Mine tailings as partial raw materials substitutes in restoration and modern mortars: converting a "waste" into a "product"

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Abstract

During the restoration and reuse of monuments and monumental structures, it is crucial to research historic construction materials and formulate new ones to ensure the structural and historical integrity of monuments. A study of using mine tailings for construction materials is the subject of this thesis.

Mine tailings are normally considered waste, which is expensive to store in mine facilities and may impair environment and society.

However, the shortage and late price increases in some construction materials, together with the increasingly more restrictive environmental regulations, making this “ground dust”, a by-product of mining activities, an attractive alternative for construction materials.

Many studies have been carried out on the use of mine tailings as construction material in the past, but a comprehensive study including tailings originating from different ore ore-forming processes and therefore having varied mineralogical and chemical compositions has not yet been carried out. Moreover, to date, there have been no known instances of mortars specifically designed for use in the restoration of historical buildings or modern structures.

In this work, mine tailings from different deposits have been studied (Zinkgruvan, Kiruna and Vale). The experiments involve the analytical characterization of the tailings (mineralogical, chemical), formulation in mortars, testing (mechanical, physical) and optimization of the mix designs over the whole process to obtain the best-fitting solution for the tailings from the deposit studied.

Concrete monuments and buildings, that already use cement as a construction material, can be restored with these products. The tailings used as substitute are used as a partial replacement of cement, and/or aggregates, where in grout when cement is substituted by Zinkgruvan or Kiruna tailings, in the presence of an activator, the 1d compressive strengths increased from 24.5MPa to 40MPa and from 21.4MPa to 39MPa respectively in comparison with the reference 1d strength 50MPa. Whereas, when they were used as an aggregate’s replacement the 28d strengths reached 96MPa (Zinkgruvan) and 93.7MPa (Kiruna).

When Vale tailings are used as cement and/or aggregate’s replacement for repair mortars the values obtained are comparable with the reference, and no cracks are observed when applied on a concrete substrate.

Περίληψη

Κατά την αποκατάσταση και την επάναχρηση των ιστορικών μνημείων και αρχαιολογικών κατασκευών, είναι απαραίτητη η διεξαγωγή έρευνας σχετικά με τα ιστορικά δομικά υλικά, καθώς και η ανάπτυξη νέων υλικών, προκειμένου να διασφαλιστεί η διατήρηση της δομικής και ιστορικής ακεραιότητας των μνημείων. Η παρούσα διπλωματική εργασία στοχεύει στην έρευνα των καταλοίπων που προέρχονται από τις εξορύξεις των ορυχείων και στην εξερέυνηση της χρήσης τους ως δομικών υλικών.

Συνήθως, τα κατάλοιπα αυτά θεωρούνται απόβλητα, τα οποία είναι δαπανηρό να αποθηκευτούν στις εγκαταστάσεις των ορυχείων και μπορεί να προκαλέσουν περιβαλλοντικές και υγειονομικές επιπτώσεις.

Ωστόσο, η έλλειψη που παρατηρείται σε ορισμένα δομικά υλικά, η αύξηση των τιμών και οι όλο και αυστηρότεροι περιβαλλοντικοί κανονισμοί, κάνουν τα κατάλοιπα αυτά μία ελκυστική εναλλακτική λύση για δομικά υλικά.

Διάφορες έρευνες έχουν διεξαχθεί για την χρήση των καταλοίπων αυτών ως δομικών υλικών, αλλά μέχρι σήμερα, δεν υπάρχει μία εκτενής και ολοκληρωμένη έρευνα που να περιλαμβάνει κατάλοιπα από διαφορετικά είδη κοιτασμάτων με διαφορετικές ορυκτολογικές και χημικές συστάσεις. Επίσης, δεν συναντώνται περιπτώσεις κονιαμάτων που έχουν σχεδιαστεί ειδικά για την αποκατάσταση ιστορικών κτιρίων ή τη χρήση τους σε μοντέρνες κατασκευές.

Σε αυτή την έρευνα, πραγματοποιήθηκε μελέτη των καταλοίπων που προέρχοναι από διαφορετικά κοιτάσματα μεταλλευμάτων (Zinkgruvan, Kiruna, Vale). Οι πειραματικές διαδικασίες περιλαμβάνουν λεπτομερή χαρακτηρισμό των αποβλήτων με την χρήση φυσικοχημικών και αναλυτικών τεχνικών (ορυκτολογική, χημική ανάλυση), την ενσωμάτωση τους σε κονιάματα (μηχανικές, φυσικές αντοχές), και δοκιμές για την βελτιστοποίηση των συνθέσεων των μιγμάτων. Ο στόχος ήταν να επιτευχθεί η βέλτιστη λύση για τη διαχείριση των αποβλήτων από τα επιλεγμένα κοιτάσματα μεταλλευμάτων.

Μνημεία και κτίρια από σκυρόδεμα, που χρησιμοποιούν ήδη τσιμέντο ως δομικό υλικό, μπορούν να αποκατασταθούν με αυτά τα προϊόντα. Τα απόβλητα που χρησιμοποιούνται ως υποκατάστατα χρησιμοποιούνται ως μερική αντικατάσταση του τσιμέντου ή των αδρανών, όπου σε ενέματα όταν το τσιμέντο αντικαθίσταται από απόβλητα Zinkgruvan ή Kiruna, παρουσία ενεργοποιητή, οι αντοχές σε θλίψη 1d αυξάνονται από 24.5MPa σε 40MPa και από 21.4MPa σε 39MPa αντίστοιχα σε σύγκριση με την αντοχή αναφοράς 1d 50MPa. Ενώ, όταν χρησιμοποιήθηκαν ως υποκατάστατο αδρανών, οι αντοχές 28d έφθασαν τα 96MPa (Zinkgruvan) και 93.7MPa (Kiruna). Όταν τα υπολείμματα Vale χρησιμοποιούνται ως υποκατάστατο τσιμέντου ή/και αδρανών για κονιάματα αποκατάστασης, οι τιμές που λαμβάνονται είναι συγκρίσιμες με τις τιμές αναφοράς και δεν παρατηρούνται ρωγμές όταν εφαρμόζονται σε υπόστρωμα σκυροδέματος.

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1.1 Theoretical Framework

1.1.1 What are mine tailings-mineralogical and chemical composition:

Mining is fundamental for human society, playing a pivotal role in the economic growth of numerous countries worldwide. The unquestionable significance of mining in shaping our civilization is evident. Nevertheless, the mining, processing, and metallurgical operations unavoidably result in an increasing volume of solid wastes, primarily comprising waste rock, tailings and slag [1].

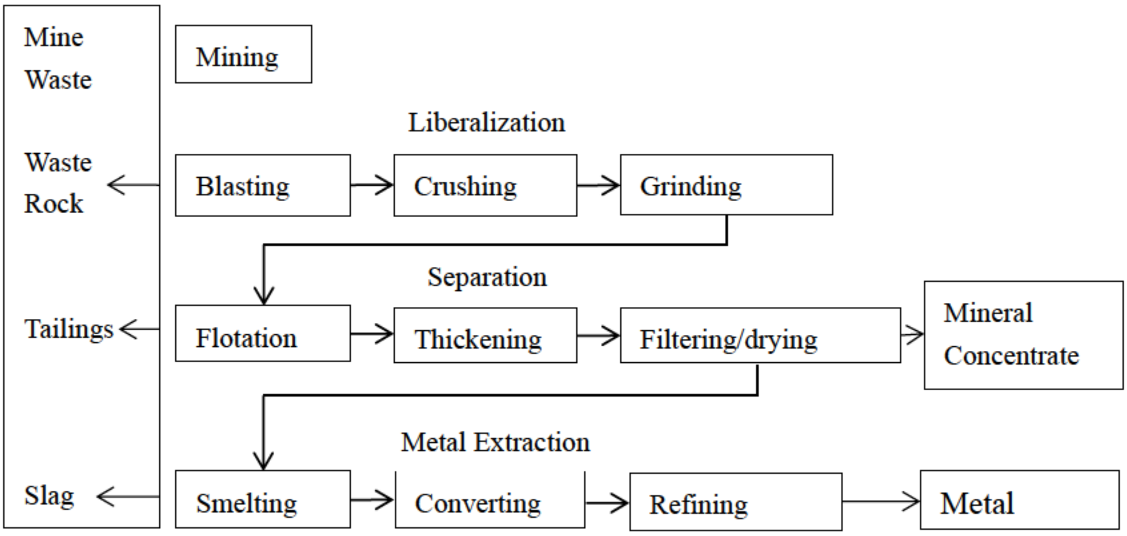

Figure 1: Mineral extraction from mining to metal. [1]

Mine tailings refer to the residual materials left behind after valuable minerals have been extracted from ore during mining operations. These tailings typically consist of a mixture of crushed rock, waste, and various chemicals and minerals used in the extraction process.

Depending on the type of mining activity and local environmental requirements, the storage solutions for tailings may include open pits, impoundments, or piling them up into dams. Despite the fact that tailings contain precious minerals, they are typically regarded as waste due to the impossibility of economically recovering these materials. In addition, tailings may include potentially dangerous materials like solvents and heavy metals utilized in extraction. Tailings provide substantial dangers to the environment and public health when improperly managed. They might cause air, water, and soil contamination as well as including landslides and dam leaks.

The chemical composition of tailings can vary depending on several factors, including the mineralogy of the ore body, processing methods, weathering, and impoundment conditions.

[1] Mifeng Gou, "Utilization of tailings in cement and concrete: A review", p.g.449

The major and trace elements found in tailings can have significant environmental implications, especially with respect to potential toxicity and environmental contamination.

- Si (SiO2): Silica is commonly found in tailings and is a major component of many mineral ores.
- Iron (Fe): Iron is another abundant element in tailings, often present in different mineral forms.
- Oxygen (O): Oxygen is naturally abundant due to its presence in various mineral oxides.
- Aluminum (Al): Aluminum is often present in significant amounts in certain types of tailings.
- Calcium (Ca), Potassium(K), Magnesium (Mg), Sodium (Na): These elements can be present due to the mineral composition of the ore.
- Phosphorous (P): Phosphorous may be present, especially in tailings associated with phosphate ore deposits.
- Titanium (Ti): Titanium can be found in certain ore types and subsequently present in their tailings.
- Sulfur (S): Sulfur can be present in various mineral sulfides commonly found in tailings.
- Arsenic (As), Copper (Cu), Lead (Pb), Zinc (Zn): These trace elements are often quantified due to their potential toxicity and environmental impact. They can be enriched in tailings, particularly in sulfidic ore deposits.
- Cadmium (Cd): When zinc concentrations are high in tailings, cadmium is also measured due to their chemical similarities and potential environmental risks.
- Mercury (Hg), Antimony (Sb), Thallium (Tl): these elements may also be monitored, especially if there is evidence of elevated concentrations or environmental concerns.
- Other trace elements: Depending on the specific ore body and its mineralogy, other trace elements like chromium (Cr), nickel (Ni), cobalt (Co), molybdenum (Mo), and others may also be present in tailings.

Tailings' minerals can be categorized into three main groups: the gangue fraction; the residual uneconomic sulfide-oxide fraction, and the secondary mineral fraction. In sulfide tailings from metal extraction, the gangue fraction is dominated by minerals like quartz (SiO_2), K-feldspar, Na-feldspar, Ca-feldspar, sericite ($Kal_2(AlSi_3O_{10})(OH)_2$, chlorite, calcite ($CaCO_3$), and dolomite ($CaMg(CO3)_2$)[2]. The sulfide-oxide fraction commonly contains pyrite (FeS_2), pyrrhotite, arsenopyrite (FeAsS), marcasite, magnetite (Fe_3O_4), sphalerite ((Zn,Fe)S), chalcopyrite ($CuFeS_2$), and galena (PbS). Secondary mineral formation occurs when fresh tailings are exposed to oxygen-rich conditions, leading to the development of minerals such as goethite (A-FeOOH), gypsum ($CaSO_4 \cdot 2H_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$, scorodite ($FeASO_4 \cdot 2H_2O$), and kaolinite $Al_2Si_2O_5(OH)_4$. These secondary minerals act as hosts for contaminant metals and

[2] Lottermoser, "Mine wastes-Characterization, Treatment, and environmental impact", p.g.4-7

metalloids through structural incorporation and surface sorption. The negatively charged oxygen atoms on secondary mineral surfaces are important sorption sites for ions. Understanding the mineralogy and formation of secondary minerals in tailings is crucial for effective tailings management and environmental impact mitigation in base and precious metal extraction industries[3].

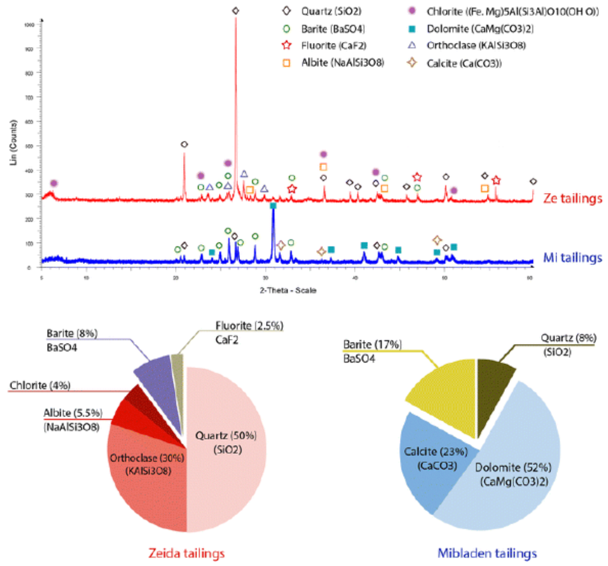

Figure 2: XRD patterns of lead-zinc tailings. Utilization of mine tailings in cement and concrete: A review, Gou et.al

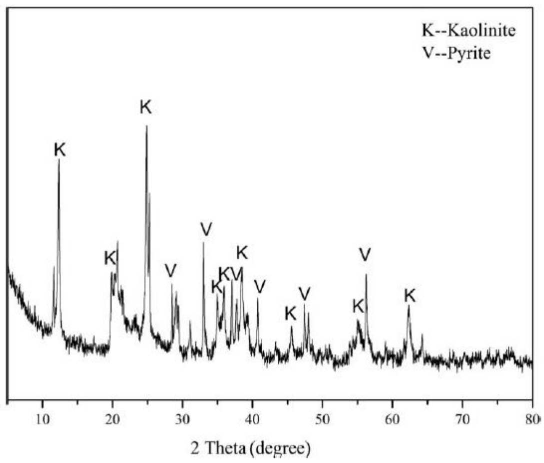

Figure 3: XRD patterns of pyrite tailings. Utilization of mine tailings in cement and concrete: A review, Gou et.al.

