and 0.951 kWh per kg of treated LS5 tailing. Water released to the air is 0.065 kg per kg of treated OP1 and 0.069 kg per kg of treated LS5. Release of CO_2 due to decarboxylation of carbonates represents 0.014 per kg of treated OP1 and 0.044 per kg of treated LS5.

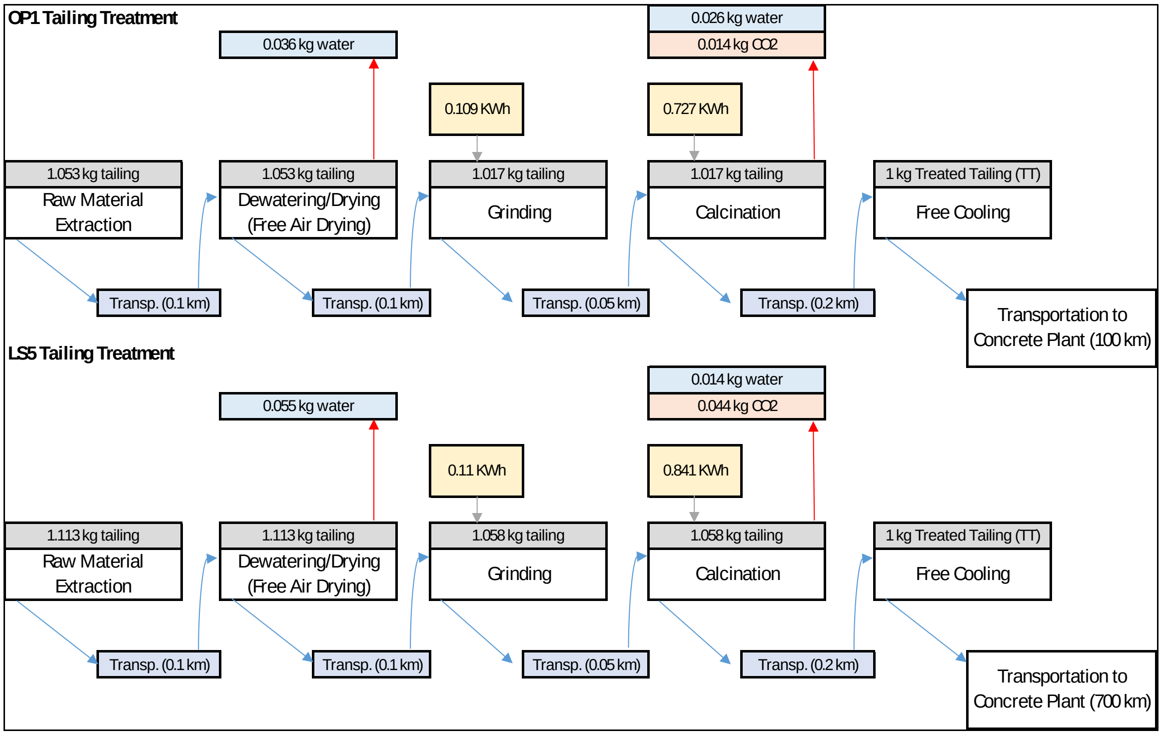

Figure 4.3 Model system for production of the treated tailings starting from OP1 and LS5 tailings, with energy requirements and emissions of water and carbon dioxide to air.

Due to the absence of a national database for Chile, data from ecoinvent 3.1 database was selected and then modified with specific chilean data. First of all, energy production matrix for Chile was used and datasets were adjusted properly (Table A.2). Then, data about energy and emissions for cement production was obtained from an ecoinvent dataset related to the United States, adjusted and complemented with information obtained from Chilean producers about distances, types of transportation, type of production and energy. The clinker considered was imported due to current trend of the market and that most of the Chilean cement industry produces blended cement (Instituto Chileno del Cemento y el Hormigón, 2018) instead of the portland cement used for this research. Data for aggregates was obtained from a global ecoinvent dataset and adjusted to production in Chile: mining and river embankment production. Changes were made on type of production, transportation distances, and energy requirements for all materials. Extraction and handling of tailing inside the plant were modelled based on information obtained from ecoinvent database, using site-specific data for limestone and calcined clay processing systems. All transportation inside the country was modelled by truck. a sensitivity analysis was made on the transportation distance of TT. A summary about the modelling of the production of the different raw materials is reported in **Table 4.2**.

Table 4.2 Information about the modelling of the production of raw materials.

Raw Material	Details	Location	Transportation distance	Source
Tailing	-	Chile	700 km (LS5); 100 km (OP1)	Site-specific data applied to existing ecoinvent datasets for limestone production and calcined clay production.
Cement	OPC CEM Type I	USA mod. Chile	100 km	ecoinvent 3 for USA, modified for Chile (based on data collected from producers)
Coarse Aggregate	Crushed rock	Global	100 km	ecoinvent 3, modified with in-situ data for Santiago, Chile
Fine Aggregate	River sand	Global	100 km	ecoinvent 3, modified with in-situ data for Santiago, Chile
Water	Tap water	Chile	N/A	ecoinvent 3

When tailing is added to a concrete mixture, the final disposal is avoided (Figure 1). The main issue with the tailing, from an environmental point of view related with the tailing final disposal, is the release of toxic elements to the environment, affecting the human health and water toxicity; and therefore, it should be considered in despite of the difficulty to model this kind of environmental impact (Beylot and Villeneuve, 2017). To accurately model the savings in the tailing final disposal (i.e., tailing dam), specific data of each tailing was considered. For this, an ecoinvent dataset was modified with specific data about concentration of leachable elements on each tailing. The dataset also considers assumptions on the behaviour for short-term and long-term leaching from the tailings based on the model by Althaus et al. (2004), which is also used in the used dataset.

4.3 Results

4.3.1 Potential environmental impacts

The results for concrete mixtures with equivalent mechanical performance; i.e., 34 MPa (scenario 1) are shown in Figure 4 (complete data on Table A.3). The use of TT shows equal or lower environmental impacts for 8 out of the 11 impact categories with stratospheric ozone depletion, fine particle matter and terrestrial acidification showing slightly higher impact values. Due to the numerous assumptions made in the study, only differences above 10% can be considered as significant. Therefore, the three impact categories where concrete with TT show higher impact values than concrete without TT can be neglected.

OP1 TT stands as the one with the lower overall impact for this scenario, with impacts ranging between 80 and 90% of those of the concrete without TT for categories such as global warming and ozone formation, while in stratospheric ozone depletion, particle matter formation or terrestrial acidification, BC-34 and OP1-34 show similar results. Consequently, the higher temperatures needed to obtain the TT from the LS5 tailing compared to OP1 tailing generates similar results for all the impact categories, but with lower environmental benefits for this scenario. The avoided disposal of both tailings generates an important benefit in the freshwater eutrophication indicator due to avoided leaching. This effect is more relevant at higher replacement level (i.e. for OP1).

The results for concrete mixtures with maximum mechanical performance (scenario 2) are shown in Figure 5 (complete data on Table A.4), where it can be seen that the environmental benefits of the use of TT are more relevant than that of scenario 1 (complete data on Table A.3), with impacts raging between 70% and 90% of those of the concrete without TT for categories such as global warming, ozone formation or particle matter formation. This better environmental performance at higher mechanical performances is due to the increase in cement dosages needed to reach the maximum strength in the case without TT (see Table 2), and cement is the most relevant material in increasing the environmental indicators. This in despite that the addition of TT is relatively low (OP1 replacement level of 20% and LS1 replacement level of 10%) to be important as contribution to the indicators.

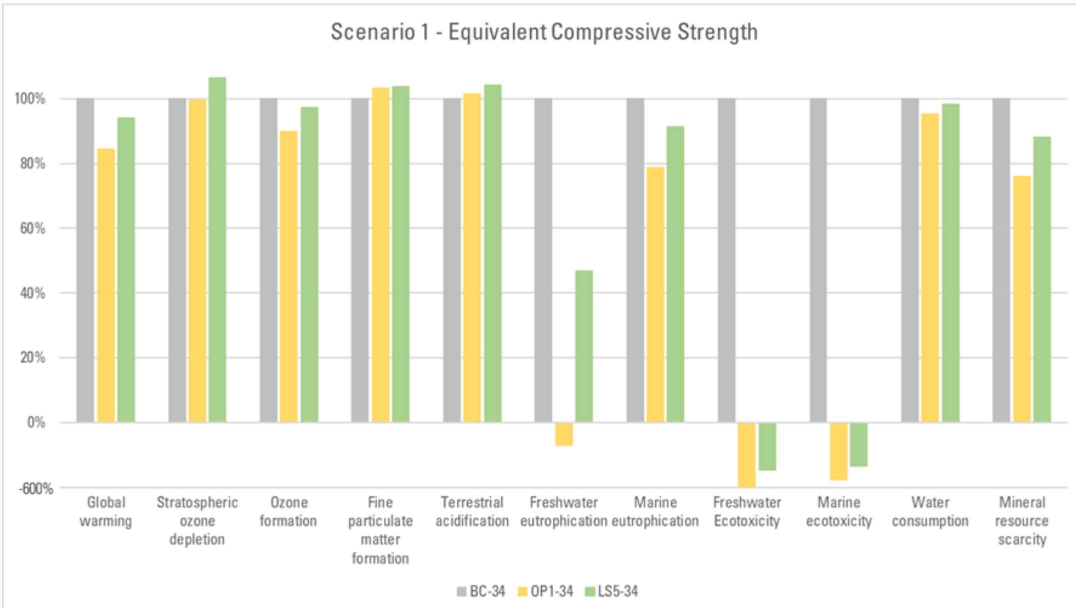

Figure 4.4 Relative comparison of the analysed mixtures (concrete mixture without TT is 100%). Scenario 1: equivalent mechanical performance.

The fact that OP1 shows better mechanical performance than LS5 (41 versus 37 MPa) means that BC-41 requires more cement than the respective BC-37 and this difference allows OP1 concrete to perform between 10% and 20% better environmentally than their LS5 counterpart when compared with the case without TT. Note that the direct comparison between tailings is not possible in scenario 2 because of their different mechanical performance level.

The use of OP1 TT shows lower environmental impacts than the counterpart without TT for all the 11 impact categories. Some relevant results are the global warming, freshwater eutrophication and marine eutrophication with values of 74, 20 and 69% of that of concrete without TT, respectively. The freshwater and marine ecotoxicity are both negative with values of -300% approximately.

Concrete with LS5 had a global warming indicator and freshwater eutrophication of 91 and 61% of that of concrete without TT. The freshwater and marine ecotoxicity are also both negative with values of -150% approximately.

The results for concrete mixtures with minimum allowable mechanical performance; (scenario 3) are shown in Figure 5 (complete data on Table A.5), where it can be seen that the environmental benefits of the use of TT are less relevant than that of scenarios 1 and 2 (complete data on Tables A.3 and A.4) with some impacts even reaching 137% of those of the concrete without TT for the terrestrial acidification impact indicator.

Impact indicators of categories such as global warming (only for the mixture with LS5 TT), stratospheric ozone depletion, ozone formation, particle matter formation, and terrestrial acidification are higher than those for a mixture without TT. Indeed, there is a decrease in the environmental performance for LS5 concrete compared with the mixture without the TT, due to higher energy requirements for the treatments and distance of transportation of tailings, which is no countered by the lower cement content of LS5-20 compared to BC-20. For the OP1 concrete, with a 43.9% replacement level, the environmental impacts of the production of TT for the mixture are higher than those associated with the saving associated with the cement production. Therefore, the use of TT implies an increase of the environmental impacts. On the contrary, the indicators for eutrophication (marine and freshwater) are much better and water consumption and mineral resource scarcity slightly better, thanks to the benefit of the avoided deposit of tailings.