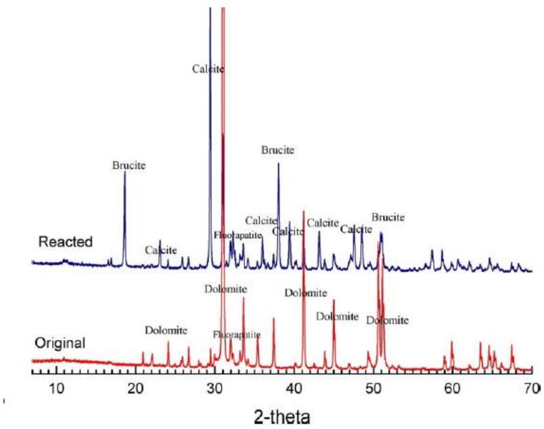

Figure 4: XRD patterns of phosphate tailings before and after alkali treatment. Utilization of tailings in cement and concrete: A review, Gou et.al.

The ore deposit from which each type of mine tailings originates determines the tailings' mineralogical and chemical composition. In metallic ore deposits, where copper, gold, iron ore, lead-zinc, nickel-cobalt, and uranium mine tailings are present, the various types of mine waste can primarily be classified. There are also non-metallic ore deposits that also contain coal ash or coal tailings and mine tailings containing phosphate minerals. The industrial mineral deposits are the last group, where mine tailings with residual potash salt and diamond content are produced.

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[3] Kontopoulos, "Environmental characterization of the sulfidic tailings in Lavrion"

It is crucial to mention the volcanogenic massive sulfide (VMS) deposits which are a specific type of ore deposit formed at the seafloor through hydrothermal processes associated with volcanic activity. These deposits contain a combination of valuable metals such as copper, zinc, lead, and sometimes precious metals like gold and silver. When these VMS deposits are mined and processed, the resulting tailings contain residual minerals and materials from the ore extraction and beneficiation processes. VMS tailings come from deposits that are rich in base metals.

Zinc in VMS tailings is often present as sphalerite ((Zn, Fe)S). Lead is often present as galena (PbS). This type of deposit can also contain various other sulfide minerals, such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and arsenopyrite (FeAsS). Finally, barite is often associated with VMS deposits and can be present in tailings as well.

1.1.2 Mine tailings dam facilities:

Mining waste is a significant environmental concern in the EU, constituting one of the largest waste streams. To manage these waste materials, tailings are typically stored in various ways, including dammed impoundments with different methods such as riverine disposal, submarine disposal, wetland retention, backfilling, dry stacking, and storage behind dammed impoundments [4]. Currently, the predominant method employed is the use of dammed impoundments, often referred to as “tailings pond” or “tailings dams.” In this approach, the tailings are stored underwater to prevent the formation of surface dust and the occurrence of acid mine drainage, which is cause by oxidation. This is especially important when there are substantial quantities of acid-generating minerals such as pyrite and pyrrhotite in the tailings.

Worldwide, billions of tons of water produced by mining operations are stored in tailings storage facilities (TSFs). Traditionally, these facilities have been wet mixtures of water, mine waste, and ground rock. However, in recent decades, dewatering technologies such as hydro-cycloning, thickening, filtration and paste facilities have been introduced to enhance the geotechnical and geochemical stability of conventional wet tailings. These advancements aim to reduce the risk of collapse associated with traditional wet tailings facilities that lack water removal processes. Despite the potential benefits of adopting advanced dewatering technologies, there is limited data available regarding their widespread implementation in the industry. A recent disclosure on tailings management revealed that only thirteen dry stack facilities had been constructed since 2000. Dry stacking is one of the methods that involve removing water from tailings to create a more stable and secure storage structure. While each tailings storage method has its own costs and benefits, it is evident that conventional wet tailings facilities pose the highest risk. By transitioning to dewatering technologies and incorporating methods like dry stacking, the industry can significantly improve the safety and stability of tailings storage facilities. However, further efforts are needed to promote the

[4] Kossof, “Mine tailings dams: Characteristics, failure, environmental impacts, and remediation”, p.g.232

adoption of these advanced technologies and to collect comprehensive data on their uptake across the mining sector[5].

For instance, one research focused on, developing different financial models and time-independent costing metrics, to understand the actual cost of tailings dams from pre-feasibility to closure. Some results showed that in the cost model of a specific case study, about the Teck Quebrada Balance Phase 2 (QB2) project, the overall capital cost (the cost that is depleted at the outset of the TSF construction period), was USD 4.739 billion. So, it is safe to say that building and preserving the tailings dams can be extremely costly[6].

Mine tailings have been used in paste backfill (cement paste backfill or hydraulic backfill), cement free concrete, concrete with aggregates substitution by tailings and as a road construction material. There is also some research done, about the utilization of mine waste in mortars as cement, filler, and aggregates replacement and in tiles.

1.1.3 Paste backfill:

Two prevalent types of tailings used in underground mine backfilling are paste fills and hydraulic fills. When the parent rock is crushed, its porosity can rise from insignificant levels to 40-45% when transformed into tailings for underground placement. Given the dry unit weight of waste tailings is approximately 15-20kN/m^3 and the porosity lies within 40-45%, slightly over 50% of the tailings can be effectively disposed of underground[7].

Backfills can exist as either uncemented or cemented geomaterials, encompassing tailings, sands, or waste rocks. Uncemented backfills include hydraulic fills, sand fills, aggregate fills, and rock fills, with rock fills and hydraulic fills constituting the majority. In contrast, cemented backfills include paste fills, cemented hydraulic fills, cemented aggregate fills, and cement rock fills. Notably a mining company might consume up to 100.000 tons of cement annually. Beyond the substantial carbon footprint tied to cement production, the high transportation costs to the mine site contribute significantly to the expense of incorporating cement into backfill formulations, even in modest proportions like 3-6% [8].

1.1.4 Cement paste backfill:

To effectively manage mineral tailings while considering technical, environmental, and economic factors, the cemented paste backfill (CPB) technology offers a promising solution and has gained widespread adoption. This innovative approach has the capacity to significantly transform and enhance the role of tailings in the mining industry [9]. The global production of concrete surpasses a staggering 10 billion cubic meters, as indicated by cement

[5] Cox, "A unified metric for costing tailings dams and the consequences for tailings management", p.g.1
[6] Cox, "A unified metric for costing tailings dams and the consequences for tailings management", p.g.7
[7] Sivakugan, "Underground Mine Backfilling in Australia Using Paste Fills and Hydraulic Fills", p.g.2 of 7
[8] Sivakugan, "Underground Mine Backfilling in Australia Using Paste Fills and Hydraulic Fills", p.g.4 of 7

[9] Qi, "Cemented paste backfill for mineral tailings management: Review and future perspectives".

output figures. This prolific output is occurring in tandem with ongoing innovations in cement and concrete mix components, presenting a unique opportunity for the repurposing and recycling of solid waste materials. Among these waste materials, tailings can play a crucial role when incorporated into cement and concrete formulations. This integration serves a dual purpose: mitigating the need for excessive tailings storage and contributing to the advancement of sustainability within the cement and concrete sector. This progressive approach aligns with the principles of sustainable development, fostering a more responsible and eco-friendlier trajectory for the industry [10].

The cemented paste backfill (CPB) technology comprises several essential components: dewatered mine tailings (with a solid content of 70-85% by weight), hydraulic binders (constituting 3-7% of the dry paste weight), and mixing water, which can be either fresh or processed. In certain cases, waste rocks and admixtures, such as superplasticizers, are incorporated to enhance particle size distribution and consistency. This versatile technology offers numerous benefits, including the safe disposal of tailings, mitigation of surface subsidence, reduced rehabilitation costs, and ground support-challenges that conventional tailings disposal methods often struggle to address effectively or at significant operational expense. Moreover, CPB has demonstrated its capacity to curtail water infiltration, stabilize heavy metals, and control the formation of acid mine drainage when employed as surface paste disposal [11].

1.1.5 Hydraulic backfill:

Backfilling has emerged as an environmentally friendly, economically efficient, and well-established approach for the sustainable management of mine waste. Beyond its waste management benefits, backfilling can also offer passive support and contribute to stabilizing the surrounding rock mass [12].

Hydraulic fills, often referred to as deslimed tailings or classified tailings, involve the removal of the clay fraction from total tailings by employing hydroclones[13]. This process of fines elimination significantly enhances drainage properties and expedites the consolidation of tailings. Rigorous laboratory examinations conducted on hydraulic fills sourced from various mines have indicated that, during self-weight consolidation, these fills slurries settle to a porosity level of approximately 40%, while their relative densities span the range of 40-70%[14].

In cases where the drainage of hydraulic fills is suboptimal, the accumulation of decant water above the fill leads to elevated pore water pressures. This, in turn, escalates the risks

[10] Gou, "Utilization of tailings in cement and concrete: A review", p.g.450
[11] Qi, "Cemented paste backfill for mineral tailings management: Review and future perspectives".
[12] Qi, "Cemented paste backfill for mineral tailings management: Review and future perspectives".
[13] Hydroclones or cyclones, are devices used in various industries for the separation, classification, and concentration of solid particles suspended in liquids or gates based on their size, density, and shape. They operate on the principle of centrifugal force generated by a high-speed flow of the fluid inside the cyclone.
[14] Sivakugan, "Underground Mine Backfilling in Australia Using Paste Fills and Hydraulic Fills", p.g.6 of 7

associated with liquefaction and places greater loads on dams. It is widely recognized that hydraulic fills should possess robust drainage characteristics to facilitate the swift removal of excess water from the stope, typically accomplished through barricades [15].

Throughout the filling operations, the hydraulic fill attains a state of saturation. During this phase, Darcy's law[16] can be aptly applied to calculate the flow rate, aiding in the determination of phreatic head at different time intervals. Following the completion of filling, the phreatic surface recedes, causing the fill above it to transition into an unsaturated state. Even after the passage of several months, residual moisture persists due to the presence of residual water within the voids [17].

1.1.6 What is Concrete:

Concrete, a fundamental construction material, plays a pivotal role in facilitating global infrastructure and construction endeavors. Its significance stems from its extensive application as a foundational substrate. The environmental ramifications of concrete are contingent upon its composition, encompassing the type of concrete and the proportion of cement employed. Given the diverse components constituting concrete, their ecological impacts vary considerably. The sustained viability of concrete raises pertinent long-term concerns, amplified by its ubiquitous utilization on a global scale.

1.1.7 Cement free concrete:

In the process of cement substitution in concrete production, the utilization of copper mine tailings as a partial cement replacement has been studied. Within this domain of exploration, the study focused on the incorporation of copper mine tailings into the mix, while designing concrete of M25 grade, conforming to IS:10262-2009 (the Indian standard code of practice for guidelines) [18].

A pivotal aspect in this context is the quantification of leached heavy metals form the tailings, which exhibits a strong correlation with variations in pH levels. To address this, a pre-incorporation assessment of the pH of mine tailings was conducted. The outcomes of this examination revealed a pH range spanning from 8.0 to 8.5. In the pursuit of optimal concrete performance, the granular attributes of cement emerge as a critical factor. These properties intricately regulate the pace at which cement solidifies and attains strength. To achieve desirable workability of cement, a diverse spectrum of particle sizes and angular shapes is

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[15] Sivakugan, "Underground Mine Backfilling in Australia Using Paste Fills and Hydraulic Fills", p.g.6 of 7

[16] Dracy's law is typically expressed in the following form:
$Q = -k \cdot A \cdot \frac{\Delta h}{L}$, where: *Q* is the volumetric flow rate of fluid through the porous medium, *k* is the hydraulic conductivity of the porous medium, representing its ability to transmit fluid, *A* is the cross-section area perpendicular to the flow direction, *Δh* is the difference in hydraulic head (elevation of the fluid) between two points along the flow path and *L* is the length of the flow path between the two points.

[17] Sivakugan, "Underground Mine Backfilling in Australia Using Paste Fills and Hydraulic Fills", p.g.7 of 7

[18] Kundu, "Stabilization characteristics of copper mine tailings through its utilization as a partial substitute for cement in concrete: preliminary investigations" p.g.2 of 9

sought after. This diversity contributes to the favorable properties necessary for the effective setting and strengthening of the cementitious material [19].

It is imperative that any partial replacement of cement maintains comparable properties to cement, to a certain extent. Considering this, the investigation into granular properties becomes crucial. In the context of this study, where mine tailings are employed as a partial cement replacement, an analysis of granular attributes has been undertaken. This scrutiny delves into the variety of irregular angular shapes and the extensive range of sizes present, a facet elucidated through Scanning Electron Microscopy (SEM) analysis. Notably, these granular characteristics bear a striking resemblance to Ordinary Portland Cement (OPC). This resemblance is further corroborated by the grain size distribution of mine tailings particles, which exhibits a pattern very similar to that of cement, but slightly coarser than cement. This alignment in granular attributes reinforces the viability of utilizing mine tailings as a partial cement substitute [20].

The assessment of compressive strength in concrete blocks, containing varying proportions of mine tailings, was conducted over durations of 3,7, and 28 days. These analyses served to validate the strength characteristics of the concrete compositions. The outcomes, showcase-a discernible trend: the substitution of cement with the mine tailings leads to a decline in compressive strength, a trend that persists across different concrete ages.

In specific, the 3-day compressive strength displayed a sequence of reductions at rates of 40% to 4%, corresponding to the mine tailings ratios of 50% to 10% respectively. In a similar pattern, the 28-day compressive strength decreased from 36% to 6% as the mine tailings proportions increased from 10% to 50%.

This decline in strength can be attributed to two primary factors. Firstly, the gradual decrease in cement content due to the inclusion of mine tailings results in a reduced quantity of hydration products, impacting overall strength. Secondly, the relatively inert nature of mine tailings, characterized by their larger size and non-reactive properties in contrast to ordinary Portland cement, contributes to the observed weakening effect.

However, it is noteworthy that the compressive strength for the 10% MT concrete showcased a pattern similar to that of the 0% mine tailings concrete, suggesting a more moderate impact. From these findings, a prudent approach when utilizing mine tailings in concrete entails employing it moderately, up to 10% by mass. This approach ensures a balance between

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[19] Kundu, "Stabilization characteristics of copper mine tailings through its utilization as a partial substitute for cement in concrete: preliminary investigations" p.g.5 of 9

[20] Kundu, "Stabilization characteristics of copper mine tailings through its utilization as a partial substitute for cement in concrete: preliminary investigations" p.g.5 of 9

concrete's mechanical properties and the potential benefits of cost reduction in binding agent materials [21].

The outcomes of the semi-dynamic leaching tests revealed a consistent pattern: The quantity of metal release decreased as the proportion of mine tailings replacing cement increased. Furthermore, a recurring observation was that the immobilization of elements became more pronounced as curing time increased.

Moreover, when focusing on the elements that raised concerns in the context of TCLP and ASTM tests, namely Zn, Co, Mn, and Ni, it is noteworthy that these elements demonstrated absolute immobility within the scope of the semi-dynamic leach tests. This finding underscores the potential effectiveness of the studied treatment in immobilizing these particular elements [22].

1.1.8 Concrete with mine tailings as an aggregate's replacement:

Environmental scholars and advocates, express apprehension regarding the escalating utilization of riverbed-derived sand and gravel for construction purposes. Notably, this trend is exacerbated by the proliferation of concrete deployment, concomitant with the rapid urbanization and industrialization witnessed across the global demographic landscape, consequently leading to the escalated extraction of natural sand deposits from riverbed environments. The escalation in demand for natural resources parallels the steady ascent of living standards, contributing to a commensurate upsurge in industrial waste generation. In response to this environmental challenge, the prospect of repurposing waste materials as secondary resources emerges as a pragmatic stratagem, poised to alleviate ecological pressures and foster the attainment of sustainability objectives [23].

To leverage mine tailings effectively as aggregates within concrete formulations it is imperative to comprehensively examine their particle size distribution, morphological characteristics, and loss on ignition (LOI) attributes. In particular, the particle size distribution, encompassing a spectrum of sizes, delineates the proportion of aggregates present. This gradational aspect significantly influences the compactness of the resultant concrete matrix. Notably, a lower fineness modulus corresponds to heightened water requisites, invariably impacting concrete's strength adversely [24]. Given the inherently fine nature tailings, their particle size distribution necessitates amelioration before suitability as aggregates can be

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[21] Kundu, "Stabilization characteristics of copper mine tailings through its utilization as a partial substitute for cement in concrete: preliminary investigations" p.g.6 of 9
[22] Kundu, "Stabilization characteristics of copper mine tailings through its utilization as a partial substitute for cement in concrete: preliminary investigations" p.g.8,9 of 9
[23] Arbili, "Concrete Made with Iron Ore Tailings as a Fine Aggregate: A Step towards Sustainable Concrete", p.g.2
[24] Li, "The Study on used properties of mine tailings sand", p.g.88

ascertained. This necessitates the implementation of an agglomeration process, also termed as granulation [25].

For example a study underscores the potential for judiciously exploiting substantial quantities of mine tailings through their transformation into synthetic aggregates via granulation. These tailings, predominantly comprising calcite and quartz, underwent rigorous mixing within a high-intensity mixer alongside a cementitious binding agent. Notably, optimal strength outcomes, achieved with minimal cement clinker content, were observed when employing a specific type of cement. By modulating the proportion of the cement, the granule's crushing strength could be meticulously controlled. Intriguingly, a 5 wt% infusion of the cement (corresponding to 95 wt% tailings) proved adequate in yielding robust aggregates applicable across a spectrum of concrete products.

Critical to this process is the particle size distribution of the tailings, which exerts a pivotal influence on the resultant aggregate's crushing strength. It is recommended that an effective aggregate quality post-granulation is achieved by maintaining a particle size distribution characterized by $d50<10\mu m$ and $d90<50\mu m$. Optimizing granulation parameters, achieved through a systematic screening process, entailed determining optimal water content, pan speed, and rotor speed. By implementing specific parameters-specifically, water content of 16 wt%, pan speed of 1.1m/s, and rotor speed ranging from 3-5 m/s- a granule crushing strength of 3.1 MPa was realized after 28 days. Notably, such granules displayed a water absorption capacity of 14%, while a stable granule size was achieved within a total mixing duration of 10 minutes [26].

Tailings, characterized by their irregular and amorphous aggregate nature, offer distinct advantages in terms of robust strength and a favorable adherence to concrete, setting them apart from conventional natural sands. However, they are accompanied by certain limitations, including deficient water retention, a modest degree of slip resistance, and suboptimal grading. Consequently, when tailings are incorporated into concrete mixes, a dual objective is achieved: not only does the resulting concrete exhibit commendable performance characteristics but is also attains elevated fluidity while minimizing slump loss, thereby adhering to the specified goals [27].

Intrinsically, tailings comprise a discernible proportion of fine powder, which, when combined with cement and water, culminates in the formation of a slurry. This synergistically enhances the workability of the concrete matrix, concomitantly ameliorating the likelihood of bleeding and segregation phenomena. However, a caveat exists, exceeding a tailings content threshold

[25] Peys,"Transformation of mine tailings into cement-bound aggregates for use in concrete by granulation in a high intensity mixer", p.g.2
[26] Peys,"Transformation of mine tailings into cement-bound aggregates for use in concrete by granulation in a high intensity mixer", p.g.8,9
[27] Li, "The Study on used properties of mine tailings sand", p.g.88

of 60% amplifies the powder concentration, potentially leading to an overly viscous and dry concrete mixture, thereby heightening the potential for segregation [28].

In assessing the ignition loss, a crucial parameter in tailings evaluation, the quantification stems for the evaluation of liberated crystallization water during the billet firing process. The computation of loss on ignition within mine tailings arises from the decarbonization of the carbonate constituents and the subsequent sulfate decomposition, with the exclusion of organic impurities from the volumetric analysis post-loss [29].

Iron Ore Tailings are very well known to be used as aggregates substitution in concrete. A comprehensive examination of concrete performance upon the inclusion IOT has been undertaken through an assessment of multiple studies conducted over the past decade. The synthesized findings yield the following insights:

In terms of physical attributes, the coarse and angular nature of IOT particles inherently diminishes the concrete's flowability. Chemically, the composition and XRD analysis of IOT demonstrate its capacity to function as a binding material. Fresh concrete properties, such as slump flow and compactability, undergo a reduction with the introduction of IOT. Notably, up to a 40% substitution level of IOT appears to maintain satisfactory flowability and compactability. For higher substitution rates, the supplementation of a plasticizer is advocated to mitigate potential changes. Mechanically, the incorporation of IOT generally is attributed to micro-filling voids and potential pozzolanic reactions. Divergent optimal dosages are suggested by various researchers, albeit a consensus emerges around an optimal range of 30-40%. It is noteworthy, however, hat exceeding the 40% IOT substitution threshold detrimentally impacts concrete's mechanical strength. Impressively, a concrete mixture with 20% IOT substitution showcases a 14% boost in compressive strength compared to reference concrete.

Furthermore, the substitution of IOT manifests notable benefits in terms of water absorption reduction, diminished chloride penetration, and mitigated dry shrinkage. Scanning Electron Microscopy (SEM) analyses shed light on the reinforcement of crack mitigation resulting from IOT substitution, attributed to the filling of voids and instigation of pozzolanic reactions [30].

1.1.9 Mine tailings used as road construction materials:

A promising avenue for the utilization of mining waste as alternative aggregates is in the domain of road construction. This approach not only holds the potential to conserve precious natural resources but also carries the capacity to significantly curtail the ecological footprint of mining activities. The study underscores the imperative need for the establishment of tailored legislation and comprehensive guidelines to facilitate the widespread integration of

[28] Li, "The Study on used properties of mine tailings sand", p.g.88, 89
[29] Li, "The Study on used properties of mine tailings sand", p.g.89
[30] Arbili, "Concrete Made with Iron Ore Tailings as a Fine Aggregate: A Step towards Sustainable Concrete", p.g.20

mining wastes in road construction endeavors, a regulatory void that presently impedes progress in this area. By leveraging mining wastes as construction materials for roads, a dual advantage of waste volume reduction and sustainable waste management is envisaged, fostering a more environmentally responsible mining industry. Furthermore, the practice contributes to the sustainable advancement of exploited regions, aligning with eco-friendly principles across diverse facets of mining, including exploration, methodologies to encourage the adoption of alternative materials through by-product recovery or recycling strategies stand to foster resource conservation, harmoniously resonating with the core tenets of sustainable development.

The extensive review done on the utilization of mine tailings as road construction materials, highlights instances where mining wastes have been judiciously employed to address inadequate soil properties, such as low bearing capacity and frost susceptibility, thereby bolstering the infrastructure projects. Various techniques were harnessed to utilize the potential of mining wastes, encompassing direct use and the application of hydraulic binders through geopolymerization or bituminous treatments. This innovative approach not only presents an opportunity to abate natural resource depletion and environmental degradation linked to mining but also underscores the importance of enacting precise legal frameworks and guidelines conductive to the large-scale adoption of mining waste-based road construction. In summary, the study unveils a pathway towards sustainable development by harnessing mining wastes for road construction, ultimately steering the mining industry towards more ecologically conscious and progressive practices, while concurrently securing the longevity of exploited regions and mitigating waste-related environmental pressures [31].

1.1.10 Utilization of sulfidic mine tailings in tiles:

Comparative analyses were conducted among ceramic roof tile samples with varying MT percentages (5%, 10%, and 20%) to assess properties such as density, water absorption, and firing shrinkage. Additionally, the research done assessed the firing temperature and potential energy conservation facilitated by the integration of MT into the ceramic formulation. Notably, the research introduced a pragmatic approach to tackle sulphate gas emissions during firing: By inducing a reaction with water, sulfuric acid by-products are generated, suggesting a means to mitigate the environmental consequences of sulfuric acid formation. The investigation revealed that the inclusion of sulfidic mine tailings positively impacted the properties of ceramic roof tiles, including density, water absorption, and firing shrinkage. This effect was most pronounced with the addition of 20% MT, which led to a reduction in firing temperature form 1150^{o}C to 1050^{o}C, subsequently yielding energy savings and reduced costs. The study also identified the optimal temperature range for sulphate decomposition within mine tailings, particularly around 700^{o}C, beyond which sulphates were not present in the composition. From an environmental perspective, the study's proposal for sulphate gas emission management through sulfuric acid by-product generation offers a

[31] Segui, "Mining Wastes as Road Construction Material: A Review", p.g.13-18

potential avenue for mitigating the ecological impact of sulfuric acid formation, thus rendering it a feasible alternative, particularly for regions where ceramic plants are situated within 50km radius of mine sites [32].

1.1.11 Utilization of mine tailings in mortars as cement replacement:

There many studies conducted about the utilization of mine tailings as a partial replacement for cement in mortar formulations, where mine tailings are analyzed and then incorporated into mortars, of which the mechanical performance is tested afterwards.

In one study, two distinct types of mine tailings, from Zinkgruvan and Nalunaq mines, were harnessed to partially replace cement in mortar specimens. The research entailed a comparative assessment of the compressive strength of mortar specimens containing mine tailings against reference specimens and those incorporating coal fly ash (CFA), a common cement substitute. Initial chemical examination of leaching tendencies from both the mine tailings and the mortar specimens. Detailed characterization efforts encompassed particle size distribution, pH levels, conductivity, carbonate content, water content, solubility, loss on ignition, and mineral composition profiling of the mine tailings. The interplay between mine tailings and cement's calcium content was probed to discern potential influences on the mechanical properties of the mortar specimens [33].

Key findings indicated that the compressive strength of mortar specimens incorporating mine tailings as partial cement replacement lagged that of reference specimens at curing intervals of 7, 14, and 28days. Both types of mine tailings exhibited contribution to pozzolanic activity, with Zinkgruvan demonstrating a more pronounced tendency. Notably, the compressive strength of mortar specimens integrating mine tailings surpassed that of coal fly ash-containing counterparts, signifying the potential of mine tailings, attributed to their amorphous volcanic-derived content, to enhance compressive strength through heightened pozzolanic activity. Most importantly, no indications of toxic chemical element leaching were evident from either the pure tailings or the corresponding mortar specimens. The study concluded that mine tailings hold promise as mineral admixture for cement substitution in mortar formulations, thereby curbing tailings deposition and mitigating CO2 emissions linked to cement production [34].

Another example of a study is focusing on the viability of repurposing copper mine tailings (CMT) as a partial substitute for cement within paste, mortar, ad concrete mixtures. The enhanced performance of CMT-modified mortar composition is evidenced by higher strength, heightened sulfate resistance, and bolstered environmental sustainability compared with reference mortar formulations. The successful integration of CMT as a partial cement

[32] Paiva, "Production of ceramic construction materials as an environmental management solution for sulfidic mine tailings".
[33] Sigvardsen, "Utilization of Mine tailings as partial cement replacement", p.g.272, 274
[34] Sigvardsen, "Utilization of Mine tailings as partial cement replacement", p.g.276-277

substitute in mortar formulations was demonstrated, with CMT-modified mortar meeting minimum SAI (strength activity index) requirements on the 28th and 90th days. Enhanced mechanical strength was particularly notable in CMT-blended concrete, especially when incorporating 5%-20% CMT. Also, the sulfate resistance of CMT-blended formulations surpassed that of the reference. XRD results corroborated CMT's potential as a robust cement replacement. Although minor impacts on water demand and setting time were observed, their influence remained negligible [35].

1.1.12 Utilization of mine tailings in mortars as filler replacement:

Mine tailings can also be used as filler replacement in mortar formulations. More specifically, there an examination done that delves into the utilization of molybdenum mine tailings as an augmenting filler material within cement mortar, aiming to bolster its mechanical attributes and durability. The infusion of molybdenum mine tailings yields tangible enhancements in the performance of cement mortar, as evidence through augmented compressive strength, flexural strength, ultrasonic pulse velocity, dynamic modulus of elasticity, and density. Moreover, the incorporation of these mine tailings contributes to the reinforced resilience of the mortar against water absorption and chemical aggressions, such as sulfate and acid attacks, while concurrently mitigating total voids within the mortar structure [36].

The outcomes of this study reveal a notable enhancement in the mechanical properties and durability of cement mortar upon the infusion of molybdenum mine tailings as a filler material. This effect is particularly evident in the compressive strength, where the dosage of mine tailings demonstrates a discernible influence, corresponding to improved mechanical performance as tailings content increases. Remarkably, the introduction of 20% mine tailings yields a 16% upswing in mechanical efficacy after 28 days, whereas a 10% tailings incorporation translates to a remarkable 20% reduction in total voids within the mortar. Moreover, the integration of mine tailings leads to decreased water absorption via capillaries, underscoring its enhanced resistance against water infiltration. Consequently, the study contends that a prudent usage of up to 10% molybdenum mine tailings effectively facilitates the production of masonry mortar closely mirroring the properties of conventional mortar. In essence, this strategic integration offers a sustainable solution for recycling these materials while contributing to reinforced mechanical traits and enduring performance of cement mortar [37].