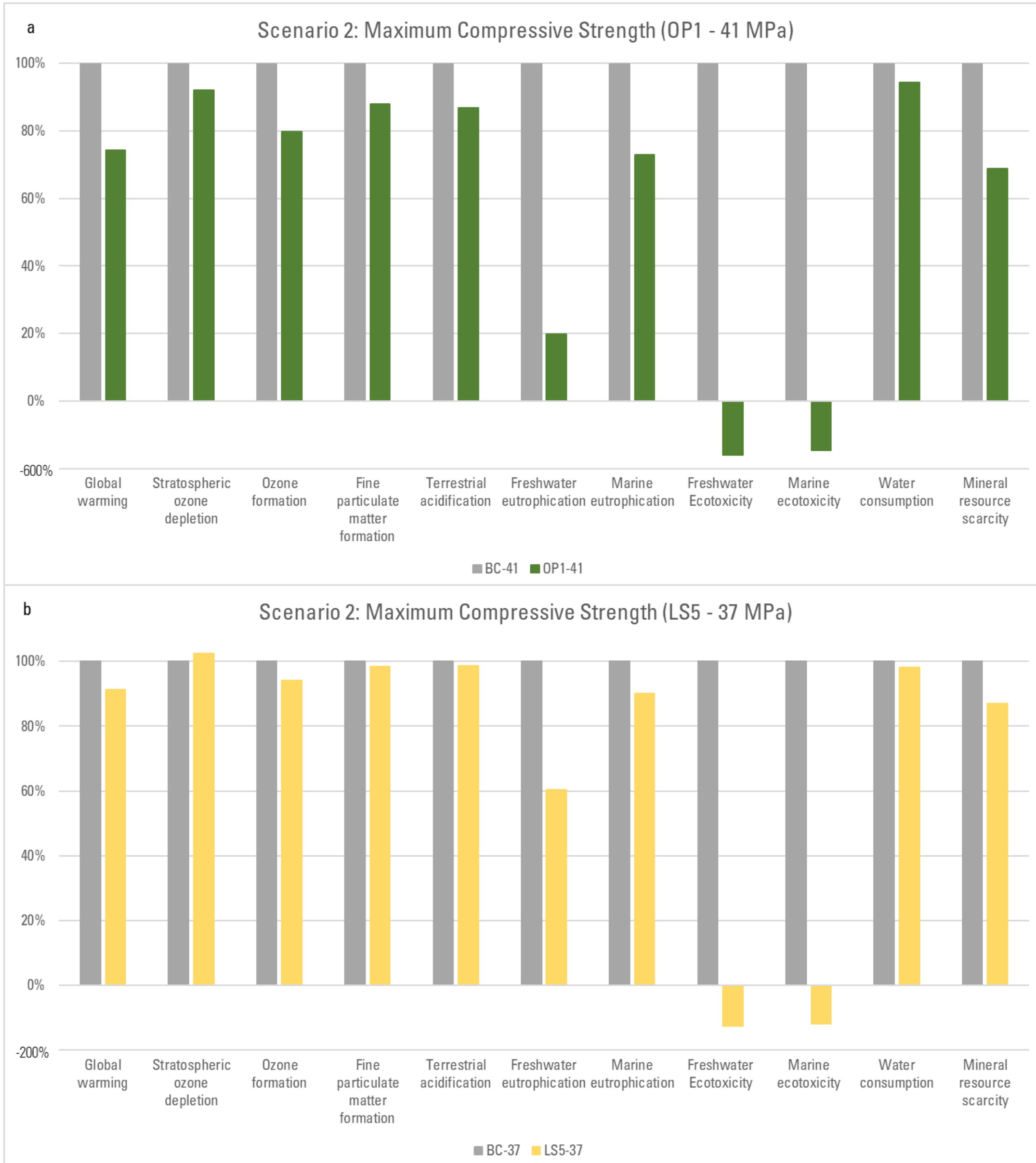

Figure 4.5 Relative comparison of the analysed mixtures (concrete mixture without treated tailing is 100%). Scenario 2: maximum mechanical strength. a. OP1 comparison with base case 41 MPa. b. LS5 comparison with base case 37 MPa.

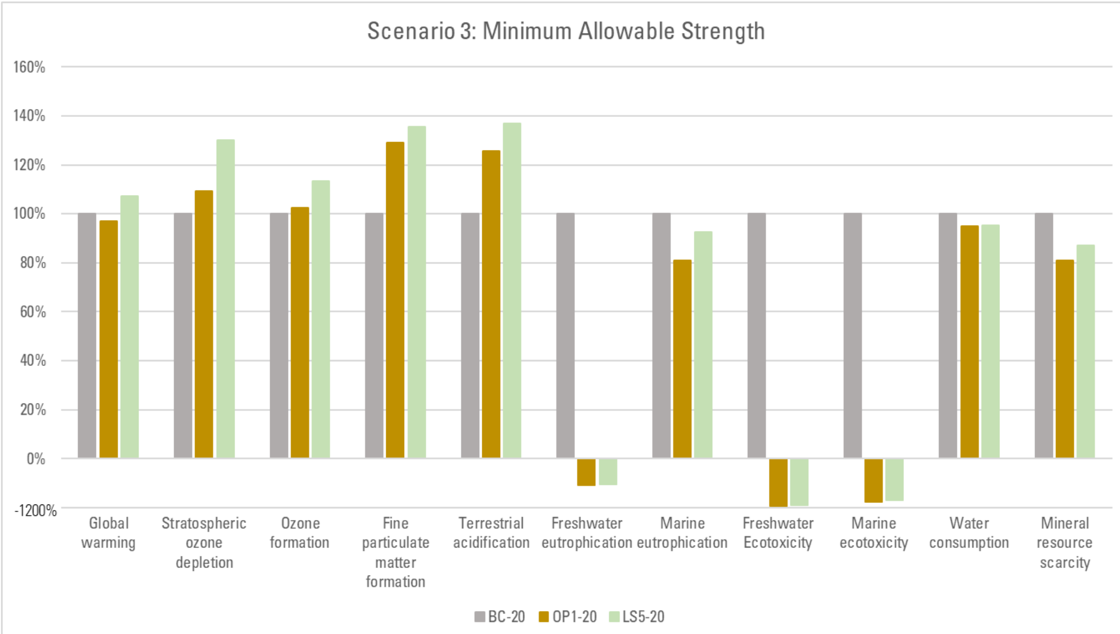

Figure 4.6 Relative comparison of the analysed mixtures (concrete mixture without TT is 100%). Scenario 3: minimum allowable compressive strength.

4.3.2 Interpretation of the results

4.3.2.1 Contribution analysis

The contribution of the processes to each indicator is shown in the following results. The main processes were cement production, treated tailing production, avoided tailing disposal, gravel production, sand production and concrete production (the last considering mixing of concrete, transportation inside plant, tap water, and other minor processes).

For the global warming impact category, Figure 7.a shows the contribution of each process to the overall indicator. The cement production possesses the most important contribution to the indicator, ranging from 61.4% on the concretes with higher replacement levels to 88% on the concretes without TT and higher mechanical performance. In the case of concretes with TT, the contribution of the production of TT rises from 4.6% on the concretes with higher mechanical performance to 21.2% on the concretes with higher replacement level, and lower mechanical performance. Concretes with OP1 TT shows lower impacts for the global warming indicator than concretes with LS5 TT; even though, the contribution of the production of TT is more important in the OP1 TT than in the LS5 TT concretes (scenario 1 for example, 9.7% OP1 TT versus 6.8% LS5 TT). This is due to the fact that mixtures with OP1 TT get higher mechanical performance at higher replacement levels, so at a specific scenario there is more tailing on each mixture.

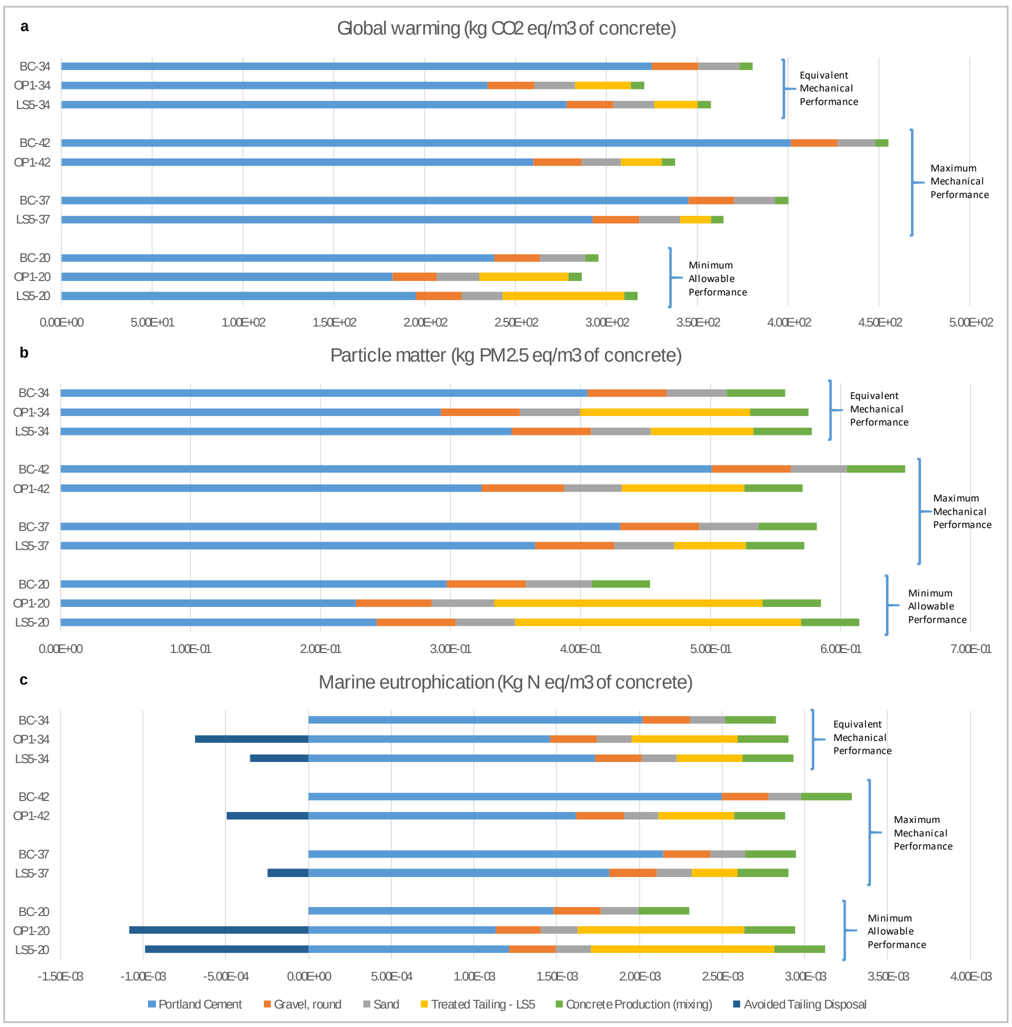

Figure 4.7 Contribution of each process to the indicator of a. Global warming impact category. b. Marine eutrophication impact category for the analysed scenarios. c. Particle formation impact category.

In the case of the Marine Eutrophication impact category (Figure 7.b), the effect of the avoided tailing disposal is relevant. The avoided tailing disposal contribution represents 23.4% for OP1 concrete and 12% of the LS5 concrete with equivalent mechanical performance. Contribution of TT production to the indicator rises from 8.4% of mixtures with higher mechanical performance (scenario 2, LS5) to 31.4% for concretes with LS5 TT in scenario 3. The same trend can be seen for concretes with OP1 (17% in scenario 2 to 36.5% in scenario 3). In this impact category, cement production contribution is countered by the effect of the avoided tailing disposal.

The particle matter formation impact category shows equal or lower environmental performance of concretes with TT compared with those without TT. This is due to the proposed processes for the TT extraction and handling. Figure 7.c shows that the higher the amount of tailings used in the mixture (i.e., an increase in the replacement level) the worse the indicator, rising from 9.6% for LS5-37 concrete to 35.7% for LS5-20. This effect is countered by the increase in the use of cement into the mixtures with higher mechanical performance. Nevertheless, this could be avoided by the use of less invasive extraction techniques of the tailings or by the collection of the tailing while they are being generated before reaching the tailing dam.

4.3.2.2 Sensitivity analysis

It is important to understand and quantify the contribution of the avoided deposit on the results. Table 3 shows the change in the indicators affected by the exclusion of the avoided tailing disposal in the analysis.

Table 4.3 Percentage change of the indicator of some impact categories compared with Base Case for each scenario and mixture, with or without the inclusion of the avoided tailing disposal.

		Impact category							
		Freshwater eutrophication		Marine eutrophication		Freshwater ecotoxicity		Marine ecotoxicity	
1 m3 of concrete	Type of Mix	With Avoided Tailing Disposal	Without Avoided Tailing Disposal	With Avoided Tailing Disposal	Without Avoided Tailing Disposal	With Avoided Tailing Disposal	Without Avoided Tailing Disposal	With Avoided Tailing Disposal	Without Avoided Tailing Disposal
Equivalent Mechanical Performance	OP1-34	-7%	103%	79%	103%	-590%	98%	-462%	98%
	LS5-34	47%	104%	91%	104%	-273%	102%	-202%	102%
Maximum Mechanical Performance	OP1-41	20%	88%	73%	88%	-355%	88%	-274%	89%
	LS5-37	60%	98%	90%	98%	-155%	98%	-107%	99%
Minimum Allowable Mechanical Performance	OP1-20	-85%	129%	81%	127%	-1137%	111%	-898%	110%
	LS5-20	-59%	136%	93%	135%	-1078%	121%	-845%	122%

The percentage is shown as comparison with the base case (concrete without TT). It can be stated that the exclusion of the avoided tailing disposal generates an important effect on each category decreasing the environmental performance importantly. This is clearly shown by the freshwater eutrophication, marine eutrophication, freshwater ecotoxicity and marine ecotoxicity indicators, where they show equal values than those of concretes without TT when excluding the avoided tailing disposal for scenarios 1 and 2 and as media 30% higher for scenario 3.