1.1.13 Utilization of mine tailings in mortars as aggregates replacement:

[35] Esmaeli, "Reuse potentials of copper mine tailings in mortar and concrete composites".
[36] Salman, "Assessing of molybdenum mine tailings as filler in cement mortar", p.g.2.
[37] Zhao, "An evaluation of iron ore tailings characteristics and iron ore tailings concrete properties", p.g.7

Ore-sand refers to a specialized form of processed sand acquired either as a co-product during the mechanical processes of mineral ore extraction, involving techniques such as crushing, grinding, and beneficiation. There are various studies done in the utilization of mine tailings as an aggregate's replacement in mortar formulations.

For example, in a specific study, the investigation done encompassed the partial replacement of natural sand with gold mine tailings in the formulation of masonry mortars, with replacement percentages of 10%, 20%, and 30%. The analysis focused on properties of masonry mortars, including water retentivity, drying shrinkage, and compressive strength. The study examined the influence of partially substituting natural sand with gold mine tailings on masonry mortar properties. Findings revealed that water retentivity heightened with sand fineness across all sand types, while drying shrinkage escalated as sand fineness increased. With the incorporation of gold mine tailings, the compressive strength of the mortar decreased, with reductions of 31%, 35%, and 57% for replacement levels of 10%, 20%, and 30%, respectively. Notably, after 56 days of curing, the compressive strength displayed an augmentation for all sand types, with increases of 70%, 65%, and 100% for 10%, 20%, and 30% tailings replacement, respectively. The presence of CaO in gold mine tailings was attributed to the enhanced compressive strength, based on its contribution to cement hydration [38].

1.1.14 The potential pozzolanic activity of mine tailings:

Pozzolanic activity of a substance is characterized by its capacity to interact with portlandite ($Ca(OH)_2$) when exposed to water. This property is particularly depended on several characteristics, among which the material's chemical and mineralogical composition are the determining factors. Equally impactful are the content of the amorphous phase, the extent of dehydroxylation, the surface area, the concentration of $Ca(OH)_2$ within the paste, the admixture composition, and the water-to-binder ratio in the mortar mix [39].

In the field of solid waste research, certain solid residues, like blast furnace slag and fly ash, have gained widespread utilization in cementitious materials due to their notable pozzolanic activity. Divergent from amorphous solid waste, mine tailings possess stable crystalline attributes at ambient temperatures, rendering their application as active additives in cementitious substances questionable. In pursuit of enhancing their reactivity, researchers have explored effective strategies such as thermal, chemical, and mechanical activation. Among these, mechanical activation through grinding, a pivotal physical pre-treatment technique for minerals, is commonly employed to induce crystal defects during the grinding

[38] Vignesh, "Effect of partial replacement of natural sand with gold mine tailings on some properties of masonry mortars", p.g.585
[39] Bakolas, "Evaluation of pozzolanic activity and physico-mechanical characteristics in metakaolin lime pastes", p.g.158

process. This approach thereby enhances the reactivity of minerals that exhibit insufficient interaction with other elements.

Past investigations into the mechanical activation of minerals indicate its efficacy in increasing the reactivity of mineral powders. For instance, in one research where it was studies the impact of mechanical grinding media on the surface physicochemical attributes of scheelite and fluorite minerals revealed a substantial alteration in morphological parameters, reactivity, and flotation behavior induced by mechanical activation. This has significant implication for guiding particle surface modification through mechanical activation. Furthermore, another research detailed how mechanical activation resulted in modification to the crystal structure of quartz, enhancing its reactivity via mechanical griding. Ground quartz exhibited a tendency to react with calcium hydroxide to form a limited amount of C-S-H gel, owing to its pozzolanic reaction at ambient temperatures [40].

1.1.15 *Activation of mine tailings:*

There are various strategies assessed for activating mine tailings with the intension of enhancing their cementitious properties and mitigating their adverse environmental consequences. The activation techniques encompass physical, chemical, and thermal methodologies, all aimed at augmenting the reactivity and mechanical strength of the tailings for potential utilization as either a cement replacement or an additive in concrete production. The investigative approach involves a comprehensive review of methodologies aimed at enhancing the cementitious characteristics and reusability of mine tailings.

- Physical activation methodologies encompass procedures such as grinding, sieving, and blending, tailored to intensify the tailings' reactivity.
- Chemical activation methodologies involve the integration of chemical additives or activators to facilitate the pozzolanic reaction and ameliorate the cementitious attributes of the tailings.
- Thermal activation methodologies encompass subjecting the tailings to elevated temperatures to induce chemical reactions and enhance their reactivity.

Further enhancement of tailings properties is contemplated through the integration of diverse activation techniques, including mechanochemical, mechanical-thermal, and thermal-chemical amalgamations. The findings underscore the potential environmental conservation and economic advantages associated with the effective management and repurposing of mineral waste and tailings. The activation of mineral tailings emerges as a promising avenue to enhance their cementitious properties and alleviate the detrimental ecological ramifications linked with cement manufacturing [41].

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[40] Saedi, "A review on different methods of activating tailings to improve their cementitious property as cemented paste and reusability", p.g.8.
[41] Saedi, "A review on different methods of activating tailings to improve their cementitious property as cemented paste and reusability".

1.2 Research questions

- Can mine tailings effectively function as partial replacement for cement in mortar formulations?
- Can mine tailings effectively serve as partial replacements for aggregates in mortar formulations?
- Is it feasible to use mine tailings to partially substitute both cement and aggregates in a mortar formulation?
- To what extend does the particle size of the tailings affect mortar properties, such as workability, and physical and mechanical performance?
- Do problematic phases within the tailings play a significant role in the workability, physical characteristics, and mechanical behaviour of the mortars?
- Are mine tailings reactive materials, and if so, what factors contribute to their reactivity?
- Do mine tailings exhibit pozzolanic activity, and how does this property impact mortar performance?

1.3 Thesis objective

The primary aim of this thesis is to explore the potential utilization of mine tailings as partial replacement for cement and/or aggregates in mortar formulations. These innovative mortars could serve two main purposes: the rehabilitation of contemporary infrastructures (grouts) and the restoration of cementitious monuments using compatible repair mortars. Through this research the comprehensive goal is to repurpose mine tailings, considered as waste material, and benefit from their properties as substitutes for cement and/or aggregates in mortar formulations.

It is important to note that this research focuses on mine tailings sourced from two distinct deposits: Vulcanogenic massive sulfides (VMS) and Iron ore tailings (IOT). The specific tailings analysed in this study include:

1. Zinkgruvan tailings (VMS) from Askersud in Sweden. The Zinkgruvan mine is owned by a company called Lundin Mining and it extracts zinc, lead, copper and silver.
2. Kiruna tailings (IOT) from Kiruna in Norbotten County, Lapland, Sweden. The Kiruna mine is owned by the company Luossavaara-Kiirunavaara AB (LKAB). The minerals extracted from this mine are mainly magnetite and apatite and in smaller amounts actinolite, calcite, diopside and biotite.
3. Brucutu mine tailings (IOT) from Brazil. The Brucutu mine tailings are owned by the company Vale, where they extract iron, nickel, copper, manganese & alloys and coal.

2 Literature review:

The theoretical framework presented above draws upon scholarly contributions found in scientific journals, conference proceedings, and a book. However, the existing literature primarily centres on the mineralogical and chemical analysis of mine tailings in a general context, focusing on individual tailings deposit types in separate studies.

Numerous investigations have explored the application of mine tailings in paste backfill and concrete usage, with fewer studies delving in their incorporation into mortar formulations. Yet, a comprehensive exploration encompassing the characterization of mine tailings from various ore deposits, coupled with an evaluation of the physical and mechanical attributes of mortars containing such tailings, remains absent.

Moreover, a research gap exists in the examination of how mine tailings can be integrated to formulate diverse mortar types suitable for rehabilitating modern structures (grouts) and restoring cementitious historical buildings from the 19^{th}-20^{th} century (repair mortars). Furthermore, a detailed investigation into the pozzolanic activity of mine tailings derived from distinct ore deposits has yet to be undertaken.

This thesis is focused on analytical investigations, involving the mineralogical, chemical, and pozzolanic assessment of different tailings types. More specifically, tailings sourced from VMS and IOT ore deposits are used for the design of two distinct mortar formulations replacing cement/filler and/or aggregates. This research achieves in the successful activation of both tailings types, thereby enhancing the overall performance of the resulting mortars. Rigorous workability, mechanical and physical evaluations are subsequently conducted on these mortars.

Significantly, these formulated mortars are intended for application in the rehabilitation of modern structure and the preservation of historic cement-based monuments. This multifaceted exploration fills critical gaps in the existing research represents a step ahead for advancing practices in sustainable construction and restoration sectors.

3 Methodology:

3.1 Characterization techniques of mine tailings:

3.1.1 XRD, Xray diffraction

X-Ray diffractometers consist of three fundamental elements: an X-Ray tube, a sample holder, and an X-Ray detector.

The generation of X-rays within a cathode ray tube follows a process whereby a filament is heated to emit electrons. These electrons are subsequently accelerated towards a designated target through the application of voltage, resulting in the bombardment of the target material by electrons. As the energy of the electrons surpasses the threshold required to displace inner shell electrons of the target material, distinct X-ray spectra are produced. These spectra encompass various components, with Kα and Kβ being the most prevalent. The Kα component includes $K\alpha_1$ and $K\alpha_2$, whereby $K\alpha_1$ exhibits a marginally shorter wavelength and twice the intensity of $K\alpha_2$. These wavelengths are indicative of the chosen target material (such as Cu, Fe, Mo, or Cr). To generate the monochromatic X-Rays essential for diffraction, filtration through foils or crystal monochromators is necessary. Due to the slight proximity of $K\alpha_1$ and $K\alpha_2$ wavelengths, a weighted average of the two is commonly employed. Notably, copper (Cu) is frequently utilized as the target material for single-crystal diffraction, utilizing CuKα radiation with a wavelength of 1.5418 Å. These collimated X-rays are then directed onto the sample. During the rotation of both the sample and the detector, the intensity of reflected X-rays is meticulously recorded. Constructive interference and the subsequent intensity peak emerge when the incident X-rya geometry aligns with the Bragg Equation[42]. The resulting X-ray signal is detected and processed by a detector, ultimately transforming into a count rate. This count rate is subsequently outputted to a designated device, such as a printer or a computer monitor.

The geometrical configuration of an X-ray diffractometer is such that the sample is subjected to rotation within the collimated X-ray beam's trajectory at an angle θ. Simultaneously, the X-ray detector, affixed to an arm, captures the diffracted X-rays, and undergoes rotation at an angle of 2θ. The apparatus responsible for maintaining the angle and managing the sample's rotation in known as a goniometer [43].

For the measurements taken for this study a Brucker D8 ADVANCE diffractometer was used, the angle range was 3-65° 2θ, the step size: 0.015°, the time per step was 1.0s (BL), and the radiation was Cu-kα.

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[42] $n \times \lambda = 2 \times d \times \sin(\theta)$, where n is the order of diffraction, λ is the wavelength of the X-ray or electron beam, d is the spacing between crystal lattice planes, and θ is the angle between the incident X-ray or electron beam and the lattice planes

[43] [X-ray Powder Diffraction (XRD) (carleton.edu)]

3.1.2 XRF, Xray fluorescence

An X-ray fluorescence (XRF) spectrometer serves as an X-ray instrument pivotal for conducting routine, minimally intrusive chemical analyses of a variety of substances including rocks, minerals, sediments, and fluids. Operating on principles rooted in wavelength-dispersive spectroscopy similar to those employed in an electron microprobe (EPMA), an XRF instrument offers a comparable approach. However, the spatial resolution of an XRF is typically not conducive to performing analyses at the fine spot sizes commonly associated with EPMA work (ranging from 2 to 5 microns). As a result, the XRF method is typically harnessed for comprehensive analyses of larger quantities of geological materials.

The capability to analyze major and trace elements within geological materials via XRF is enabled by the interaction of atoms with X-radiation. The functioning of an XRF spectrometer relies on the response of a sample when subjected to an intense X-ray beam, referred to as the incident beam. As the incident X-ray beam interacts with the sample, a portion of its energy is scattered, while another portion is absorbed within the sample in a manner contingent upon its chemical composition. Conventionally, the incident X-ray beam originates from a rhodium (Rh) target; however, alternative materials such as tungsten (W), molybdenum (Mo), chromium (Cr), and others can also be employed, based on the specific application.

Upon illumination by the primary X-ray beam, the sample becomes excited. This excited state prompts the sample to emit X-rays spanning a spectrum of characteristic wavelengths corresponding to the atoms present within it. The underlying mechanism involves the absorption of X-ray energy by atoms sample, leading to the ionization of electrons from lower energy levels (typically K and L levels). These ejected electrons are subsequently replaced by electrons from higher energy orbitals. This transition results in the release of energy due to the outer one. This energy manifests as the emission of characteristic X-rays indicative of the type of atom within the sample [44].

X-ray fluorescence (XRF) was determined using a WDXRF Rigaku Supermini200 equipped with Pd- x-ray tube. The samples were prepared as pressed powder pellets or by using the borate fusion method.

[44] X-Ray Fluorescence (XRF) (carleton.edu)

3.1.3 PSD, particle size distribution

The technique involves illuminating a collection of particles with laser light and deriving the particle size distribution through analysis of the emitted diffracted/scattered light's distribution pattern.

The following outlines the fundamental principle underlying the measurement of particle size distribution as employed in the SALD Series Laser Diffraction Particle Size Analyzer. Upon exposure to a laser beam, particles emit light in diverse directions-forward/backwards, upwards/downwards, and horizontally termed as "diffracted/scattered light." The intensity of diffracted/scattered light forms a consistent spatial arrangement aligned with the light's emission direction, referred to as the "light intensity distribution pattern." The pattern of light intensity distribution is recognized to vary in accordance with particle size.

A direct and proportional relationship between particle size and the light intensity distribution pattern becomes apparent. In essence, discerning particle size becomes feasible by detecting the light intensity distribution pattern. In practical particle size distribution analysis, the focus extends beyond a solitary particle to encompass a conglomerate of particles. Such an aggregate comprises diverse particles of varying sizes, with the resultant intensity distribution pattern of emitted diffracted/scattered light being the outcome of overlapping contributions from individual particles. Through the detection analysis of this light intensity distribution pattern, insight into the particle size distribution is attainable-specifically, the range of particle sizes, and their respective proportions [45].

For the determination of the particle size distribution (PSD) using laser diffraction of tailings a Sympatec HELOS device was used in wet dispersion with distilled water (QUIXEL).