Concerning the sensitivity analysis about the transport distances, changes in the distance of consumption of the TT do not show an important influence, mainly due to the relatively high energy requirements of the processing of tailing. Figure 11 shows the relative increase on each indicator for four relevant impact categories when adding 100 km of transportation to the baseline considered in the analysis. It can be seen that transportation has an impact of less than 3.5% in all impact categories, also due to the low levels of use of each TT (156 kg as maximum, approx. 0.05 m3) compared with the total volume of materials for each mixture.

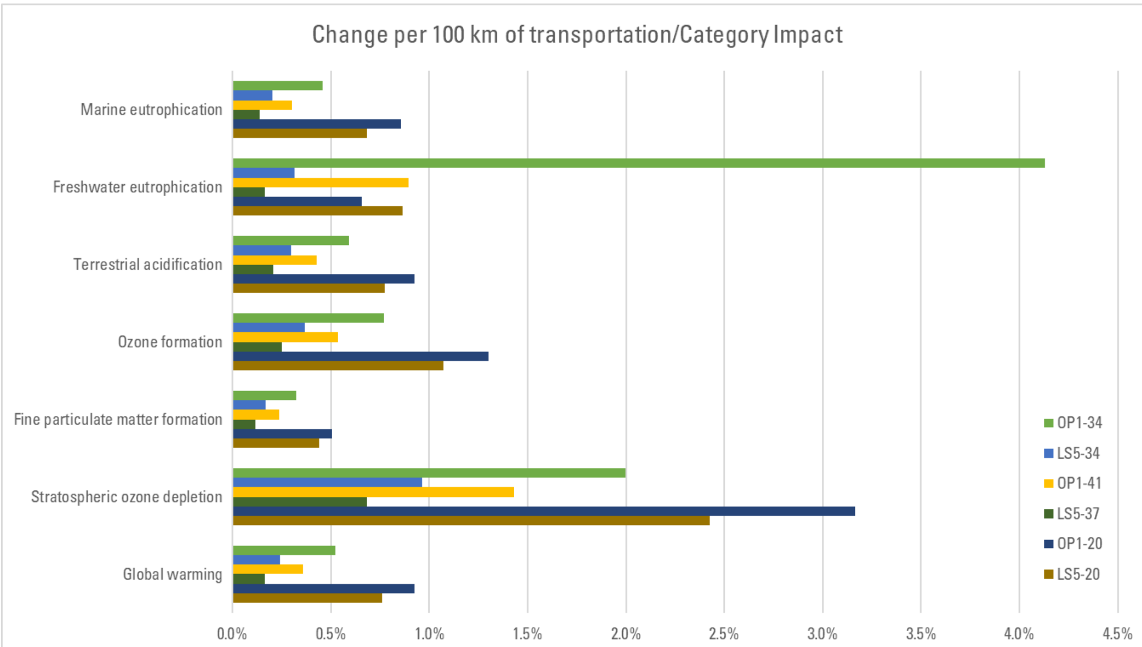

Figure 4.8 Percentage increase on each indicator per 100 km of transportation of TT added to the system on four selected impact category indicators.

4.4 Conclusions and future work

In the present study, concrete mixtures including two treated tailings from Chile used as SCM were compared, from an environmental point of view, to concrete mixtures without TT at the same performance level. All performances were measured as mechanical performance. Three different scenarios were considered: equivalent compressive strength, maximum mechanical performance and minimum allowable mechanical performance.

Results show that the environmental indicators are dependent on the characteristics of each tailing. Nevertheless, some general conclusions can be driven. At higher mechanical performance, the concretes with TT show better environmental indicators than those without TT. As the mechanical performance decreases, the environmental benefits of the use of TT decrease or disappear showing a consistent reduction in the environmental performance of the concrete with TT. This is due to the relatively low amount of cement that is necessary to obtain the same mechanical performance al low strength levels. Moreover, due to a higher performance level and a lower distance of transportation, OP1 appears as the most attractive tailing to work for as SCM.

From the results obtained in this LCA study, it can be stated that:

- The use of treated tailings as replacement of cement in concrete mixtures can be a promissory way to reduce the use of cement and reduce the impact of the deposit of tailings. Nevertheless, studies need to be carried out to analyse and determine what would be the best use and replacement level of those tailings to improve mechanical and environmental performance.

- It is not evident whether a tailing will produce an environmental benefit by its use as replacement of cement or not. Calculations on the effect of the treatment of tailings and the performance of the mixtures are relevant. Also, the performances are not linear, so it is not simple to translate mechanical performance into environmental performance for this type of material.

- Related with the previous, the analysis shows that cement is the most important contributor to impact indicators of each concrete, but this is relative to the impact itself and the way the SCM is considered into the model. Considering only cement content can give erroneous conclusions.

- The environmental benefits of the inclusion of TT decreases as the replacement level of cement by TT increases. This can make concrete with TT to show equal or worst environmental performance than concretes without TT. Nevertheless, it is shown that using energy and processes to improve the mechanical performance of an SCM (thus, increasing the environmental impact of a concrete mix with SCM) can benefit the environmental comparison when is made with a concrete mix without SCM at the same mechanical performance.

- The inclusion of the contribution related to the avoided disposal of tailings improves the environmental indicators related with the release of elements to water. If this contribution is not considered, mixtures with TT can show similar or even poorer results than concretes without TT.

Conclusions are valid under the following limitations of the LCA carried out in this study:

- The data used for the modelling of the treatments were primary data acquired at a laboratory level. Upscaling the processes could allow to reduce the environmental impact of the treatments of the tailings.

- Due to lack of information for the Chilean context, processes were modelled based on foreign models that were modified to the Chilean context.

Studies on new SCMs need to consider the environmental performance to fully assess the benefits from the replacement of cement. Many new potential cementitious materials need treatments or new processes to be fully functional SCMs, and even allocation for materials considered as by-products would affect the environmental indicators of concrete mixtures, changing the perception of the benefits of replacing cement.

In this study a new methodology of comparing performance has been proposed to decide whether a mixture with an SCM is environmentally better than a mixture without SCM. This new methodology allows for direct comparisons for mixtures with SCM for specific levels of performance; and this can be a powerful tool to decide the optimum level of replacement and performance for a specific SCM on a green concrete mixture. This is especially useful for SCMs that need an additional processing and also for materials with low performance level as cement replacement, but that can function well where a low mechanical performance level is required or where durability is not an issue (as occurs in temporally structures). Other performances variables should be included in future works such as durability, workability and rheological properties.

4.5 Acknowledgments

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4.6 References

Adjoudj, M., Ezziane, K., Kadri, E. H., Ngo, T.-T., & Kaci, A. (2014). Evaluation of rheological parameters of mortar containing various amounts of mineral addition with polycarboxylate superplasticizer. *Construction and Building Materials*, *70*, 549–559. https://doi.org/10.1016/j.conbuildmat.2014.07.111

Ahmari, S., & Zhang, L. (2012). Production of eco-friendly bricks from copper mine tailings through geopolymerization. *Construction and Building Materials*, *29*, 323–331. https://doi.org/10.1016/j.conbuildmat.2011.10.048

Aïtcin, P.-C. (2016). Supplementary cementitious materials and blended cements. In *Science and Technology of Concrete Admixtures*. https://doi.org/10.1016/B978-0-08-100693-1.00004-7

Antiohos, S., & Tsimas, S. (2004). Activation of fly ash cementitious systems in the presence of quicklime. *Cement and Concrete Research*, *34*(5), 769–779. https://doi.org/10.1016/j.cemconres.2003.08.008

Apodaca, L. E. (2016). Mineral Commodity Summaries. In *Mineral Commodity Summaries* (Vol. 1). https://doi.org/http://dx.doi.org/10.3133/70140094.

Argane, R., Benzaazoua, M., Hakkou, R., & Bouamrane, A. (2015). Reuse of base-metal tailings as aggregates for rendering mortars: Assessment of immobilization performances and environmental behavior. *Construction and Building Materials*, *96*, 296–306. https://doi.org/10.1016/j.conbuildmat.2015.08.029

Avet, F., Snellings, R., Alujas Diaz, A., Ben Haha, M., & 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. https://doi.org/10.1016/j.cemconres.2016.02.015

Bentz, D. P., Jones, S. Z., & Snyder, K. A. (2015). Design and performance of ternary blend high-volume fly ash concretes of moderate slump. *Construction and Building Materials*, *84*, 409–415. https://doi.org/10.1016/j.conbuildmat.2015.03.082

Bentz, D. P., Sato, T., de la Varga, I., & Weiss, W. J. (2012). Fine limestone additions to regulate setting in high volume fly ash mixtures. *Cement and Concrete Composites*, *34*(1), 11–17. https://doi.org/10.1016/j.cemconcomp.2011.09.004

Bui, P. T., Ogawa, Y., Nakarai, K., & Kawai, K. (2015). A study on pozzolanic reaction of fly ash cement paste activated by an injection of alkali solution. *Construction and Building Materials*, *94*, 28–34. https://doi.org/10.1016/j.conbuildmat.2015.06.046

Burgos, D. M., Cardona, L. M., & Delvasto, S. (2014). Estudio de dos materiales volcánicos y efecto del tipo de molienda en su reactividad. *Revista Ingeniería de Construcción*, *29*(2), 159–174. https://doi.org/10.4067/S0718-50732014000200003

Burris, L. E., & Juenger, M. C. G. (2016). Milling as a pretreatment method for increasing the reactivity of natural zeolites for use as Supplementary cementitious materials. *Cement and Concrete Composites*, *65*, 163–170. https://doi.org/10.1016/j.cemconcomp.2015.09.008

Cao, Z., Cao, Y., Dong, H., Zhang, J., & Sun, C. (2016). Effect of calcination condition on the microstructure and pozzolanic activity of calcined coal gangue. *International Journal of Mineral Processing*, *146*, 23–28. https://doi.org/10.1016/j.minpro.2015.11.008

Carkovic, A. B., Calcagni, M. S., Vega, A. S., Coquery, M., Moya, P. M., Bonilla, C. A., & Pastén, P. A. (2016). Active and legacy mining in an arid urban environment: challenges and perspectives for Copiapó, Northern Chile. *Environmental Geochemistry and Health*, *38*(4), 1001–1014. https://doi.org/10.1007/s10653-016-9793-5

Celik, K., Meral, C., Petek Gursel, A., Mehta, P. K., Horvath, A., & Monteiro, P. J. M. (2015). Mechanical properties, durability, and life-cycle assessment of self-consolidating concrete mixtures made with blended portland cements containing fly ash and limestone powder. *Cement and Concrete Composites*, *56*, 59–72. https://doi.org/10.1016/j.cemconcomp.2014.11.003

EN 206 Concrete - Specification, performance, production and conformity, (2013) (testimony of CEN).

Chen, C., Habert, G., Bouzidi, Y., Jullien, A., & Ventura, A. (2010). LCA allocation procedure used as an incitative method for waste recycling: An application to mineral additions in concrete. *Resources, Conservation and Recycling*, *54*(12), 1231–1240. https://doi.org/10.1016/J.RESCONREC.2010.04.001

Choi, Y. W., Kim, Y. J., Choi, O., Lee, K. M., & Lachemi, M. (2009). Utilization of tailings from tungsten mine waste as a substitution material for cement. *Construction and Building Materials*, *23*(7), 2481–2486. https://doi.org/10.1016/j.conbuildmat.2009.02.006

CNE. (2019). *Generación Bruta SEN - Comision Nacional de Energia Chile*. https://www.cne.cl/estadisticas/electricidad/

Damineli, B. L., Kemeid, F. M., Aguiar, P. S., & John, V. M. (2010). Measuring the eco-efficiency of cement use. *Cement and Concrete Composites*, *32*(8), 555–562. https://doi.org/10.1016/J.CEMCONCOMP.2010.07.009

Davenport, W. G., King, M., Schlesinger, M., & Biswas, A. K. (2002). Overview. *Extractive Metallurgy of Copper*, 1–16. https://doi.org/10.1016/B978-008044029-3/50004-6

De Schepper, M., Van den Heede, P., Van Driessche, I., & De Belie, N. (2014). Life Cycle Assessment of Completely Recyclable Concrete. *Materials*, *7*(8), 6010–6027. https://doi.org/10.3390/ma7086010

Deng, Y., Zhang, C., & Wei, X. (2014). Influence of lithium sulfate addition on the properties of Portland cement paste. *Construction and Building Materials*, *50*, 457–462. https://doi.org/10.1016/j.conbuildmat.2013.09.058

Di Maria, A., Salman, M., Dubois, M., & Van Acker, K. (2018). Life cycle assessment to evaluate the environmental performance of new construction material from stainless steel slag. *The International Journal of Life Cycle Assessment*, *23*(11), 2091–2109. https://doi.org/10.1007/s11367-018-1440-1

Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, I. (2010). Effect of natural pozzolans as mineral admixture on the performance of cemented-paste backfill of sulphide-rich tailings. *Waste Management & Research : The Journal of the International Solid Wastes and Public Cleansing Association, ISWA*, *28*(5), 430–435. https://doi.org/10.1177/0734242X09351905

Erniati, Tjaronge, M. W., Zulharnah, & Irfan, U. R. (2015). Porosity, pore size and compressive strength of self compacting concrete using sea water. *Procedia Engineering*, *125*, 832–837. https://doi.org/10.1016/j.proeng.2015.11.045

Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC, (2006) (testimony of European Parlament and Council).

Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives, 312 Official Journal of the European Union (2008).

Fan, C., & Miller, S. A. (2018). Reducing greenhouse gas emissions for prescribed concrete compressive strength. *Construction and Building Materials*, *167*, 918–928. https://doi.org/10.1016/J.CONBUILDMAT.2018.02.092

Fuentes, M., Zúñiga, A., Díaz, M., Rocha, E., & Díaz, S. (2014). Molienda mecánica por alta energía de minerales mexicanos para producir concreto de alto desempeño (CAD). *Revista Ingeniería de Construcción*, *29*(3), 256–269. https://doi.org/10.4067/S0718-50732014000300003

Grist, E. R., Paine, K. A., Heath, A., Norman, J., & Pinder, H. (2013). Compressive strength development of binary and ternary lime–pozzolan mortars. *Materials & Design*, *52*, 514–523. https://doi.org/10.1016/j.matdes.2013.05.006

Guo, B., Liu, B., Yang, J., & Zhang, S. (2017). The mechanisms of heavy metal immobilization by cementitious material treatments and thermal treatments: A review. *Journal of Environmental Management*, *193*, 410–422. https://doi.org/10.1016/J.JENVMAN.2017.02.026

Gursel, A. P., Maryman, H., & Ostertag, C. (2016). A life-cycle approach to environmental, mechanical, and durability properties of “green” concrete mixes with rice husk ash. *Journal of Cleaner Production*, *112*, 823–836. https://doi.org/10.1016/j.jclepro.2015.06.029

Habeeb, G. A., & Mahmud, H. Bin. (2010). Study on properties of rice husk ash and its use as cement replacement material. *Materials Research*, *13*(2), 185–190. https://doi.org/10.1590/S1516-14392010000200011

Hamidi, M., Kacimi, L., Cyr, M., & Clastres, P. (2013). Evaluation and improvement of pozzolanic activity of andesite for its use in eco-efficient cement. *Construction and Building Materials*, *47*, 1268–1277. https://doi.org/10.1016/j.conbuildmat.2013.06.013

Hossain, M. M., Karim, M. R., Hossain, M. K., Islam, M. N., & Zain, M. F. M. (2015). Durability of mortar and concrete containing alkali-activated binder with pozzolans: A review. *Construction and Building Materials*, *93*, 95–109. https://doi.org/10.1016/j.conbuildmat.2015.05.094

Huang, X. Q., Hou, H. B., Zhou, M., & Wang, W. X. (2014). Mechanical Properties and Microstructure Analysis of Copper Tailings Solidifying with Different Cementitious Materials. *Advanced Materials Research*, *878*, 171–176. https://doi.org/10.4028/www.scientific.net/AMR.878.171

Ilić, B., Radonjanin, V., Malešev, M., Zdujić, M., & Mitrović, A. (2016). Effects of mechanical and thermal activation on pozzolanic activity of kaolin containing mica. *Applied Clay Science*, *123*, 173–181. https://doi.org/10.1016/j.clay.2016.01.029

NCh170.Of2016 - Hormigón - Requisitos generales, (2016) (testimony of INN).

Jain, N. (2012). Effect of nonpozzolanic and pozzolanic mineral admixtures on the hydration behavior of ordinary Portland cement. *Construction and Building Materials*, *27*(1), 39–44. https://doi.org/10.1016/j.conbuildmat.2011.08.006

Juenger, M. C. G., & Siddique, R. (2015). Recent advances in understanding the role of Supplementary cementitious materials in concrete. *Cement and Concrete Research*, *78*, 71–80. https://doi.org/10.1016/j.cemconres.2015.03.018

Juenger, M. C. G., Snellings, R., & Bernal, S. A. (2019). Supplementary cementitious materials: New sources, characterization, and performance insights. *Cement and Concrete Research*, *122*, 257–273.

https://doi.org/10.1016/J.CEMCONRES.2019.05.008

Khodabakhshian, A., de Brito, J., Ghalehnovi, M., & Asadi Shamsabadi, E. (2018). Mechanical, environmental and economic performance of structural concrete containing silica fume and marble industry waste powder. *Construction and Building Materials*, *169*, 237–251. https://doi.org/10.1016/J.CONBUILDMAT.2018.02.192

Klopffer, W., & Grahl, B. (2015). *Life Cycle Assessment: A guide to best practise (chapter 1-3)* (Issue 1995). https://doi.org/10.1016/B978-0-12-801595-7.00013-6

Küçükyıldırım, E., & Uzal, B. (2014). Characteristics of calcined natural zeolites for use in high-performance pozzolan blended cements. *Construction and Building Materials*, *73*, 229–234. https://doi.org/10.1016/j.conbuildmat.2014.09.081

Kurda, R., Silvestre, J. D., & de Brito, J. (2018). Life cycle assessment of concrete made with high volume of recycled concrete aggregates and fly ash. *Resources, Conservation and Recycling*, *139*(April 2018), 407–417. https://doi.org/10.1016/j.resconrec.2018.07.004

Lee, K.-M., & Park, P.-J. (2005). Estimation of the environmental credit for the recycling of granulated blast furnace slag based on LCA. *Resources, Conservation and Recycling*, *44*(2), 139–151. https://doi.org/10.1016/J.RESCONREC.2004.11.004

Li, J., Zhang, W., Li, C., & Monteiro, P. J. M. (2019). Green concrete containing diatomaceous earth and limestone: Workability, mechanical properties, and life-cycle assessment. *Journal of Cleaner Production*, *223*, 662–679. https://doi.org/10.1016/j.jclepro.2019.03.077

Lothenbach, B., Scrivener, K., & Hooton, R. D. (2011). Supplementary cementitious materials. *Cement and Concrete Research*, *41*(12), 1244–1256. https://doi.org/10.1016/j.cemconres.2010.12.001

Ludwig, H.-M., & Zhang, W. (2015). Research review of cement clinker chemistry. *Cement and Concrete Research*. https://doi.org/10.1016/j.cemconres.2015.05.018

Ma, X.-W., Chen, H.-X., & Wang, P.-M. (2010). Effect of CuO on the formation of clinker minerals and the hydration properties. *Cement and Concrete Research*, *40*(12), 1681–1687. https://doi.org/10.1016/j.cemconres.2010.08.009

Masi, G., Rickard, W. D. A., Vickers, L., Bignozzi, M. C., & van Riessen, A. (2014). A comparison between different foaming methods for the synthesis of light weight geopolymers. *Ceramics International*, *40*(9), 13891–13902. https://doi.org/10.1016/j.ceramint.2014.05.108

Matos, P. R. de, Foiato, M., & Prudêncio, L. R. (2019). Ecological, fresh state and long-term mechanical properties of high-volume fly ash high-performance self-compacting concrete. *Construction and Building Materials*, *203*, 282–293. https://doi.org/10.1016/J.CONBUILDMAT.2019.01.074

Mehta, P. K., & Monteiro, P. J. M. (2014). *Concrete: Microstructure, Properties, and Materials, Fourth Edition* (4th Editio). McGraw-Hill Education: New York, Chicago, San Francisco, Athens, London, Madrid, Mexico City, Milan, New Delhi, Singapore, Sydney, Toronto.

Miller, S. A. (2018). Supplementary cementitious materials to mitigate greenhouse gas emissions from concrete: can there be too much of a good thing? *Journal of Cleaner Production*, *178*, 587–598. https://doi.org/10.1016/j.jclepro.2018.01.008

Montgomery, D. C. (2017). Design and Analysis of Experiments. In *Design* (Vol. 2). https://doi.org/10.1198/tech.2006.s372

Moretti, L., & Caro, S. (2017). Critical analysis of the Life Cycle Assessment of the Italian cement industry. *Journal of Cleaner Production*, *152*, 198–210. https://doi.org/10.1016/J.JCLEPRO.2017.03.136

Moya, P. M., Arce, G. J., Leiva, C., Vega, A. S., Gutiérrez, S., Adaros, H., Muñoz, L., Pastén, P. A., & Cortés, S. (2019). An integrated study of health, environmental and socioeconomic indicators in a mining-impacted community exposed to metal enrichment. *Environmental Geochemistry and Health*. https://doi.org/10.1007/s10653-019-00308-4

Nakic, D. (2018). Environmental evaluation of concrete with sewage sludge ash based on LCA. *Sustainable Production and Consumption*, *16*, 193–201. https://doi.org/10.1016/J.SPC.2018.08.003

Oliva, M., Vargas, F., & Lopez, M. (2019). Designing the incineration process for improving the cementitious performance of sewage sludge ash in Portland and blended cement systems. *Journal of Cleaner Production*, *223*, 1029–1041. https://doi.org/10.1016/J.JCLEPRO.2019.03.147

Onuaguluchi, O., & Eren, O. (2013a). Rheology, strength and durability properties of mortars containing copper tailings as a cement replacement material. *EUROPEAN JOURNAL OF ENVIRONMENTAL AND CIVIL ENGINEERING*, *17*(1), 19–31. https://doi.org/10.1080/19648189.2012.699708

Onuaguluchi, O., & Eren, Ö. (2012). Cement mixtures containing copper tailings as an additive: durability properties. *Materials Research*, *15*(6), 1029–1036. https://doi.org/10.1590/S1516-14392012005000129

Onuaguluchi, O., & Eren, Ö. (2013b). Rheology, strength and durability properties of mortars containing copper tailings as a cement replacement material. *European Journal of Environmental and Civil Engineering*, *17*(1), 19–31. https://doi.org/10.1080/19648189.2012.699708

Onuaguluchi, O., & Eren, Ö. (2015). Reusing copper tailings in concrete: corrosion performance and socioeconomic implications for the Lefke-Xeros area of Cyprus. *Journal of Cleaner Production*. https://doi.org/10.1016/j.jclepro.2015.09.036

Panesar, D. K., Seto, K. E., & Churchill, C. J. (2017). Impact of the selection of functional unit on the life cycle assessment of green concrete. *International Journal of Life Cycle Assessment*, *22*(12), 1969–1986. https://doi.org/10.1007/s11367-017-1284-0

Peng, K., Yang, H., & Ouyang, J. (2015). Tungsten tailing powders activated for use as cementitious material. *Powder Technology*, *286*, 678–683. https://doi.org/10.1016/j.powtec.2015.09.012

Petek Gursel, A., Masanet, E., Horvath, A., & Stadel, A. (2014). Life-cycle inventory analysis of concrete production: A critical review. *Cement and Concrete Composites*, *51*, 38–48. https://doi.org/10.1016/j.cemconcomp.2014.03.005

Ramezanianpour, A. A. (2014). Cement Replacement Materials; Properties, Durability, Sustainability. In *Springer Geochemistry/Mineralogy* (Vol. 7). https://doi.org/10.1007/978-3-642-36721-2

Ramezanianpour, A. M., Esmaeili, K., Ghahari, S. A., & Ramezanianpour, A. A. (2014). Influence of initial steam curing and different types of mineral additives on mechanical and durability properties of self-compacting concrete. *Construction and Building Materials*, *73*, 187–194. https://doi.org/10.1016/j.conbuildmat.2014.09.072

Robayo-Salazar, R., Mejía-Arcila, J., Mejía de Gutiérrez, R., & Martínez, E. (2018). Life cycle assessment (LCA) of an alkali-activated binary concrete based on natural volcanic pozzolan: A comparative analysis to OPC concrete. *Construction and Building Materials*, *176*, 103–111. https://doi.org/10.1016/j.conbuildmat.2018.05.017

Rossen, J. E., Lothenbach, B., & Scrivener, K. L. (2015). Composition of C–S–H in pastes with increasing levels of silica fume addition. *Cement and Concrete Research*, *75*, 14–22. https://doi.org/10.1016/j.cemconres.2015.04.016

Saade, M. R. M., Passer, A., & Mittermayr, F. (2019). (Sprayed) concrete production in life cycle assessments: a systematic literature review. *The International Journal of Life Cycle Assessment*. https://doi.org/10.1007/s11367-019-01676-w

Sagastume Gutiérrez, A., Cabello Eras, J. J., Gaviria, C. A., Van Caneghem, J., & Vandecasteele, C. (2017). Improved selection of the functional unit in environmental impact assessment of cement. *Journal of Cleaner Production*, *168*, 463–473. https://doi.org/10.1016/J.JCLEPRO.2017.09.007

Sant, G., Kumar, A., Patapy, C., Le Saout, G., & Scrivener, K. (2012). The influence of sodium and potassium hydroxide on volume changes in cementitious materials. *Cement and Concrete Research*, *42*(11), 1447–1455. https://doi.org/10.1016/J.CEMCONRES.2012.08.012

Schlesinger, M., King, M., Sole, K., & Davenport, W. (2011). Extractive Metallurgy of Copper. In *Extractive Metallurgy of Copper*. Elsevier Ltd. https://doi.org/10.1016/C2010-0-64841-3

Schneider, M., Romer, M., Tschudin, M., & Bolio, H. (2011). Sustainable cement production—present and future. *Cement and Concrete Research*, *41*(7), 642–650. https://doi.org/10.1016/j.cemconres.2011.03.019

Schöler, A., Lothenbach, B., Winnefeld, F., & Zajac, M. (2015). Hydration of quaternary Portland cement blends containing blast-furnace slag, siliceous fly ash and limestone powder. *Cement and Concrete Composites*, *55*, 374–382. https://doi.org/10.1016/j.cemconcomp.2014.10.001

Seraj, S., Ferron, R. D., & Juenger, M. C. G. (2016). Calcining natural zeolites to improve their effect on cementitious mixture workability. *Cement and Concrete Research*, *85*, 102–110. https://doi.org/10.1016/j.cemconres.2016.04.002

SERNAGEOMIN. (2019a). *Anuario de la minerìa de Chile 2018*. https://doi.org/https://www.sernageomin.cl/wp-content/uploads/2019/06/Libro_Anuario_2018_.pdf

SERNAGEOMIN. (2019b). *Catastro de Depositos de Relaves en Chile*. https://www.sernageomin.cl/datos-publicos-deposito-de-relaves/

Seto, K. E., Churchill, C. J., & Panesar, D. K. (2017). Influence of fly ash allocation approaches on the life cycle assessment of cement-based materials. *Journal of Cleaner Production*, *157*, 65–75. https://doi.org/10.1016/J.JCLEPRO.2017.04.093

Shi, C., Meyer, C., & Behnood, A. (2008). Utilization of copper slag in cement and concrete. *Resources, Conservation and Recycling*, *52*(10), 1115–1120. https://doi.org/10.1016/j.resconrec.2008.06.008

Smuda, J., Dold, B., Spangenberg, J. E., Friese, K., Kobek, M. R., Bustos, C. A., & Pfeifer, H.-R. (2014). Element cycling during the transition from alkaline to acidic environment in an active porphyry copper tailings impoundment, Chuquicamata, Chile. *Journal of Geochemical Exploration*, *140*, 23–40. https://doi.org/10.1016/j.gexplo.2014.01.013

Smuda, J., Dold, B., Spangenberg, J. E., & Pfeifer, H.-R. (2008). Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: Implications on sources and mobility of elements during transport and early stages of deposition. *Chemical Geology*, *256*(1), 62–76. https://doi.org/10.1016/j.chemgeo.2008.08.001

Snellings, R., & Scrivener, K. L. (2015). Rapid screening tests for Supplementary cementitious materials: past and future. *Materials and Structures*, *49*(8), 1–15. https://doi.org/10.1617/s11527-015-0718-z

Souri, A., Kazemi-Kamyab, H., Snellings, R., Naghizadeh, R., Golestani-Fard, F., & Scrivener, K. (2015). Pozzolanic activity of mechanochemically and thermally activated kaolins in cement. *Cement and Concrete Research*, *77*, 47–59. https://doi.org/10.1016/j.cemconres.2015.04.017

Taylor-Lange, S. C., Lamon, E. L., Riding, K. A., & Juenger, M. C. G. (2015). Calcined kaolinite–bentonite clay blends as Supplementary cementitious materials. *Applied Clay Science*, *108*, 84–93. https://doi.org/10.1016/j.clay.2015.01.025

Taylor, H. F. W. (1997). Cement chemistry. In *Cement chemistry*. Thomas Telford Publishing. https://doi.org/10.1680/cc.25929

Teklay, A., Yin, C., Rosendahl, L., & Bøjer, M. (2014). Calcination of kaolinite clay particles for cement production: A modeling study. *Cement and Concrete Research*, *61–62*, 11–19. https://doi.org/10.1016/j.cemconres.2014.04.002

Thomas, B. S., Damare, A., & Gupta, R. C. (2013a). Strength and durability characteristics of copper tailing concrete. *Construction and Building Materials*, *48*, 894–900. https://doi.org/10.1016/j.conbuildmat.2013.07.075

Thomas, B. S., Damare, A., & Gupta, R. C. (2013b). Strength and durability characteristics of copper tailing concrete. *Construction and Building Materials*, *48*, 894–900. https://doi.org/10.1016/j.conbuildmat.2013.07.075

Thomas, M. (2013). *Supplementary Cementing Materials in Concrete*. CRC Press.

Tironi, A., Trezza, M. A., Scian, A. N., & Irassar, E. F. (2013). Assessment of pozzolanic activity of different calcined clays. *Cement and Concrete Composites*, *37*, 319–327. https://doi.org/10.1016/j.cemconcomp.2013.01.002

Turk, J., Cotič, Z., Mladenovič, A., & Šajna, A. (2015). Environmental evaluation of green concretes versus conventional concrete by means of LCA. *Waste Management*, *45*, 194–205. https://doi.org/10.1016/j.wasman.2015.06.035

U.S. EPA. (2012). Method SW-846 - 1313 : LIQUID-SOLID PARTITIONING AS A FUNCTION OF EXTRACT pH USING A PARALLEL BATCH EXTRACTION PROCEDURE SW-846. *Us. Epa*, *14429*(October).

U.S. Geological Survey. (2019). *Mineral commodity summaries 2019: U.S. Geological Survey*. https://doi.org/10.3133/70202434

United States Geological Survey. (2020). Mineral Commodity Summaries 2020. In *United States Geological Survey* (Issue 703). https://pubs.usgs.gov/periodicals/mcs2020/mcs2020.pdf

Van den Heede, P., & De Belie, N. (2012). Environmental impact and life cycle assessment (LCA) of traditional and 'green' concretes: Literature review and theoretical calculations. *Cement and Concrete Composites, 34*(4), 431–442. https://doi.org/10.1016/j.cemconcomp.2012.01.004

Vargas, F., & Lopez, M. (2018). Development of a new supplementary cementitious material from the activation of copper tailings: Mechanical performance and analysis of factors. *Journal of Cleaner Production*, *182*, 427–436. https://doi.org/10.1016/J.JCLEPRO.2018.01.223

Vargas, F., Lopez, M., & Rigamonti, L. (2020). Environmental impacts evaluation of treated copper tailings as Supplementary cementitious materials. *Resources, Conservation and Recycling*, *160*. https://doi.org/10.1016/j.resconrec.2020.104890

Wang, C., Harbottle, D., Liu, Q., & Xu, Z. (2014). Current state of fine mineral tailings treatment: A critical review on theory and practice. *Minerals Engineering*, *58*, 113–131. https://doi.org/10.1016/j.mineng.2014.01.018

Wang, F.-H., Zhang, F., Chen, Y.-J., Gao, J., & Zhao, B. (2015). A comparative study on the heavy metal solidification/stabilization performance of four chemical solidifying agents in municipal solid waste incineration fly ash. *Journal of Hazardous Materials*, *300*, 451–458. https://doi.org/10.1016/j.jhazmat.2015.07.037

Yang, D., Fan, L., Shi, F., Liu, Q., & Wang, Y. (2017). Comparative study of cement manufacturing with different strength grades using the coupled LCA and partial LCC methods—A case study in China. *Resources, Conservation and Recycling*, *119*, 60–68. https://doi.org/10.1016/J.RESCONREC.2016.06.017

Yang, K. H., Jung, Y. B., Cho, M. S., & Tae, S. H. (2015). Effect of Supplementary cementitious materials on reduction of CO2 emissions from concrete. *Journal of Cleaner Production*, *103*, 774–783. https://doi.org/10.1016/j.jclepro.2014.03.018

Yanguatin, H., Tobón, J., & Ramírez, J. (2017). Reactividad puzolánica de arcillas caoliníticasuna revisión. *Revista Ingeniería de Construcción*, *32*(2), 13–24. https://doi.org/10.4067/s0718-50732017000200002

Zhang, C., Zhou, T., Wu, Q., Zhu, H., & Xu, P. (2014). Mechanical Performances and Microstructures of Cement Containing Copper Tailings. *ASIAN JOURNAL OF CHEMISTRY*, *26*(5, A), 1371–1375.

Zhao, S., Fan, J., & Sun, W. (2014). Utilization of iron ore tailings as fine aggregate in ultra-high performance concrete. *Construction and Building Materials*, *50*, 540–548. https://doi.org/10.1016/j.conbuildmat.2013.10.019

Zheng, K., Zhou, J., & Gbozee, M. (2015). Influences of phosphate tailings on hydration and properties of Portland cement. *Construction and Building Materials*, *98*, 593–601. https://doi.org/10.1016/j.conbuildmat.2015.08.115

Zou, D., Zhang, H., Wang, Y., Zhu, J., & Guan, X. (2015). Internal curing of mortar with low water to cementitious materials ratio using a normal weight porous aggregate.

Construction and Building Materials, *96*, 209–216. https://doi.org/10.1016/j.conbuildmat.2015.08.025

Zunino, F., & Lopez, M. (2016). Decoupling the physical and chemical effects of Supplementary cementitious materials on strength and permeability: A multi-level approach. *Cement and Concrete Composites*, *65*, 19–28. https://doi.org/10.1016/j.cemconcomp.2015.10.003

Zunino, F., & Lopez, M. (2017). A methodology for assessing the chemical and physical potential of industrially sourced rice husk ash on strength development and early-age hydration of cement paste. *Construction and Building Materials*, *149*, 869–881. https://doi.org/10.1016/j.conbuildmat.2017.05.187

5. GENERAL CONCLUSIONS AND PERSPECTIVES

5.1 General Conclusions

The use of wastes and/or by-products in the concrete and cement industry is a trend that will rise in the future from actual levels of use, due to necessity of reduction of impacts of cement and construction industry. In the case of copper tailings, increasing levels of production and the increasing need of construction materials to achieve these production levels, including concrete, is relevant to propose the use of alternatives materials for most of the stages of production of a mining site. Also, this can contribute to the environmental performance of mining production sites and beyond depending on the characteristics and uses of those wastes.

This research proposed and studied the use of copper tailings as supplementary cementitious material. Results showed that it is possible to use copper tailings as SCM, in a safely way, limiting leaching of heavy metals from cementitious materials, increasing the capacity of the tailings with some treatments from a cementitious point of view and with environmental benefits from their use. Nevertheless, limitations due to heterogeneity of tailings and production systems rise as a major obstacle to generalize conclusions on the use of specific tailing.

The hypotheses proposed for the development of this research can be analysed with the perspective of the obtained results as follow:

Regarding the performance improvement of mixtures containing tailings as supplementary cementitious material:

H.Ia *Tailings cementitious capacity is improved by a combination of heat treatment under 900° C and decreasing particle size of 15%, which improve performance in mechanical strength of concrete*: has been demonstrated through analysis of mechanical performance and increased pozzolanic activity on tailings treated mechanically and by calcination. The benefits of the use of these treatments has been quantified (**Specific Objective O1.a**) and the use of treated tailings has been analysed up to 50%, increasing the use of this material (**Specific Objective O1.b**). The results and specific conclusions related with this hypothesis can be seen on chapter 2.

H.Ib *There is an environmental performance benefit on the use of concrete mixes containing copper tailings as supplementary cementitious material compared with concrete mixes without copper tailings as supplementary cementitious material up to 10% measured as CO_2 release*: the environmental performance has been measured through the development of a new methodology to compare and analyse concrete mixes with Supplementary cementitious materials based on the Life Cycle Assessment methodology. A system was proposed to simulate the production of treated tailings (**Specific Objective O3.b**). Results showed that environmental benefits depend on the performance of the tailing, this is, at higher performance levels, higher is the environmental benefit of the use the SCM (**Specific Objective O3.a**). The results and specific conclusions related with this hypothesis can be seen in chapter 4.

Regarding the form copper is incorporated into the cement hydration products:

H.IIa *The contribution of free lime and alkali at the beginning of the hydration process, in larger proportions than those in Portland cement, improves chemical entrapment of copper present in tailings*: this hypothesis has not been demonstrated, and results showed that there is no statistical correlation between leaching of copper and concentration of those materials, at the experimental region of interest proposed in this research. These results are partially related with observations shown in chapter 3 (**Specific Objective O2.b**)

H.IIb *Changes in hydration products packing due to higher concentrations of CSH due to changes on water-to-binder ratio, improves the physical entrapment of copper present in* *tailings*: no relation between hydration products of cementitious mixes and copper compound has been stablished (**Specific Objective O2.a**) due to lack of information and changes on the focus of the research: the focus was changed to prove the hypothesis: determine the way copper is entrapped into the cementitious mixes. The mechanism of entrapment of copper has been partially explained by the determination of the position of copper compounds on cementitious matrix and determination of the way copper phases change during hydration. Also, water-to-binder ratio has been shown as a factor statistically significant related with the leaching of copper phases (**Specific Objective O2.b**).

The consecution of the previous objectives and the validation of the hypotheses proposed, when successful, have made an effort to accomplish the general objective of this research:

To provide mechanical, safety and environmental information in order to increase the use of copper tailings as supplementary cementitious material.