3.1.4 FTIR, Fourier transform infrared spectroscopy.

Fourier transform infrared spectroscopy represents the prevalent variant of infrared spectroscopy. This technique operates based on the fundamental principle that when infrared (IR) radiation traverses a specimen, certain portions of the radiation are absorbed, while the transmitted radiation is captured. Owing to the distinct molecular structures of various substances, diverse spectra are generated, enabling the identification and differentiation of molecules. These spectra serve as analogous entities to human fingerprints or DNA profiles, each essentially unique.

FTIR is favored for infrared spectroscopy due to several advantageous attributes. Firstly, it avoids sample destruction. Secondly, it boasts substantially heightened speed compared to conventional methods. Thirdly, it exhibits heightened sensitivity and precision. These advantages of FTIR are underpinned by the utilization of an interferometer, the source of infrared radiation, which contributes to its enhanced speed, along with the application of

[45] Particle Size Distribution Measurement by the Laser Diffraction/Scattering Method Part1 : SHIMADZU (Shimadzu Corporation)

Fourier transform. The Fourier transform, a mathematical operation, deconstructs waveforms to derive their frequencies in relation to time. The outcome of the interferometer is not the final spectroscopy spectrum; instead, it takes the form of an "interferogram," a graph. Subsequently, the Fourier transform converts this interferogram into the recognizable and usable graph of the infrared spectroscopy spectrum.

The operational principle of FTIR is depending on a molecule's covalent bonds selectively absorb radiation at specific wavelengths, modifying the vibrational energy within the bond. The type of vibration induced (stretching or bending) by the infrared radiation hinges on the atoms constituting the bond. Diverse bonds and functional groups absorb distinct frequencies, resulting in varied transmittance patterns for different molecules [46].

Fourier-transform infrared spectroscopy (FTIR) was determined using Thermo Scientific Nicolet iS50 FT-IR Spectrometer with a wavenumber range: 4000-400cm^{-1}. The samples were analyzed as powders using the ATR method. The tailings powders were analyzed individually, then the tailings were used in to making pastes of 90%lime, 10% mine tailings. The FTIR measurements of these pastes were taken after 7days and after 30days since the pastes were made.

3.1.5 TGA, Thermogravimetric analysis

Thermogravimetric Analysis (TGA) involves a continuous measurement of the weight of a sample while subjecting it to heating within an inert gas environment. Many solid materials undergo reactions that release gaseous byproducts. In the TGA method, these gaseous byproducts are effectively eliminated, and any alterations in the residual mass of the sample are meticulously documented. Three common variations of TGA are as follows:

Dynamic TGA: In this variant, the temperature is systematically elevated over time, concomitant with the recording of changes in mass. This approach allows for the concurrent determination of the quantity of gas released and the corresponding temperature at which these changes occur.

Static TGA: In this scenario, the temperature is held at a constant level while the mass of the sample is monitored. This method is valuable for gaining deeper insights into decomposition processes that transpire at specific temperatures or for assessing a material's capacity to endure a particular temperature threshold.

Quasistatic TGA: In this approach, the sample undergoes heating across multiple discrete temperature intervals, with each interval being maintained for a period until the sample's mass stabilizes. Quasistatic TGA is particularly well-suited for the analysis of substances that are known to decompose through distinct mechanisms at varying temperatures. This

[46] Was ist FTIR-Spektroskopie? (sigmaaldrich.com)

technique facilitates a more comprehensive understanding of the decomposition pathways and behaviors exhibited by these materials [47].

Thermogravimetric analysis (TGA) was operated using Setaram Labsys Evo 1600°C thermal analyzer, where each individual tailings were measured as powders. TGA measurements of the pastes with lime and tailings mentioned above, were taken in the Institute of Geoenergy at the Foundation for Research & Technology, after 30 days that the pastes were produced.

3.1.6 Luxan Test for assessing pozzolanic activity.

The assessment of pozzolanic activity in natural products was accomplished through conductivity measurement, which proved to be the most suitable parameter for this purpose. The methodology centered on determining the compensated conductivity of a solution saturated with calcium hydroxide, into which the material was introduced progressively. Impressively rapid results, achievable within a mere two-minute timeframe, were attained using this technique [48].

For assessing the pozzolanic activity of mine tailings the following process took place: a polyethylene flask with a capacity of 600ml was utilized, equipped with a thermometer and a conductivity measurement cell, which is connected to a conductometer. This setup is placed within a water bath that is thermostatted at 40 ± 1°C.

An initial step involves adding 200ml of a $Ca(OH)_2$ solution that is saturated and maintained at a temperature of 40 ± 1°C. The initial compensated conductivity of this solution is recorded. Following this a specific amount of the material, weighing 5.00g, is introduced. This material has been previously dried in an oven at a temperature of 105 ± 5°C. The solution is kept under continuous stirring throughout the procedure.

Conductivity measurements are then conducted for a duration of 120 seconds. Subsequently, the variation between the initial and final compensated conductivity values is ascertained. If a sample is pozzolanic or not is determined due to the following table:

Material classification	Conductivity variation-ΔC (mS/cm)
Non pozzolanic	**< 0.4**
Variable pozzolanicity	**0.4 - 1.2**
Good pozzolanicity	**> 1.2**

[47] Thermogravimetric analysis (TGA) - Chemistry LibreTexts
[48] Luxan, "Rapid evaluation of pozzolanic activity of natural products by conductivity measurement".

Table 1: Material classification as non-pozzolanic to pozzolanic using the Luxan Method.

Where ΔC is calculated by the conductivity of the $Ca(OH)_2$ solution minus the conductivity measurement when the sample is added to the solution.

3.1.7 Determination of calcium carbonate with the Bernard calcimeter method:

Figure 5: The experimental arrangement

The Bernard calcimeter method is employed to determine the quantity of free calcium carbonate present in a sample. This method relies on measuring the volume of carbon dioxide (CO2) liberated through the reaction of hydrogen chloride solution (HCl) with the carbonates within the test sample. The chemical reaction driving this process is as follows:

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$

Initially, a 0.1g sample is introduced into a container. In a separate test tube, 5ml of hydrogen chloride (HCl) is added. Subsequently, the test tube containing HCl is placed within the container. The container is then sealed using a cap until both tubes reach the same level. The container is gently rotated to expel the HCl form the test tube, allowing it to react with the sample. If the sample indeed contains calcium carbonate, the ensuing release of carbon dioxide leads to a shift in the liquid level within the tube. The lowest point that the liquid level attains is meticulously recorded [49].

3.1.8 Calorimetry:

Calorimetry encompasses the measurement of heat change occurring during a chemical reaction, indicating the amount of heat released or absorbed. This quantification assists in discerning whether a reaction is exothermic (releasing heat) or endothermic (absorbing heat). Calorimetry stands as a pivotal component of thermodynamics, given its role in heat measurement during reactions. Isolation of the reaction to prevent heat loss to the surroundings is essential for accurate measurement. This is facilitated through the use of calorimeters, devices that insulate reactions to contain heat [50].

For measuring the calorimetry of the mix designs containing mine tailings, a Calmetrix device was used, where 50g of each sample were measured at constant temperature 23°C.

[49] "Determination of carbonates in soils by the Bernard Calcimeter method (UNE 7-367).
[50] Calorimetry - Chemistry LibreTexts

3.1.9 *Toxicity measurement using ICP-MS:*

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) is an analytical method utilized for the determination of trace concentrations of multiple elements and isotopes in liquid, solid, or gaseous samples. It combines an ion-generating argon plasma source with the high sensitivity of mass spectroscopy detection. While ICP-MS finds applications in various elemental analyses, including pharmaceutical testing and reagent production, this discussion will concentrate on its relevance in mineral and water research.

The ICP-MS instrument comprises several essential components, including a sampling interface, a peristaltic pump connected to a nebulizer, a spray chamber, a plasma torch, a detector, and a vacuum chamber maintained by turbo molecular pumps. The operational process is as follows: a liquid sample is introduced into the nebulizer, transforming it into spray. An internal standard, such as germanium, is introduced into a mixer along with the sample before nebulization to counterbalance matrix effects. Larger droplets are eliminated, allowing smaller ones to progress into the plasma torch where they convert into ions. These ions are subsequently separated based on their mass-to-charge ratios by the mass-separation device. An ion detector converts these ions into an electrical signal, which is amplified and read by computer software.

ICP-MS employs horizontal plasma for ion generation and separates ions based on their mass-to-charge ratios (m/z). Rigorous measures are taken to prevent photons form reaching the detector and introducing background noise. This divergence in ion formation and detection significantly influences the relative sensitivities of these techniques. While both methods enable swift, high-throughput multi-elemental analysis (approximately 10-40 elements per minute per sample), ICP-MS boasts a detection limit ranging from a few parts per trillion (ppt) to several parts per million (ppm). A noteworthy feature is that ICP-MS can discriminate between different isotopes of an element by segregation ions based on mass [51].

[51] 1.6: ICP-MS for Trace Metal Analysis - Chemistry LibreTexts

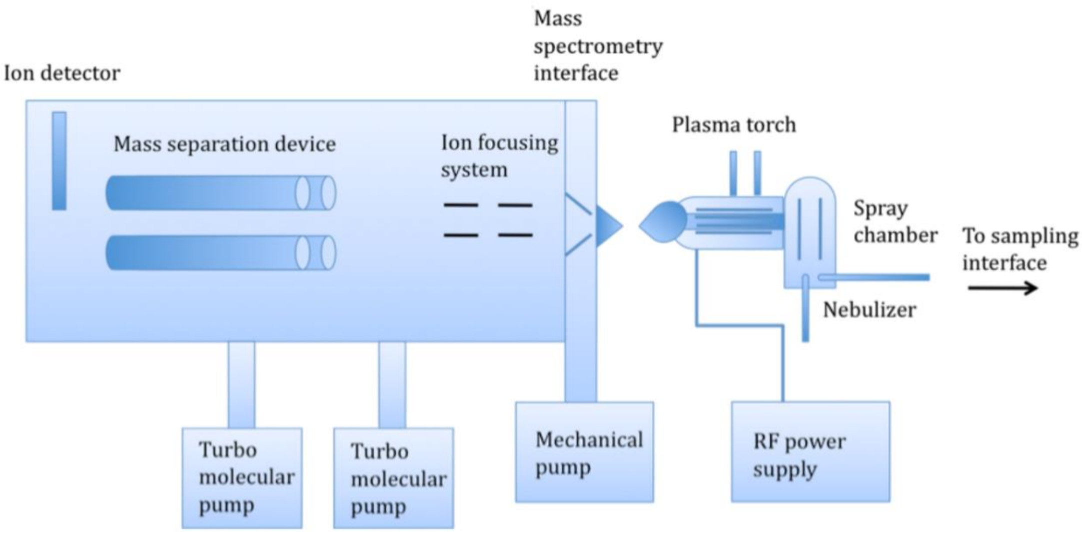

Figure 6: Scheme depicting the basic components of an ICP-MS system. Adapted from R. Thomas.

For the determination of the heavy metals' concentration in mine tailings with ICP-MS, the measurements were taken in the University of Granada, where an NexION ICP-Mass Spectrometer was used.

3.2 Performance Tests on grout:

Figure 7: Hobart Mixer

Grouts are viscous or fluid materials used in construction, civil engineering, and other applications to fill gaps, seal joints, provide support, and strengthen structures. For instance, grouts can be used in repair and rehabilitation work, filling damaged or deteriorating areas to restore structural integrity. For the performance tests that took place for this thesis there were used ready dry mix designs provided by the company Sika Technology AG, with incorporating two different type of mine tailings (VMS-Zinkgruvan, IOT-Kiruna), either as cement or aggregates replacement. The investigated grouts are composed of a mixture of cement sand, mine tailings (for cement replacement 20%-30% mine tailings, for aggregates replacement 40%-50% mine tailings), additives and water. The mortar trials were carried out using Ordinary Portland Cement. The tailings were dried in an oven at 105^{o}C for 24 hours. Mixing for the formulations was accomplished with a Hobart Mixer for 3 minutes, adhering to EN 196-1 guidelines. There were optimized 8 mortar formulations including mine tailings and one reference mortar without tailings. The mortars were as follows: *Mortar A1* with Zinkgruvan tailings as cement replacement, *Mortar B1* with Zinkgruvan tailings as cement replacement and activator, *Mortar C1* with Kiruna tailings as cement replacement, *Mortar D1* as cement replacement and activator, *Mortar E1* with Zinkgruvan tailings as aggregates replacement, *Mortar F1* with Zinkgruvan tailings as aggregates replacement and activator, *Mortar G1* with Kiruna tailings as aggregates replacement, and *Mortar H1* with Kiruna tailings as aggregates replacement and activator.

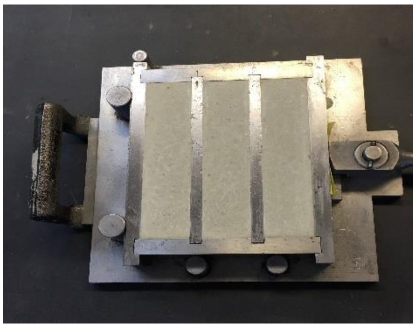

Figure 8: Mortar prisms.

3.2.1 Rheology of the grout

To assess the workability of the grouts within a time frame of up to 60minutes, a standardized steel cone (in compliance with EN 1015-3) was used to measure the spread (without strokes) diameter in to two perpendicular directions.

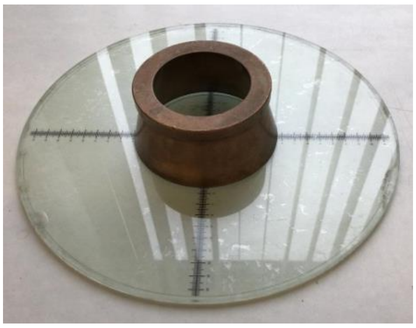

Figure 9: Standardized cone and glass plate.

The steel cone was placed on the flow table, it was filled with the mortar and removed afterwards. The flow (without strokes) was measured immediately after mixing at 4, followed by 10, 20, 30, 45 and 60 minutes. Before every measuring point the mix was remixed by hand for 10 seconds.

3.2.2 Calorimetry of the grout

When water is added to the dry mix of the mix design, the reaction of cement with water starts to take place. After the 3 minutes of mixing with the Hobart Mixer, 50g of the mortar formulation were weighed and placed in the Calmetrix box. The calorimetry measurement of the reactions that take place inside the mortar formulation was measured under constant temperature 23ºC for 24 hours.