The results of this research have shown the importance of the development of standard analysis and the resolution of methodological differences in order to study and increase the use of any supplementary cementitious material (beyond tailings as result of this investigation) to provide information and contribute to the cement and concrete industry, the construction and mining industry and finally and more important, to the environment.

5.2 Perspectives and Future Work

Results of this study provide information that can be used by the industry (construction and mining) to use this waste as supplementary cementitious material. The huge amounts of tailings generated each year makes this research mainly relevant for the mining industry and management on mining sites, but applications can extend far beyond the scope of a mining site.

The study of tailings, and this kind of materials, may be considered an extremely case-to-case approach, due to high heterogeneity of materials. Nevertheless, the proposed methods and analyses (characterization of SCM, improvement of cementitious capacity, analysis of leaching, methodology for proper comparison of concrete mixes from an environmental point of view) can be used for any supplementary cementitious material, specially wastes from industrial activities (converted into by-products). This methodological approach is a contribution independently of the specific results of this study.

As a consequence of the present work and the results obtained, the following research and development proposals can be stated as future work:

- Further research on tailings from other sources, considering the size of the copper industry on the Chilean context, but extendable to other countries and types of mining wastes.

- Development of a standardize methodology for the analysis of any material as SCM, on a rapid way to achieve the industrial standards of development.

- Development of a standard for leaching of cementitious materials, considering the use of new wastes and the low levels observed during this research.

- Extension of this work to other uses of tailings, such as bricks and manufactured aggregates through geopolymerization process. This can lead to the use of higher volumes of tailings in concrete mixes or other uses such as road bases and other construction applications.

- Development and extension of the methodology for a consistent environmental comparison of concrete mixes, using other Supplementary cementitious materials and validating for other geographical contexts and scenarios.

GENERAL REFERENCES

Adjoudj, M., Ezziane, K., Kadri, E. H., Ngo, T.-T., & Kaci, A. (2014). Evaluation of rheological parameters of mortar containing various amounts of mineral addition with polycarboxylate superplasticizer. *Construction and Building Materials*, *70*, 549–559. https://doi.org/10.1016/j.conbuildmat.2014.07.111

Ahmari, S., & Zhang, L. (2012). Production of eco-friendly bricks from copper mine tailings through geopolymerization. *Construction and Building Materials*, *29*, 323–331. https://doi.org/10.1016/j.conbuildmat.2011.10.048

Aïtcin, P.-C. (2016). Supplementary cementitious materials and blended cements. In *Science and Technology of Concrete Admixtures*. https://doi.org/10.1016/B978-0-08-100693-1.00004-7

Antiohos, S., & Tsimas, S. (2004). Activation of fly ash cementitious systems in the presence of quicklime. *Cement and Concrete Research*, *34*(5), 769–779. https://doi.org/10.1016/j.cemconres.2003.08.008

Apodaca, L. E. (2016). Mineral Commodity Summaries. In *Mineral Commodity Summaries* (Vol. 1). https://doi.org/http://dx.doi.org/10.3133/70140094.

Argane, R., Benzaazoua, M., Hakkou, R., & Bouamrane, A. (2015). Reuse of base-metal tailings as aggregates for rendering mortars: Assessment of immobilization performances and environmental behavior. *Construction and Building Materials*, *96*, 296–306. https://doi.org/10.1016/j.conbuildmat.2015.08.029

Avet, F., Snellings, R., Alujas Diaz, A., Ben Haha, M., & 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. https://doi.org/10.1016/j.cemconres.2016.02.015

Bentz, D. P., Jones, S. Z., & Snyder, K. A. (2015). Design and performance of ternary blend high-volume fly ash concretes of moderate slump. *Construction and Building Materials*, *84*, 409–415. https://doi.org/10.1016/j.conbuildmat.2015.03.082

Bentz, D. P., Sato, T., de la Varga, I., & Weiss, W. J. (2012). Fine limestone additions to regulate setting in high volume fly ash mixtures. *Cement and Concrete Composites*, *34*(1), 11–17. https://doi.org/10.1016/j.cemconcomp.2011.09.004

Bui, P. T., Ogawa, Y., Nakarai, K., & Kawai, K. (2015). A study on pozzolanic reaction of fly ash cement paste activated by an injection of alkali solution. *Construction and Building Materials*, *94*, 28–34. https://doi.org/10.1016/j.conbuildmat.2015.06.046

Burgos, D. M., Cardona, L. M., & Delvasto, S. (2014). Estudio de dos materiales volcánicos y efecto del tipo de molienda en su reactividad. *Revista Ingeniería de Construcción*, *29*(2), 159–174. https://doi.org/10.4067/S0718-50732014000200003

Burris, L. E., & Juenger, M. C. G. (2016). Milling as a pretreatment method for increasing the reactivity of natural zeolites for use as Supplementary cementitious materials. *Cement and Concrete Composites*, *65*, 163–170. https://doi.org/10.1016/j.cemconcomp.2015.09.008

Cao, Z., Cao, Y., Dong, H., Zhang, J., & Sun, C. (2016). Effect of calcination condition on the microstructure and pozzolanic activity of calcined coal gangue. *International Journal of Mineral Processing*, *146*, 23–28. https://doi.org/10.1016/j.minpro.2015.11.008

Carkovic, A. B., Calcagni, M. S., Vega, A. S., Coquery, M., Moya, P. M., Bonilla, C. A., & Pastén, P. A. (2016). Active and legacy mining in an arid urban environment: challenges and perspectives for Copiapó, Northern Chile. *Environmental Geochemistry and Health*, *38*(4), 1001–1014. https://doi.org/10.1007/s10653-016-9793-5

Celik, K., Meral, C., Petek Gursel, A., Mehta, P. K., Horvath, A., & Monteiro, P. J. M. (2015). Mechanical properties, durability, and life-cycle assessment of self-consolidating concrete mixtures made with blended portland cements containing fly ash and limestone powder. *Cement and Concrete Composites*, *56*, 59–72. https://doi.org/10.1016/j.cemconcomp.2014.11.003

EN 206 Concrete - Specification, performance, production and conformity, (2013) (testimony of CEN).

Chen, C., Habert, G., Bouzidi, Y., Jullien, A., & Ventura, A. (2010). LCA allocation procedure used as an incitative method for waste recycling: An application to mineral additions in concrete. *Resources, Conservation and Recycling*, *54*(12), 1231–1240. https://doi.org/10.1016/J.RESCONREC.2010.04.001

Choi, Y. W., Kim, Y. J., Choi, O., Lee, K. M., & Lachemi, M. (2009). Utilization of tailings from tungsten mine waste as a substitution material for cement. *Construction and Building Materials*, *23*(7), 2481–2486. https://doi.org/10.1016/j.conbuildmat.2009.02.006

CNE. (2019). *Generación Bruta SEN - Comision Nacional de Energia Chile*. https://www.cne.cl/estadisticas/electricidad/

Damineli, B. L., Kemeid, F. M., Aguiar, P. S., & John, V. M. (2010). Measuring the eco-efficiency of cement use. *Cement and Concrete Composites*, *32*(8), 555–562. https://doi.org/10.1016/J.CEMCONCOMP.2010.07.009

Davenport, W. G., King, M., Schlesinger, M., & Biswas, A. K. (2002). Overview. *Extractive Metallurgy of Copper*, 1–16. https://doi.org/10.1016/B978-008044029-3/50004-6

De Schepper, M., Van den Heede, P., Van Driessche, I., & De Belie, N. (2014). Life Cycle Assessment of Completely Recyclable Concrete. *Materials*, *7*(8), 6010–6027. https://doi.org/10.3390/ma7086010

Deng, Y., Zhang, C., & Wei, X. (2014). Influence of lithium sulfate addition on the properties of Portland cement paste. *Construction and Building Materials*, *50*, 457–462. https://doi.org/10.1016/j.conbuildmat.2013.09.058

Di Maria, A., Salman, M., Dubois, M., & Van Acker, K. (2018). Life cycle assessment to evaluate the environmental performance of new construction material from stainless steel slag. *The International Journal of Life Cycle Assessment*, *23*(11), 2091–2109. https://doi.org/10.1007/s11367-018-1440-1

Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, I. (2010). Effect of natural pozzolans as mineral admixture on the performance of cemented-paste backfill of sulphide-rich tailings. *Waste Management & Research : The Journal of the International Solid Wastes and Public Cleansing Association, ISWA*, *28*(5), 430–435. https://doi.org/10.1177/0734242X09351905

Erniati, Tjaronge, M. W., Zulharnah, & Irfan, U. R. (2015). Porosity, pore size and compressive strength of self compacting concrete using sea water. *Procedia Engineering*, *125*, 832–837. https://doi.org/10.1016/j.proeng.2015.11.045

Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC, (2006) (testimony of European Parlament and Council).

Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives, 312 Official Journal of the European Union (2008).

Fan, C., & Miller, S. A. (2018). Reducing greenhouse gas emissions for prescribed concrete compressive strength. *Construction and Building Materials*, *167*, 918–928. https://doi.org/10.1016/J.CONBUILDMAT.2018.02.092

Fuentes, M., Zúñiga, A., Díaz, M., Rocha, E., & Díaz, S. (2014). Molienda mecánica por alta energía de minerales mexicanos para producir concreto de alto desempeño (CAD). *Revista Ingeniería de Construcción*, *29*(3), 256–269.

https://doi.org/10.4067/S0718-50732014000300003

Grist, E. R., Paine, K. A., Heath, A., Norman, J., & Pinder, H. (2013). Compressive strength development of binary and ternary lime–pozzolan mortars. *Materials & Design*, *52*, 514–523. https://doi.org/10.1016/j.matdes.2013.05.006

Guo, B., Liu, B., Yang, J., & Zhang, S. (2017). The mechanisms of heavy metal immobilization by cementitious material treatments and thermal treatments: A review. *Journal of Environmental Management*, *193*, 410–422. https://doi.org/10.1016/J.JENVMAN.2017.02.026

Gursel, A. P., Maryman, H., & Ostertag, C. (2016). A life-cycle approach to environmental, mechanical, and durability properties of “green” concrete mixes with rice husk ash. *Journal of Cleaner Production*, *112*, 823–836. https://doi.org/10.1016/j.jclepro.2015.06.029

Habeeb, G. A., & Mahmud, H. Bin. (2010). Study on properties of rice husk ash and its use as cement replacement material. *Materials Research*, *13*(2), 185–190. https://doi.org/10.1590/S1516-14392010000200011

Hamidi, M., Kacimi, L., Cyr, M., & Clastres, P. (2013). Evaluation and improvement of pozzolanic activity of andesite for its use in eco-efficient cement. *Construction and Building Materials*, *47*, 1268–1277. https://doi.org/10.1016/j.conbuildmat.2013.06.013

Hossain, M. M., Karim, M. R., Hossain, M. K., Islam, M. N., & Zain, M. F. M. (2015). Durability of mortar and concrete containing alkali-activated binder with pozzolans: A review. *Construction and Building Materials*, *93*, 95–109. https://doi.org/10.1016/j.conbuildmat.2015.05.094

Huang, X. Q., Hou, H. B., Zhou, M., & Wang, W. X. (2014). Mechanical Properties and Microstructure Analysis of Copper Tailings Solidifying with Different Cementitious Materials. *Advanced Materials Research*, *878*, 171–176.

https://doi.org/10.4028/www.scientific.net/AMR.878.171

Ilić, B., Radonjanin, V., Malešev, M., Zdujić, M., & Mitrović, A. (2016). Effects of mechanical and thermal activation on pozzolanic activity of kaolin containing mica. *Applied Clay Science*, *123*, 173–181. https://doi.org/10.1016/j.clay.2016.01.029

NCh170.Of2016 - Hormigón - Requisitos generales, (2016) (testimony of INN).