3.2.3 Mechanical performance of the grout

For subsequent evaluation of mechanical performance, the samples were prepared following EN 12 190, comprising prismatic molds 40mm x 40mm in cross section, 160mm in length, and 40mm cube test specimens. After 1 day, the samples were demolded and stored for specifically flexural and compressive strength measurements at intervals of 1, 7, and 28 days after preparation.

Figure 10: Measurement of flexural strength.

Figure 11: Measurement of compressive strength.

3.2.4 Physical performance of the grout

For the evaluation of physical performance, the sample were prepared following EN 12 617-4, comprising prismatic moulds 40mm x 40mm in cross section, 160mm in length, with steel bolts at the ends. After 1 day, the sample were demolded and stored for specifically shrinkage-.20ºC/68% relative humidity and expansion under water at 20ºC according to the standard.

The physical performance (shrinkage and expansion) was determined after 1,2,3,7,14,21,28, 56, 91, 181 and 365 days.

3.2.5 Porosity measurement of the grout (Mercury intrusion porosimetry)

Mercury intrusion porosimetry (MIP) is valuable technique for measuring pore sizes in various porous solids. This method employs the penetration of non-wetting liquid, mercury, to assess both the size and volume of pores present in a wide array of porous materials. MIP stands as noteworthy approach in the characterization of porous substances, offering insights into pore sizes spanning a range from approximately 3nm to about 1000 µm, contingent on the specific contact angle between the solid surface and mercury. This technique surpasses the capability of gas physisorption, enabling the sizing of pores exceeding 500 nm in diameter [52].

For the MIP measurement 4 different types of mortars were prepared with Kiruna tailings either as cement or aggregates replacement with and without activator. The mortars were stored under water, and after 28 days they were taken out to air dry, they were cut into small cubes. The MIP measurement took place at the Institute for Geotechnics at ETH Zurich.

Prior to conducting the measurements, the samples underwent freeze-drying. The determination of porosity was performed using the Hg pressure porosimeter Pascal 140 + 440 (POROTEC), adhering to the ISO 15901/1 standard. This combination of instruments enables the measurement of meso- and microporosity within a pore size range spanning from a radius of 58 µm to 1.8 nm.

The measurement principle involves the application of increasing pressure to press mercury, a non-wetting liquid, into progressively smaller pores. The pore volume is deduced from the amount of injected mercury, while the pressure requires for each case reveals the distribution of pore sizes.

Porosity signifies the ratio of pore volume to the total sample volume. The pore radius r is calculated utilizing the Washburn equation formulated for cylindrical pores:

$$r = \frac{-2\,\gamma\,cos\theta}{p}$$

Where: p represents pressure, γ corresponds to the surface tension of mercury (4800 N/m), and θ denotes the wetting angle of mercury.

For the measurement procedure, fragments weighing approximately 3g were placed within a dilatometer flask and subjected to a 10minute evacuation in the macropore unit of the pressure porosimeter. Subsequently, the dilatometer flask was vacuum filled with mercury to a predetermined volume in the measuring capillary. The pressure was then gradually increased up to 400 kPa.

Following this, the dilatometer flask was removed from the macropore unit and weighed under ambient air pressure. It was then transferred to the mesopore unit of the pressure

[52] Mercury Intrusion Porosimetry Basics: Measuring Pores in Solids | Anton Paar Wiki (anton-paar.com)

porosimeter. In this phase, the pressure on the mercury within the dilatometer was increased using a specific oil in the autoclave, reaching up to 400MPa. The rate of pressure augmentation was automatically controlled using the PASCAL process, which adjusted the speed of pressure increase based on lower pressure levels and intrusion processes during measurement.

3.2.6 SEM, scanning electron microscopy.

Electron microscopes, as the name suggests, utilize an electron beam to generate images. The diverse outcomes arising from SEM derive from the interaction between electrons and matter. Each of these distinct signal types carries valuable information about the sample.

As an example, backscattered electrons yield images featuring contrast that convey details regarding variations in atomic number. Conversely, secondary electrons offer topographic insight into the sample. Moreover, the combination of SEM with an Energy-Dispersive X-ray (EDX) detector allows X-rays to serve as a signal, providing valuable chemical information [53].

The samples were prepared with two different types of ways to be tested using SEM, as cross sections and as fractures, in both ways the samples were oven dried at 50°C and then they were immersed into ethanol for 24 hours so that the hydration reaction of cement would stop.

The cross sections were prepared by cutting the mortars into cubes and incorporating them into epoxy resin, after 24 hours that the resin was hardened, the cross sections were polished using different grain sizes of glass paper (from coarser to finer) and diamond spray. Lastly, the cross sections were spattered and platinated with 5nm coating, the samples were measured at 100, 500, 2000, 5000 magnifications. From the cross sections where information was obtained about the elements existent in the mortars by the mapping of specific areas and the EDX spectra derived from these mappings.

The fractures were obtained by breaking the samples and collecting thin, small, and flat pieces. These pieces are then placed and glued in circular plates with the help of a glue containing silver. The fractures are left into a desiccator with nitrogen gas inside so that the glue will harden. After 10minutes the fractures are put for spattering, with a 10nm platinum coating. The fractures were measured in 2000, 10000, 20000, and 25000 magnifications, the data obtained give information about the microstructure of the mortars.

[53] Scanning Electron Microscopy (SEM) - Surface Science Western

3.3 Performance Tests on repair mortar:

Repair mortars are precisely formulated to restore or substitute the initial profile and purpose of the deteriorated concrete. These mortars play a crucial role in repairing concrete defects, enhancing aesthetics, renewing structural soundness, enhancing longevity, and augmenting durability of the structure.

For the performance tests of the repair mortars there were used ready dry mix designs provided by the company Sika Technology AG, with incorporating IOT tailings from the Vale mine, as cement and/or aggregates replacement. The examined repair mortars are composed of a mixture of cement sand, mine tailings (for cement replacement 20%-30% mine tailings, for aggregates replacement 40%-50% mine tailings), additives and water. The mortar trials were carried out using Ordinary Portland Cement. The tailings were dried in an oven at 105^{o}C for 24 hours. Mixing for the formulations was accomplished with a Hobart Mixer for 3 minutes, adhering to EN 196-1 guidelines. Four different mortar formulations containing mine tailings as cement and/or aggregates replacement and one reference mortar with no tailings were tested, in the dry mix of the formulation were two different types of Ordinary Portland Cement (Cem.1 and Cem. 2). The repair mortars were as follows: *Mortar A2* with Vale tailings as Cem. 1 replacement, Mortar B2 with Vale tailings as Cem. 2 replacement, Mortar C2 with Vale tailings as aggregates replacement, and Mortar D2 with Vale tailings as CEM A and aggregates replacement. The presence of an activator wasn't necessary.

3.3.1 Rheology of the repair mortar

To assess the workability of the repair mortar within a time frame of up to 60minutes, a standardized steel cone was placed on the flow table, it was filled with the mortar and removed afterwards. After 15 strokes of the flow table the spread diameter in to two perpendicular directions was measured. The flow was measured at 10, 20, 30, 45, and 60 minutes.

3.3.2 Calorimetry of the repair mortar

For the calorimetry of the repair mortar the same procedure that is mentioned above was followed.

3.3.3 Mechanical performance of the repair mortar

For subsequent evaluation of mechanical performance, the samples were prepared following EN 12 190, comprising prismatic molds 40mm x 40mm in cross section, 160mm in length, and 40mm cube test specimens. The molds containing the mortar inside were placed on a vibrating table for 120s for the excess air to be released from the mortar. After 1 day, the samples were demolded and stored for specifically flexural and compressive strength were measured at intervals of 1, 7, and 28 days after preparation.

3.3.4 *Physical performance of the repair mortar*

The samples were produced as described in 3.1.4. The physical performance (shrinkage and expansion) was determined after 1,2,3,7,14,21,28, 56, 91, 181 and 365 days.

3.3.5 *Application on concrete substrate*

By the end of the 60 minutes time frame the remaining repair mortar was applied on a prewetted concrete substrate to observe the possible formation of cracks after the drying of the mortar.

4 Results and Discussion

XRD: The XRD analysis of Zinkgruvan, Kiruna and Vale mine tailings is presented in the Tables 2, 3, and 4 respectively. All investigated samples are measured as powder specimen. The investigated tailings were subjected to Rietveld analysis:

Table 2: XRD Analysis of Zinkgruvan tailings.

Mineral	Percentage %
Quartz	42
Diopside	14
Orthoclase	11
Chlorite	9
Microcline	8
Albite	7
Cordierite	6
Biotite	2
Dolomite	1
Chalcopyrite	1
Galena	traces
Sphalerite	traces
Pyrite	traces
Pyrophyllite	traces

As shown in the table the Zinkgruvan tailings consists mostly of quartz (SiO_2), minor phases such as diopside ($MgCaSi_2O_6$), k-feldspar (i.e. orthoclase $KAlSi_3O_8$), chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$), plagioclase ($NaAlSi_3O_8CaAl_2Si_2O_8$), cordierite ($(Mg,Fe)_2Al_4Si_5O_8$), micas ($AB_{2-3}(X,Si)_4O_{10}(O,F,OH)_2$, and traces of chalcopyrite ($CuFeS_2$), galena (PbS), and sphalerite (Zn,Fe)S.

The total content of phyllosilicates is around 12%. Overall, no swelling clays, known for their adverse effect on concrete/mortar, were detected.

Table 3: XRD Analysis of Kiruna tailings.

Mineral	Percentage %
Quartz	35
Calcite	14
Apatite	12
Muscovite	9
Albite	7
Gypsum	5
Hornblende	4
Dolomite	4
Anorthite	2
Chlorite	2
Annite	1
Tremolite	1
Titanite	1
Magnetite	traces
Talc	traces
Ilmenite	traces
Actinolite	traces

The analysed Kiruna tailings is composed of quartz (SiO2), calcite ($CaCO_3$), apatite ($Ca_5(PO_4)_3(F, Cl, OH)$), micas ($AB_{2-3}(X,Si)_4O_{10}(O,F,OH)_2$, plagioclase, gypsum $CaSO_4 \cdot 2H_2O$)),

dolomite ($CaMg(CO_3)_2$), hornblende (Ca_2(Mg,Fe,Al)5$(Al,Si)_8O_{22}(OH)_2$, chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$), and traces of tremolite (Ca(Mg5.0-4.5Fe^{2+}0.0-0.5)$Si_8O_{22}(OH)_2$, titanite ($CaTiSiO_5$), magnetite (Fe^{2+}Fe3+2O_4), talc ($Mg_3Si_4O_{10}(OH)_2$ and ilmenite ($FeTiO_3$).

The total content of phyllosilicates is around 11%. Overall, no swelling clays, known for their adverse effect on concrete/mortar, were detected.

Table 4: XRD Analysis of Vale tailings.

Mineral	Percentage %
Quartz	88
Chlorite	2
Biotite	2
Cordierite	2
Hematite	1.5
Microcline	1
Albite	1
Diopside	1
Muscovite	traces
Calcite	traces

The analysed Vale tailings is composed mainly of quartz (SiO_2), and there is a small amount of chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$), biotite $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$, cordierite ($(Mg,Fe)_2Al_4Si_5O_8$), hematite ($Fe_2O_3$), microcline ($KAlSi_3O_8$), plagioclase, diopside ($MgCaSi_2O_6$), muscovite $KaI_2(AlSi_3O_{10})(F,OH)_2$ present.

The total content of phyllosilicates is around 2%. Overall, no swelling clays, known for their adverse effect on concrete/mortar, were detected.

It is observed that Vale tailings have a different composition than Kiruna tailings even though they are both categorized as IOT. This is since the ore the two mines is extracting is different.

XRF: The XRF analyses indicate that the mine tailings samples contain abundant amounts of SiO_2 (55% Zinkgruvan, 36% Kiruna, 72% Vale), Al_2O_3 (10%, Zinkgruvan, 6% Kiruna, 1% Vale) and Fe_2O_3 (7% Zinkgruvan, 16% Kiruna, 7% Vale), and Zinkgruvan and Kiruna tailings are

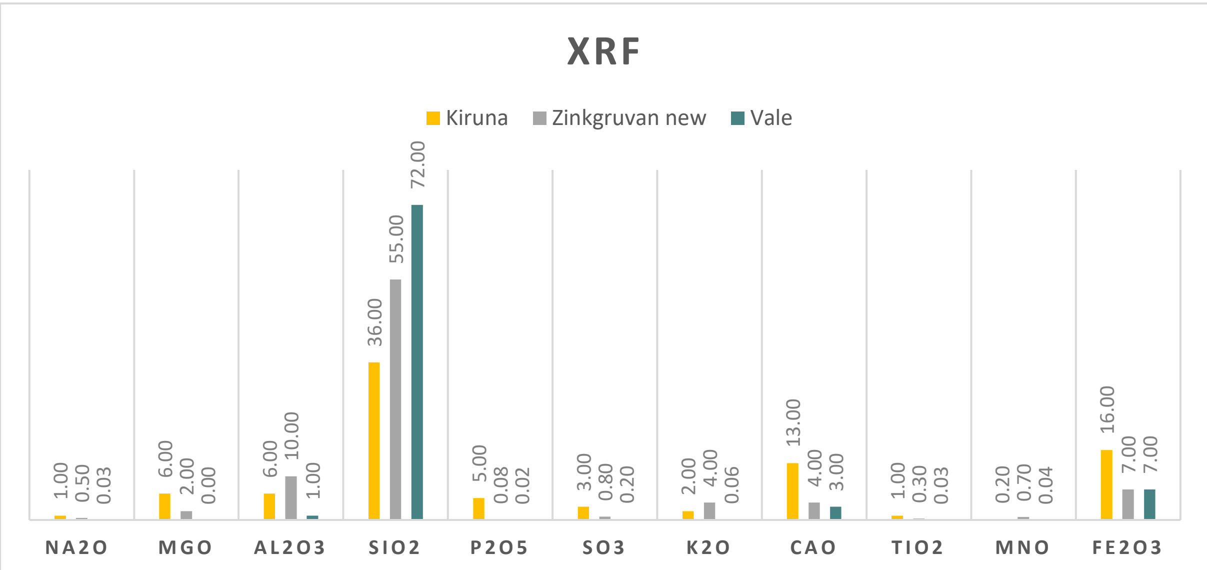

Figure 12: XRF analysis of Zinkgruvan, Kiruna and Vale tailings.

appropriate for serving as SCMs, Vale tailings can be used as SCMs but in lower percentages because of their low amount of Al_2O_3 [54].

PSD: Generally speaking, tailings possess the potential to serve as aggregates owing to their substantial quartz composition. Additionally, their relatively inert characteristics within particle dimensions comparable to those of sand facilitate the avoidance of extracting natural sands from riverbeds. Nonetheless, it's important to note that the existence of exceedingly fine particles might result in the residual material behaving similarly to supplementary substances within cement-based matrices. Consequently, a straightforward modification of particle dimensions could be necessary [55]. The particle size distribution of Zinkgruvan, Kiruna and Vale tailings is shown in the Figure 13.

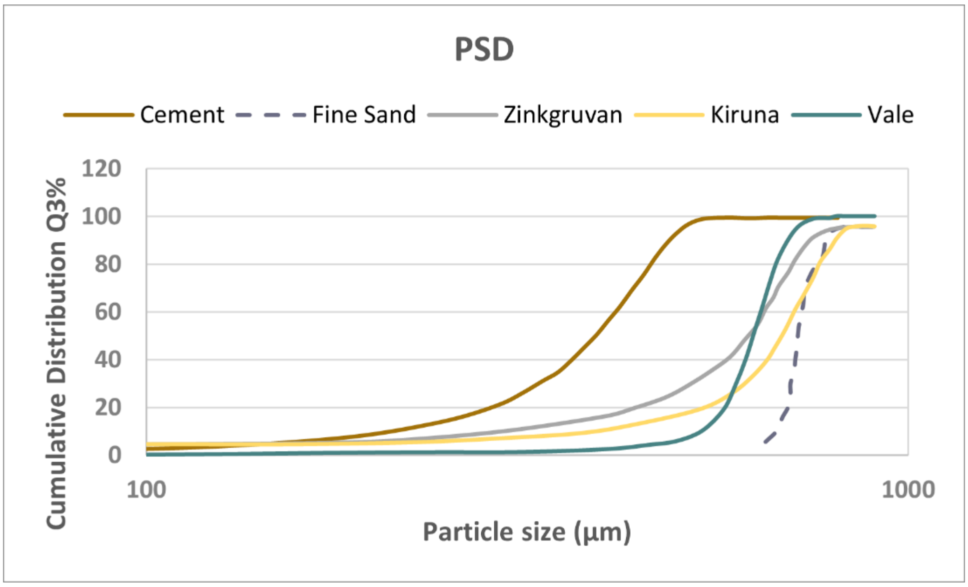

Figure 13: PSD analysis of tailings in comparison with cement and fine sand.

FTIR: The FTIR spectra of Zinkgruvan mine tailings (Figure 14.) show the presence of silicates originating from clays in the tailings (peak around 1000cm^{-1}). The presence of quartz is also revealed (double peak around 800cm^{-1}).

[54] De Castro, "Influence of Addition Contents of Iron Ore Tailings on Structural Mortar".
[55] Peys, "Transformation of mine tailings into cement-bound aggregates for use in concrete by granualzion in a high intensity mixer".

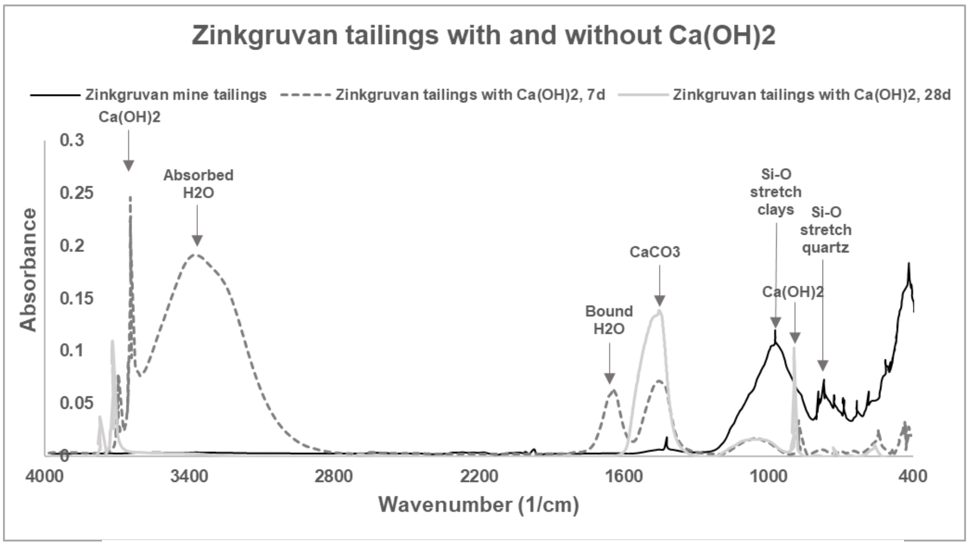

Figure 14: FTIR spectra of Zinkgruvan tailings.

The FTIR spectra of Kiruna mine tailings (Figure 15.) reveal similar behavior to Zinkgruvan as shown below.

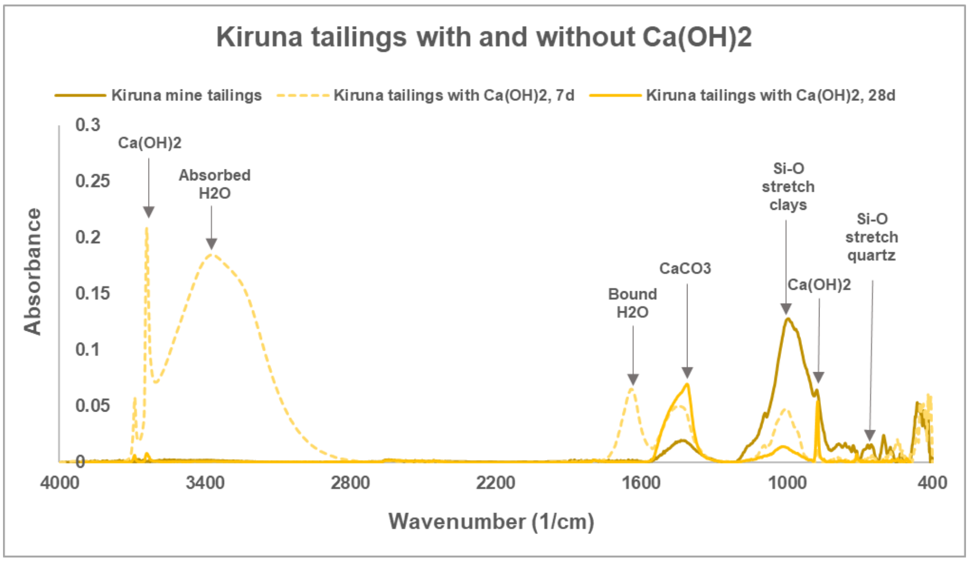

Figure 15: FTIR spectra of Kiruna tailings.

The FTIR spectra of Vale tailings (Figure 16.) show a similar behavior, however the peak corresponding to the vibration of quartz is more intense, as the Vale tailings have a higher content of quartz also indicated in the XRD measurements.

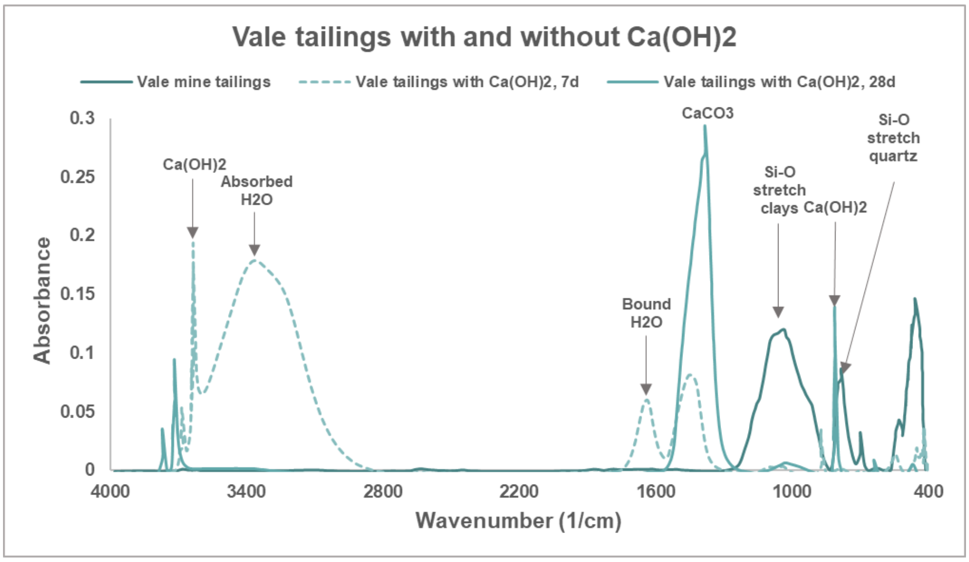

Figure 16: FTIR spectra of Vale tailings.

The FTIR analyses of Zinkgruvan, Kiruna and Vale tailings reveal that Calcite ($CaCO_3$) is produced when the raw tailings are mixed with lime ($Ca(OH)_2$). The calcite formation is the ongoing carbonation process. However, in the spectra illustrated in Figs 14-16, the hydraulic component formation is evidenced by the Si-O stretching peak shifted to higher wavenumbers after reaction with lime. The low intensity of this peak compared to the corresponding one of the mine tailings without lime, is due to the low amount of the tailing in the mixture with lime. This peak is more intensive in the IOT tailings with $Ca(OH)_2$ after 28 days of curing.

TGA: TGA analysis of Zinkgruvan raw tailings shows an endothermic peak at around 850°C which is the characteristic peak representing the carbonates, and more specifically calcite. The Total Mass Loss of the raw Zinkgruvan tailings was 2.3mg (22% loss).

When Zinkgruvan is incorporated with lime there are presented three endothermic peaks in the TGA analysis. A change in mass is observed around 100°C-400°C due to the release of bound water from the hydraulic components. This implies that the clays present might possess pozzolanic properties. Common clay minerals like kaolinite, illite, and smectite undergo dehydration between 500°C-650°C [56]. Lastly, the characteristic peak for the carbonates is again present but with higher intensity. The Total Mass Loss of Zinkgruvan

[56] Moropoulou, "Characterization of ancient, byzantine and later historic mortars by thermal and X-Ray diffraction techniques".

Tailings with $Ca(OH)_2$ is 14.3mg (28.6% loss). The TGA analysis of Zinkgruvan is illustrated in the Figure 17. below.

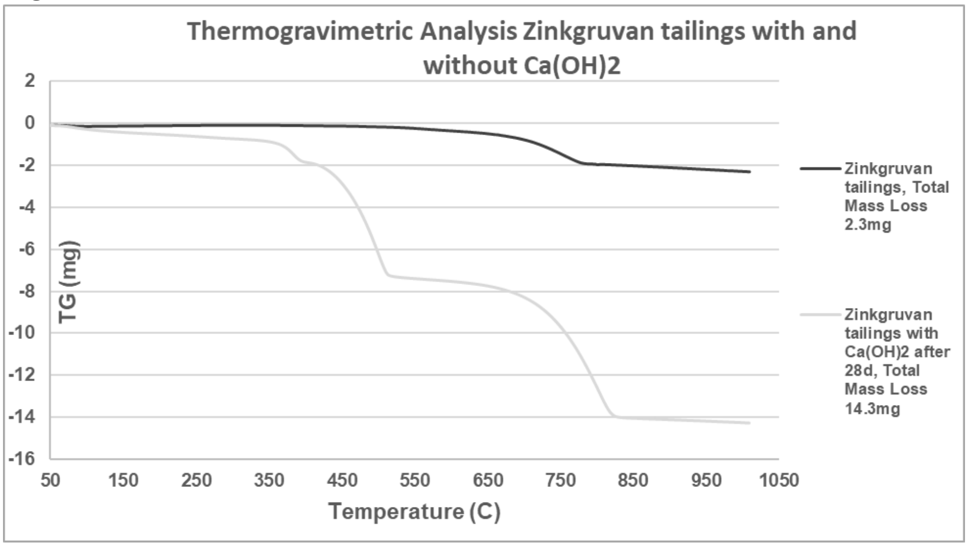

Figure 17: TGA analysis of Zinkgruvan tailings.

The TGA analysis of Kiruna raw tailings has a similar behavior to the Zinkgruvan tailings presented above. With only differences the Total Mass Loss of raw Kiruna tailings was 3.4mg (34.4% loss), and the Total Mass Loss of Kiruna tailings with $Ca(OH)_2$ is 14.8mg (29.6% loss). the TGA analysis of Kiruna tailings is shown in the Figure 18. below.

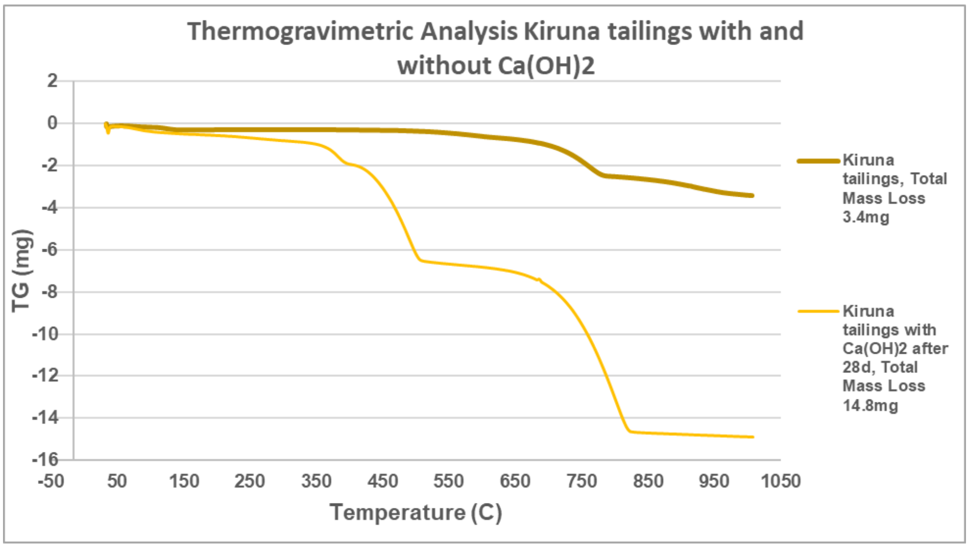

Figure 18: TGA analysis of Kiruna tailings.

The TGA analysis of Vale raw tailings does not show any big changes in mass loss, which makes sense as Vale tailings are mainly composed of quartz and a small percentage of clays. When Vale tailings are incorporated with the lime the TGA spectra obtained show a similar behavior as with the Zinkgruvan and Kiruna tailings the Total Mass Loss is 13.7mg (27.4% loss). The TGA analysis of Vale tailings is shown in the Figure 19. below.