Jain, N. (2012). Effect of nonpozzolanic and pozzolanic mineral admixtures on the hydration behavior of ordinary Portland cement. *Construction and Building Materials*, *27*(1), 39–44. https://doi.org/10.1016/j.conbuildmat.2011.08.006

Juenger, M. C. G., & Siddique, R. (2015). Recent advances in understanding the role of Supplementary cementitious materials in concrete. *Cement and Concrete Research*, *78*, 71–80. https://doi.org/10.1016/j.cemconres.2015.03.018

Juenger, M. C. G., Snellings, R., & Bernal, S. A. (2019). Supplementary cementitious materials: New sources, characterization, and performance insights. *Cement and Concrete Research*, *122*, 257–273. https://doi.org/10.1016/J.CEMCONRES.2019.05.008

Khodabakhshian, A., de Brito, J., Ghalehnovi, M., & Asadi Shamsabadi, E. (2018). Mechanical, environmental and economic performance of structural concrete containing silica fume and marble industry waste powder. *Construction and Building Materials*, *169*, 237–251. https://doi.org/10.1016/J.CONBUILDMAT.2018.02.192

Klopffer, W., & Grahl, B. (2015). *Life Cycle Assessment: A guide to best practise (chapter 1-3)* (Issue 1995). https://doi.org/10.1016/B978-0-12-801595-7.00013-6

Küçükyıldırım, E., & Uzal, B. (2014). Characteristics of calcined natural zeolites for use in high-performance pozzolan blended cements. *Construction and Building Materials*, *73*, 229–234. https://doi.org/10.1016/j.conbuildmat.2014.09.081

Kurda, R., Silvestre, J. D., & de Brito, J. (2018). Life cycle assessment of concrete made with high volume of recycled concrete aggregates and fly ash. *Resources, Conservation and Recycling*, *139*(April 2018), 407–417. https://doi.org/10.1016/j.resconrec.2018.07.004

Lee, K.-M., & Park, P.-J. (2005). Estimation of the environmental credit for the recycling of granulated blast furnace slag based on LCA. *Resources, Conservation and Recycling*, *44*(2), 139–151. https://doi.org/10.1016/J.RESCONREC.2004.11.004

Li, J., Zhang, W., Li, C., & Monteiro, P. J. M. (2019). Green concrete containing diatomaceous earth and limestone: Workability, mechanical properties, and life-cycle assessment. *Journal of Cleaner Production*, *223*, 662–679. https://doi.org/10.1016/j.jclepro.2019.03.077

Lothenbach, B., Scrivener, K., & Hooton, R. D. (2011). Supplementary cementitious materials. *Cement and Concrete Research*, *41*(12), 1244–1256. https://doi.org/10.1016/j.cemconres.2010.12.001

Ludwig, H.-M., & Zhang, W. (2015). Research review of cement clinker chemistry. *Cement and Concrete Research*. https://doi.org/10.1016/j.cemconres.2015.05.018

Ma, X.-W., Chen, H.-X., & Wang, P.-M. (2010). Effect of CuO on the formation of clinker minerals and the hydration properties. *Cement and Concrete Research*, *40*(12), 1681–1687. https://doi.org/10.1016/j.cemconres.2010.08.009

Masi, G., Rickard, W. D. A., Vickers, L., Bignozzi, M. C., & van Riessen, A. (2014). A comparison between different foaming methods for the synthesis of light weight geopolymers. *Ceramics International*, *40*(9), 13891–13902. https://doi.org/10.1016/j.ceramint.2014.05.108

Matos, P. R. de, Foiato, M., & Prudêncio, L. R. (2019). Ecological, fresh state and long-term mechanical properties of high-volume fly ash high-performance self-compacting concrete. *Construction and Building Materials*, *203*, 282–293. https://doi.org/10.1016/J.CONBUILDMAT.2019.01.074

Mehta, P. K., & Monteiro, P. J. M. (2014). *Concrete: Microstructure, Properties, and Materials, Fourth Edition* (4th Editio). McGraw-Hill Education: New York, Chicago, San Francisco, Athens, London, Madrid, Mexico City, Milan, New Delhi, Singapore, Sydney, Toronto.

Miller, S. A. (2018). Supplementary cementitious materials to mitigate greenhouse gas emissions from concrete: can there be too much of a good thing? *Journal of Cleaner Production*, *178*, 587–598. https://doi.org/10.1016/j.jclepro.2018.01.008

Montgomery, D. C. (2017). Design and Analysis of Experiments. In *Design* (Vol. 2). https://doi.org/10.1198/tech.2006.s372

Moretti, L., & Caro, S. (2017). Critical analysis of the Life Cycle Assessment of the Italian cement industry. *Journal of Cleaner Production*, *152*, 198–210. https://doi.org/10.1016/J.JCLEPRO.2017.03.136

Moya, P. M., Arce, G. J., Leiva, C., Vega, A. S., Gutiérrez, S., Adaros, H., Muñoz, L., Pastén, P. A., & Cortés, S. (2019). An integrated study of health, environmental and socioeconomic indicators in a mining-impacted community exposed to metal enrichment. *Environmental Geochemistry and Health*. https://doi.org/10.1007/s10653-019-00308-4

Nakic, D. (2018). Environmental evaluation of concrete with sewage sludge ash based on LCA. *Sustainable Production and Consumption*, *16*, 193–201. https://doi.org/10.1016/J.SPC.2018.08.003

Oliva, M., Vargas, F., & Lopez, M. (2019). Designing the incineration process for improving the cementitious performance of sewage sludge ash in Portland and blended cement systems. *Journal of Cleaner Production*, *223*, 1029–1041. https://doi.org/10.1016/J.JCLEPRO.2019.03.147

Onuaguluchi, O., & Eren, O. (2013a). Rheology, strength and durability properties of mortars containing copper tailings as a cement replacement material. *EUROPEAN*

JOURNAL OF ENVIRONMENTAL AND CIVIL ENGINEERING, *17*(1), 19–31. https://doi.org/10.1080/19648189.2012.699708

Onuaguluchi, O., & Eren, Ö. (2012). Cement mixtures containing copper tailings as an additive: durability properties. *Materials Research*, *15*(6), 1029–1036. https://doi.org/10.1590/S1516-14392012005000129

Onuaguluchi, O., & Eren, Ö. (2013b). Rheology, strength and durability properties of mortars containing copper tailings as a cement replacement material. *European Journal of Environmental and Civil Engineering*, *17*(1), 19–31. https://doi.org/10.1080/19648189.2012.699708

Onuaguluchi, O., & Eren, Ö. (2015). Reusing copper tailings in concrete: corrosion performance and socioeconomic implications for the Lefke-Xeros area of Cyprus. *Journal of Cleaner Production*. https://doi.org/10.1016/j.jclepro.2015.09.036

Panesar, D. K., Seto, K. E., & Churchill, C. J. (2017). Impact of the selection of functional unit on the life cycle assessment of green concrete. *International Journal of Life Cycle Assessment*, *22*(12), 1969–1986. https://doi.org/10.1007/s11367-017-1284-0

Peng, K., Yang, H., & Ouyang, J. (2015). Tungsten tailing powders activated for use as cementitious material. *Powder Technology*, *286*, 678–683. https://doi.org/10.1016/j.powtec.2015.09.012

Petek Gursel, A., Masanet, E., Horvath, A., & Stadel, A. (2014). Life-cycle inventory analysis of concrete production: A critical review. *Cement and Concrete Composites*, *51*, 38–48. https://doi.org/10.1016/j.cemconcomp.2014.03.005

Ramezanianpour, A. A. (2014). Cement Replacement Materials; Properties, Durability, Sustainability. In *Springer Geochemistry/Mineralogy* (Vol. 7). https://doi.org/10.1007/978-3-642-36721-2

Ramezanianpour, A. M., Esmaeili, K., Ghahari, S. A., & Ramezanianpour, A. A. (2014).

Influence of initial steam curing and different types of mineral additives on mechanical and durability properties of self-compacting concrete. *Construction and Building Materials*, *73*, 187–194. https://doi.org/10.1016/j.conbuildmat.2014.09.072

Robayo-Salazar, R., Mejía-Arcila, J., Mejía de Gutiérrez, R., & Martínez, E. (2018). Life cycle assessment (LCA) of an alkali-activated binary concrete based on natural volcanic pozzolan: A comparative analysis to OPC concrete. *Construction and Building Materials*, *176*, 103–111. https://doi.org/10.1016/j.conbuildmat.2018.05.017

Rossen, J. E., Lothenbach, B., & Scrivener, K. L. (2015). Composition of C–S–H in pastes with increasing levels of silica fume addition. *Cement and Concrete Research*, *75*, 14–22. https://doi.org/10.1016/j.cemconres.2015.04.016

Saade, M. R. M., Passer, A., & Mittermayr, F. (2019). (Sprayed) concrete production in life cycle assessments: a systematic literature review. *The International Journal of Life Cycle Assessment*. https://doi.org/10.1007/s11367-019-01676-w

Sagastume Gutiérrez, A., Cabello Eras, J. J., Gaviria, C. A., Van Caneghem, J., & Vandecasteele, C. (2017). Improved selection of the functional unit in environmental impact assessment of cement. *Journal of Cleaner Production*, *168*, 463–473. https://doi.org/10.1016/J.JCLEPRO.2017.09.007

Sant, G., Kumar, A., Patapy, C., Le Saout, G., & Scrivener, K. (2012). The influence of sodium and potassium hydroxide on volume changes in cementitious materials. *Cement and Concrete Research*, *42*(11), 1447–1455. https://doi.org/10.1016/J.CEMCONRES.2012.08.012

Schlesinger, M., King, M., Sole, K., & Davenport, W. (2011). Extractive Metallurgy of Copper. In *Extractive Metallurgy of Copper*. Elsevier Ltd. https://doi.org/10.1016/C2010-0-64841-3

Schneider, M., Romer, M., Tschudin, M., & Bolio, H. (2011). Sustainable cement production—present and future. *Cement and Concrete Research*, *41*(7), 642–650.

https://doi.org/10.1016/j.cemconres.2011.03.019

Schöler, A., Lothenbach, B., Winnefeld, F., & Zajac, M. (2015). Hydration of quaternary Portland cement blends containing blast-furnace slag, siliceous fly ash and limestone powder. *Cement and Concrete Composites*, *55*, 374–382. https://doi.org/10.1016/j.cemconcomp.2014.10.001

Seraj, S., Ferron, R. D., & Juenger, M. C. G. (2016). Calcining natural zeolites to improve their effect on cementitious mixture workability. *Cement and Concrete Research*, *85*, 102–110. https://doi.org/10.1016/j.cemconres.2016.04.002

SERNAGEOMIN. (2019a). *Anuario de la minerìa de Chile 2018*. https://doi.org/https://www.sernageomin.cl/wp-content/uploads/2019/06/Libro_Anuario_2018_.pdf

SERNAGEOMIN. (2019b). *Catastro de Depositos de Relaves en Chile*. https://www.sernageomin.cl/datos-publicos-deposito-de-relaves/

Seto, K. E., Churchill, C. J., & Panesar, D. K. (2017). Influence of fly ash allocation approaches on the life cycle assessment of cement-based materials. *Journal of Cleaner Production*, *157*, 65–75. https://doi.org/10.1016/J.JCLEPRO.2017.04.093

Shi, C., Meyer, C., & Behnood, A. (2008). Utilization of copper slag in cement and concrete. *Resources, Conservation and Recycling*, *52*(10), 1115–1120. https://doi.org/10.1016/j.resconrec.2008.06.008

Smuda, J., Dold, B., Spangenberg, J. E., Friese, K., Kobek, M. R., Bustos, C. A., & Pfeifer, H.-R. (2014). Element cycling during the transition from alkaline to acidic environment in an active porphyry copper tailings impoundment, Chuquicamata, Chile. *Journal of Geochemical Exploration*, *140*, 23–40. https://doi.org/10.1016/j.gexplo.2014.01.013

Smuda, J., Dold, B., Spangenberg, J. E., & Pfeifer, H.-R. (2008). Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: Implications on sources and mobility of elements during transport and early stages of deposition. *Chemical Geology*, *256*(1), 62–76. https://doi.org/10.1016/j.chemgeo.2008.08.001

Snellings, R., & Scrivener, K. L. (2015). Rapid screening tests for Supplementary cementitious materials: past and future. *Materials and Structures*, *49*(8), 1–15. https://doi.org/10.1617/s11527-015-0718-z

Souri, A., Kazemi-Kamyab, H., Snellings, R., Naghizadeh, R., Golestani-Fard, F., & Scrivener, K. (2015). Pozzolanic activity of mechanochemically and thermally activated kaolins in cement. *Cement and Concrete Research*, *77*, 47–59. https://doi.org/10.1016/j.cemconres.2015.04.017

Taylor-Lange, S. C., Lamon, E. L., Riding, K. A., & Juenger, M. C. G. (2015). Calcined kaolinite–bentonite clay blends as Supplementary cementitious materials. *Applied Clay Science*, *108*, 84–93. https://doi.org/10.1016/j.clay.2015.01.025

Taylor, H. F. W. (1997). Cement chemistry. In *Cement chemistry*. Thomas Telford Publishing. https://doi.org/10.1680/cc.25929

Teklay, A., Yin, C., Rosendahl, L., & Bøjer, M. (2014). Calcination of kaolinite clay particles for cement production: A modeling study. *Cement and Concrete Research*, *61–62*, 11–19. https://doi.org/10.1016/j.cemconres.2014.04.002

Thomas, B. S., Damare, A., & Gupta, R. C. (2013a). Strength and durability characteristics of copper tailing concrete. *Construction and Building Materials*, *48*, 894–900. https://doi.org/10.1016/j.conbuildmat.2013.07.075

Thomas, B. S., Damare, A., & Gupta, R. C. (2013b). Strength and durability characteristics of copper tailing concrete. *Construction and Building Materials*, *48*, 894–900. https://doi.org/10.1016/j.conbuildmat.2013.07.075

Thomas, M. (2013). *Supplementary Cementing Materials in Concrete*. CRC Press.

Tironi, A., Trezza, M. A., Scian, A. N., & Irassar, E. F. (2013). Assessment of pozzolanic activity of different calcined clays. *Cement and Concrete Composites*, *37*, 319–327. https://doi.org/10.1016/j.cemconcomp.2013.01.002

Turk, J., Cotič, Z., Mladenovič, A., & Šajna, A. (2015). Environmental evaluation of green concretes versus conventional concrete by means of LCA. *Waste Management*, *45*, 194–205. https://doi.org/10.1016/j.wasman.2015.06.035

U.S. EPA. (2012). Method SW-846 - 1313 : LIQUID-SOLID PARTITIONING AS A FUNCTION OF EXTRACT pH USING A PARALLEL BATCH EXTRACTION PROCEDURE SW-846. *Us. Epa*, *14429*(October).

U.S. Geological Survey. (2019). *Mineral commodity summaries 2019: U.S. Geological Survey*. https://doi.org/10.3133/70202434

United States Geological Survey. (2020). Mineral Commodity Summaries 2020. In *United States Geological Survey* (Issue 703). https://pubs.usgs.gov/periodicals/mcs2020/mcs2020.pdf

Van den Heede, P., & De Belie, N. (2012). Environmental impact and life cycle assessment (LCA) of traditional and 'green' concretes: Literature review and theoretical calculations. *Cement and Concrete Composites*, *34*(4), 431–442. https://doi.org/10.1016/j.cemconcomp.2012.01.004

Vargas, F., & Lopez, M. (2018). Development of a new supplementary cementitious material from the activation of copper tailings: Mechanical performance and analysis of factors. *Journal of Cleaner Production*, *182*, 427–436. https://doi.org/10.1016/J.JCLEPRO.2018.01.223

Vargas, F., Lopez, M., & Rigamonti, L. (2020). Environmental impacts evaluation of treated copper tailings as Supplementary cementitious materials. *Resources, Conservation and Recycling*, *160*. https://doi.org/10.1016/j.resconrec.2020.104890

Wang, C., Harbottle, D., Liu, Q., & Xu, Z. (2014). Current state of fine mineral tailings treatment: A critical review on theory and practice. *Minerals Engineering*, *58*, 113–131. https://doi.org/10.1016/j.mineng.2014.01.018

Wang, F.-H., Zhang, F., Chen, Y.-J., Gao, J., & Zhao, B. (2015). A comparative study on the heavy metal solidification/stabilization performance of four chemical solidifying agents in municipal solid waste incineration fly ash. *Journal of Hazardous Materials*, *300*, 451–458. https://doi.org/10.1016/j.jhazmat.2015.07.037

Yang, D., Fan, L., Shi, F., Liu, Q., & Wang, Y. (2017). Comparative study of cement manufacturing with different strength grades using the coupled LCA and partial LCC methods—A case study in China. *Resources, Conservation and Recycling*, *119*, 60–68. https://doi.org/10.1016/J.RESCONREC.2016.06.017

Yang, K. H., Jung, Y. B., Cho, M. S., & Tae, S. H. (2015). Effect of Supplementary cementitious materials on reduction of CO2 emissions from concrete. *Journal of Cleaner Production*, *103*, 774–783. https://doi.org/10.1016/j.jclepro.2014.03.018

Yanguatin, H., Tobón, J., & Ramírez, J. (2017). Reactividad puzolánica de arcillas caoliníticasuna revisión. *Revista Ingeniería de Construcción*, *32*(2), 13–24. https://doi.org/10.4067/s0718-50732017000200002

Zhang, C., Zhou, T., Wu, Q., Zhu, H., & Xu, P. (2014). Mechanical Performances and Microstructures of Cement Containing Copper Tailings. *ASIAN JOURNAL OF CHEMISTRY*, *26*(5, A), 1371–1375.

Zhao, S., Fan, J., & Sun, W. (2014). Utilization of iron ore tailings as fine aggregate in ultra-high performance concrete. *Construction and Building Materials*, *50*, 540–548. https://doi.org/10.1016/j.conbuildmat.2013.10.019

Zheng, K., Zhou, J., & Gbozee, M. (2015). Influences of phosphate tailings on hydration and properties of Portland cement. *Construction and Building Materials*, *98*, 593–601. https://doi.org/10.1016/j.conbuildmat.2015.08.115

Zou, D., Zhang, H., Wang, Y., Zhu, J., & Guan, X. (2015). Internal curing of mortar with low water to cementitious materials ratio using a normal weight porous aggregate. *Construction and Building Materials*, *96*, 209–216. https://doi.org/10.1016/j.conbuildmat.2015.08.025

Zunino, F., & Lopez, M. (2016). Decoupling the physical and chemical effects of Supplementary cementitious materials on strength and permeability: A multi-level approach. *Cement and Concrete Composites*, *65*, 19–28. https://doi.org/10.1016/j.cemconcomp.2015.10.003

Zunino, F., & Lopez, M. (2017). A methodology for assessing the chemical and physical potential of industrially sourced rice husk ash on strength development and early-age hydration of cement paste. *Construction and Building Materials*, *149*, 869–881. https://doi.org/10.1016/j.conbuildmat.2017.05.187

APPENDICES

Appendix A: Supplementary information for Chapter 4

Table A.1 Chemical composition of OPC and tailings. Chemical composition data are presented as oxide percentage by weight. Trace element concentrations are presented as mg/kg.

	XRF			ICP-MS (Digestion)			
Percentage of Oxides (%)	OPC	OP1	LS5	Element (mg/kg)	OPC	OP1	LS5
SiO_2	20.36%	62.9%	42.6%	As	16.68	10.4	34.04
Al_2O_3	5.82%	9.5%	8.8%	Cd	0.36	2.42	0.18
Fe_2O	2.3%	12.6%	11%	Co	6.38	70.1	48.52
CaO	62.49%	2.8%	12.7%	Cu	33.01	1280.9	1194.5
MgO	3.3%	1.1%	2.5%	Cr	90.46	24.24	14.07
SO_3	3.3%	0.7%	1.8%	Ni	27.92	27.23	31.31
Na_2O	0.89%	1.3%	1.6%	Pb	20.03	14.91	6.91
K_2O	0.15%	3.3%	1.8%	Se	0.86	0.19	0.45
TiO_2	0.28%	0.2%	0.4%	Sr	688.7	30.43	35.04
P_2O_5	0.16%	0.1%	0.1%	V	86.72	272.1	54.31
Mn_2O_3	0.04%	0.1%	0.7%	Zn	131.3	567.5	555.35
Loss on Ignition (LOI)	2.1%	4.4%	14.50%	**Specific Gravity**	3.142	3.01	2.864

Table A.2 Energy grid mixture for Chile, year 2018 (CNE, 2019).

Generation (GWh)	2018	%
Biomass	2.387	3.16%
Coal	28.867	38.16%
Coal + Petcoke	438	0.58%
Co-Generation	140	0.18%
Wind	3.568	4.72%
Fuel Oil	8	0.01%
Natural Gas	3.504	4.63%
LNG	7.955	10.52%
Hydraulic (Dam)	10.906	14.42%
Hydraulic (River)	12.238	16.18%
Diesel	297	0.39%
Geothermic	214	0.28%
Solar	5.119	6.77%
TOTAL	75.641	100%

Table A.3 Potential environmental impacts of concrete mixtures in scenario 1.

1 m3 of Concrete		Equivalent Mechanical Performance		
Category	**Unit**	**BC-34**	**OP1-34**	**LS5-34**
Global warming	**kg CO2 eq**	380.281	320.970	357.659
Stratospheric ozone depletion	**kg CFC11 eq**	6.09E-05	6.06E-05	6.48E-05
Ozone formation. Human health	**kg NOx eq**	7.7E-01	6.9E-01	7.5E-01
Fine particulate matter formation	**kg PM2.5 eq**	5.6E-01	5.8E-01	5.8E-01
Terrestrial acidification	**kg SO2 eq**	7.1E-01	7.2E-01	7.4E-01
Freshwater eutrophication	**kg P eq**	4.5E-02	-3.2E-03	2.1E-02
Marine eutrophication	**kg N eq**	2.8E-03	2.2E-03	2.6E-03
Freshwater ecotoxicity	**kg 1,4-DCB**	3.21	-18.95	-8.77
Marine ecotoxicity	**kg 1,4-DCB**	4.81	-22.22	-9.71
Water consumption	**m3**	2.510	2.391	2.462
Mineral resource scarcity	**kg Cu eq**	1.929	1.466	1.700

Table A.4 Environmental impacts of concrete mixtures in scenario 2.

1 m3 of Concrete		Maximum Mechanical Performance			
Category	**Unit**	**BC-41**	**OP1-41**	**BC-37**	**LS5-37**
Global warming	**kg CO2 eq**	455.200	337.724	399.899	364.571
Stratospheric ozone depletion	**kg CFC11 eq**	6.60E-05	6.08E-05	6.22E-05	6.37E-05
Ozone formation. Human health	**kg NOx eq**	9.0E-01	7.2E-01	8.1E-01	7.6E-01
Fine particulate matter formation	**kg PM2.5 eq**	6.5E-01	5.7E-01	5.8E-01	5.7E-01
Terrestrial acidification	**kg SO2 eq**	8.3E-01	7.2E-01	7.4E-01	7.3E-01
Freshwater eutrophication	**kg P eq**	5.3E-02	1.0E-02	4.7E-02	2.9E-02
Marine eutrophication	**kg N eq**	3.3E-03	2.4E-03	2.9E-03	2.68E-03
Freshwater ecotoxicity	**kg 1,4-DCB**	3.58	-12.72	3.31	-5.12
Marine ecotoxicity	**kg 1,4-DCB**	5.33	-14.63	4.95	-5.29
Water consumption	**m3**	2.530	2.385	2.515	2.468
Mineral resource scarcity	**kg Cu eq**	2.325	1.597	2.032	1.770

Table A.5 Environmental impacts of concrete mixtures in scenario 3.

1 m3 of Concrete		Minimum Allowable Mechanical Performance/ Max % of Replacement		
Category	**Unit**	**BC-20**	**OP1-20**	**LS5-20**
Global warming	**kg CO2 eq**	295.545	286.507	317.290
Stratospheric ozone depletion	**kg CFC11 eq**	5.52E-05	6.04E-05	7.18E-05
Ozone formation. Human health	**kg NOx eq**	6.3E-01	6.5E-01	7.2E-01
Fine particulate matter formation	**kg PM2.5 eq**	4.5E-01	5.8E-01	6.1E-01
Terrestrial acidification	**kg SO2 eq**	5.8E-01	7.2E-01	7.9E-01
Freshwater eutrophication	**kg P eq**	3.7E-02	-3.1E-02	-2.2E-02
Marine eutrophication	**kg N eq**	2.3E-03	1.89E-03	2.1E-03
Freshwater ecotoxicity	**kg 1,4-DCB**	2.79	-31.79	-30.14
Marine ecotoxicity	**kg 1,4-DCB**	4.21	-37.88	-35.63
Water consumption	**m3**	2.486	2.364	2.371
Mineral resource scarcity	**kg Cu eq**	1.480	1.197	1.291

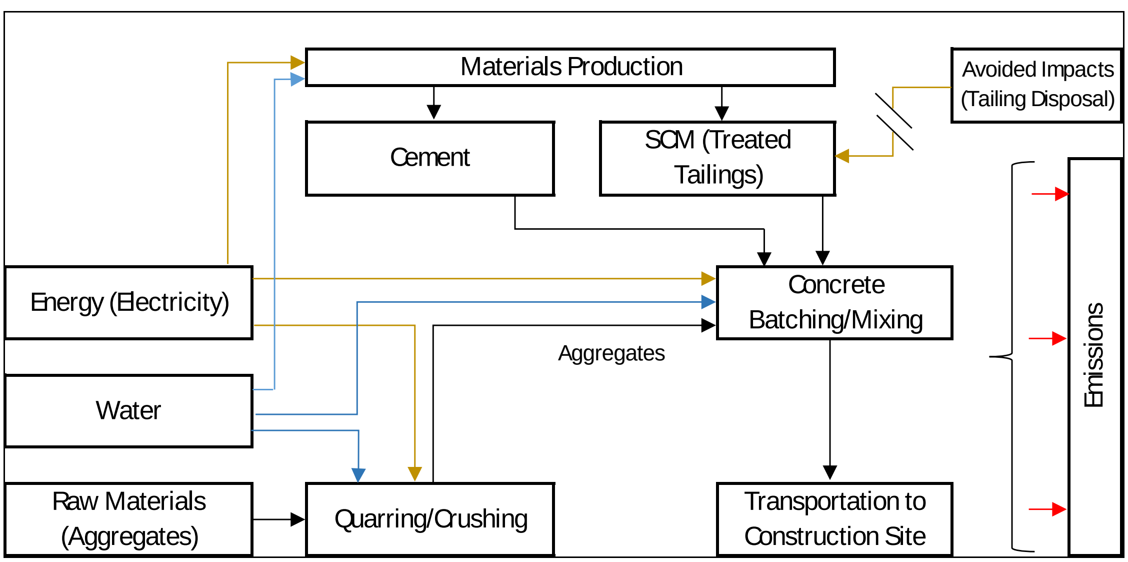

Figure A.1 Simplified process flow of concrete production for this study.