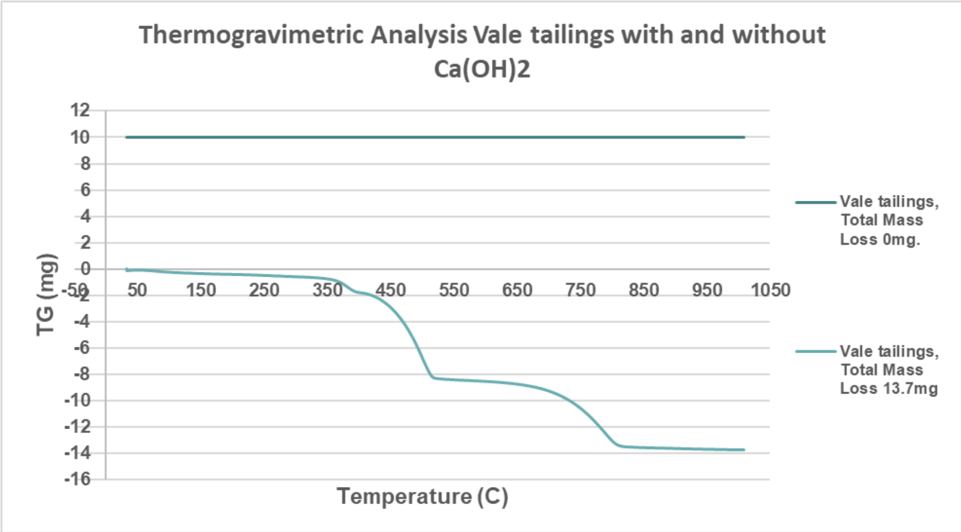

Figure 19: TGA analysis of Vale tailings.

Luxan test for assessing pozzolanic activity: The Luxan test for assessing pozzolanic activity took place for Zinkgruvan, Kiruna and Vale tailings and the results are presented in the Table 5. below:

Table 5: The Luxan Test for Zinkgruvan, Kiruna, and Vale tailings.

Sample	Conductivity Variation-ΔC (mS/cm)
Zinkgruvan	1.6
Kiruna	1.3
Vale	1.2

Comparing the results exhibited in Table 5. To Table 1., it is indicated that the Zinkgruvan tailings have good pozzolanicity, as well as the Kiruna tailings. Whereas the Vale tailings have variable pozzolanicity.

Determination of calcium carbonate: The level of carbonates present in soils is a significant factor that influences the chemical composition of the soil. Assessing this attribute is a fundamental component of standard soil analysis procedures. A majority of the techniques used rely on the interaction between carbonates and potent acids, leading to the dissolution of carbonates and generation of CO_2 [57]. The determination of calcium carbonate of Zinkgruvan, Kiruna and Vale tailings is presented in the Table 6. Below:

Table 6: Calcium carbonate of Zinkgruvan, Kiruna and Vale tailings.

Sample	%CaCO3
Zinkgruvan	10.2
Kiruna	10.8
Vale	10.3

[57] Zamanian, “Soil carbonates: The unaccounted irrecoverable carbon source”.

Toxicity measurement with ICP-MS: The heavy metal content in ppm of Zinkgruvan, Kiruna and Vale tailings is presented in the Table 7.

Table 7: Heavy metal content of Zinkgruvan, Kiruna, and Vale tailings.

	Cr	Co	Ni	As	Se	Mo	Cd	Cs	Hg	Pb	Th	U
Zinkgruvan	19.4	24.9	9.3	41.1	1.7	0.4	12.7	12.2	5.5	2622.3	17.0	4.7
Kiruna	25.0	79.3	137.8	19.2	0.9	7.8	0.1	0.9	0.1	15.2	57.8	5.8
Vale	5.2	0.8	1.1	2.0	1.8	0.3	0.004	0.01	0.1	2.6	0.1	0.5

The findings indicate that the Kiruna tailings possess potential utility in construction materials, given that their concentrations of heavy metals fall within the permissible limits for residual soils set by the U.S. EPA even though they have a high Th amount. There's a possibility that the heavy metals within Zinkgruvan tailings could become part of cement hydration products like C-S-H, ettringite, and monosulfate, aiming to minimize their leaching propensity [58]. Vale tailings show the lowest heavy metal content and are safe for use. The results obtained through ICP-MS analysis under high pH conditions closely resemble those from the untreated tailings. This suggests that the heavy metals become immobilized within the crystal lattices of the minerals during processing.

Rheology of the grout: The workability of the grout with either Zinkgruvan or Kiruna tailings as cement replacement with and without activator is presented in the Figure 20. below:

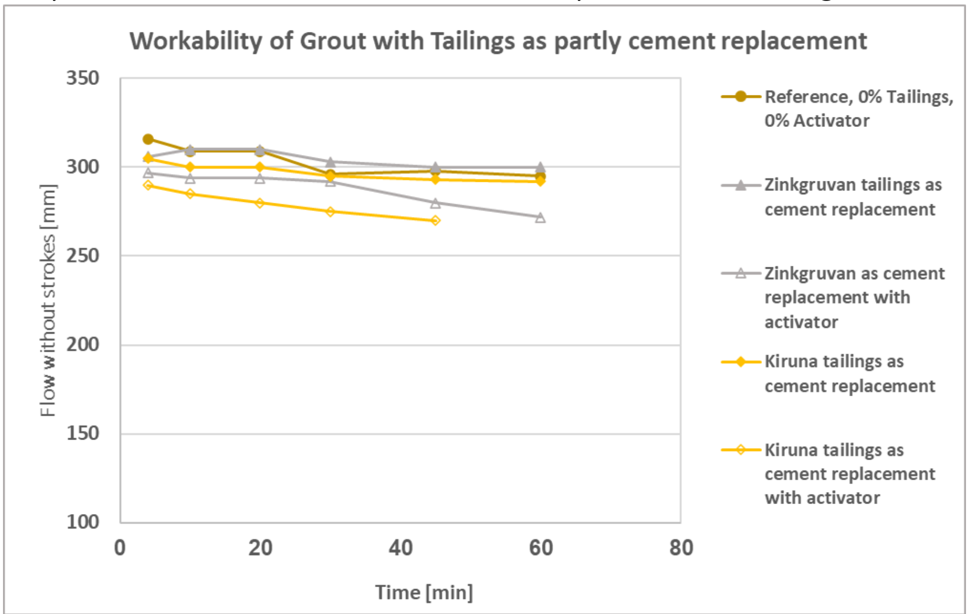

Figure 20: Workability of grout with Zinkgruvan or Kiruna tailings as partly cement replacement.

[58] Lu, "Evaluation of heavy metals leachability of incitерating recycled aggregate and solidification/stabilization products for construction reuse using TCLP, multifinal pH and EDTA mediated TCLP leaching tests".

As observed the flow of the grout when replacing cement by Zinkgruvan or Kiruna tailings is mostly constant and a bit lower than the flow of the reference. When the activator is added in the formulation the flow of the grout decreases, which makes sense as the sets faster. When the cement is replaced in the formulation by Kiruna tailings and in the presence of the activator the flow decreases more intensely so there is no measurement taken at 60 minutes.

The workability of the grout with either Zinkgruvan or Kiruna tailings as aggregates replacement with and without activator is presented in the Figure 21. below:

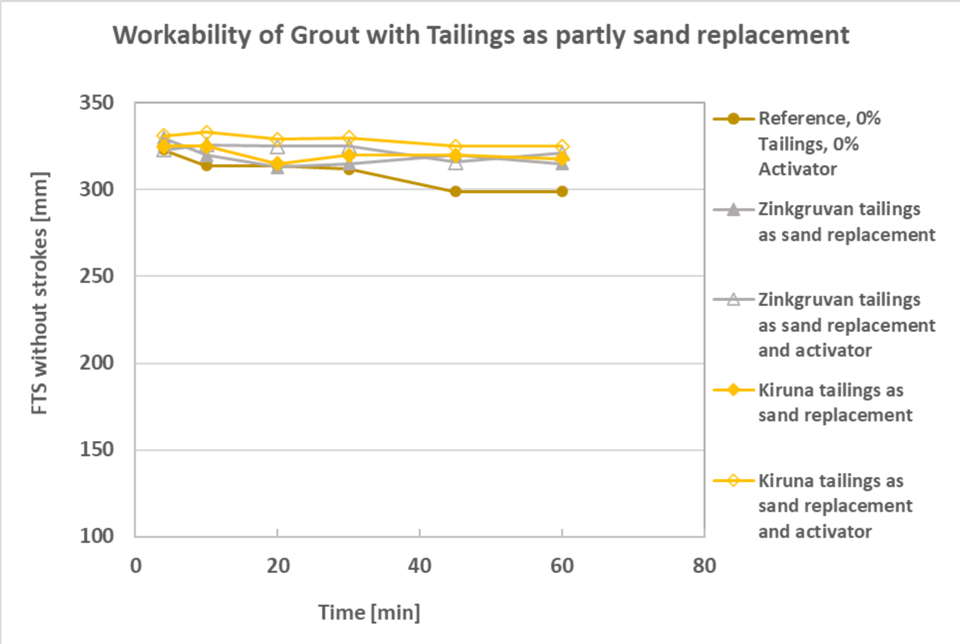

Figure 21: Workability of grout with Zinkgruvan or Kiruna tailings as partly aggregates replacement.

When sand is replaced by tailings the flow of the grout as observed from the Figure above is more stable and a bit higher. This can be explained by the fact that the tailings are finer as discussed in the PSD analysis, compared to fine sand, in order to meet the workability requirements, the superplasticizer was increased which resulted I flow comparable or bit higher as the reference.

Calorimetry: The calorimetry measurement of the grouts with Kiruna tailings as cement or aggregates replacement with or without activator are presented in the Figure 22. below:

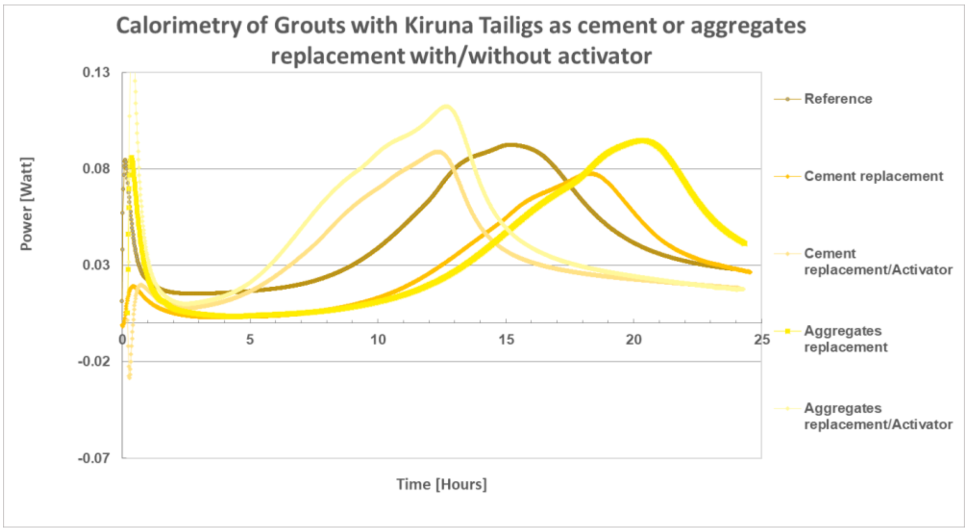

Figure 22: Calorimetry of grouts with Kiruna tailings as cement or aggregates replacement.

From the calorimetry measurements it can be observed that the peak of the reaction of the cement with the water inside the fresh mix of the formulation, when the activator is present takes place earlier (between 10-15 hours) compared to a formulation without activator (around 20 hours). Also, it can be noted that the reaction takes place later when part of the cement or the aggregates is replaced in the formulation and no activator is present.

Mechanical performance: The mechanical performance of the grout with Zinkgruvan or Kiruna tailings as cement replacement with or without activator (1d strengths) is presented in the Figure 23 below:

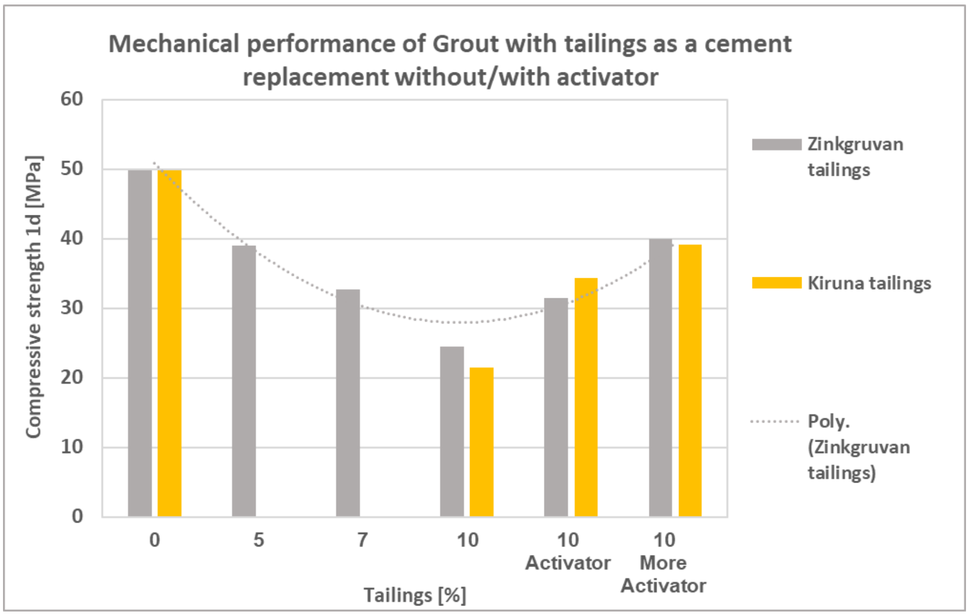

Figure 23: Mechanical performance of grout with Zinkgruvan or Kiruna tailings as cement replacement.

When the cement in the grout formulation is replaced by Zinkgruvan or Kiruna tailings the first day compressive strength is lowered, as expected from the lower amount of cement in the mortar formulation. The more the amount of tailings is increased in the formulation the more the compressive strength of the mortars is decreased from 50MPa (reference) to 24.5MPa when the cement is replaced by Zinkgruvan, and 21.4MPa when the cement is replaced by Kiruna tailings. When an activator is added the compressive strength of the grout with Zinkgruvan as cement replacement increases to 40MPa, whereas the compressive strength of the grout with Kiruna tailings as cement replacement can reach 39MPa.

The mechanical performance of the grout with Zinkgruvan or Kiruna tailings as aggregates replacement with or without activator (1d strengths) is presented in the Figure 24. below:

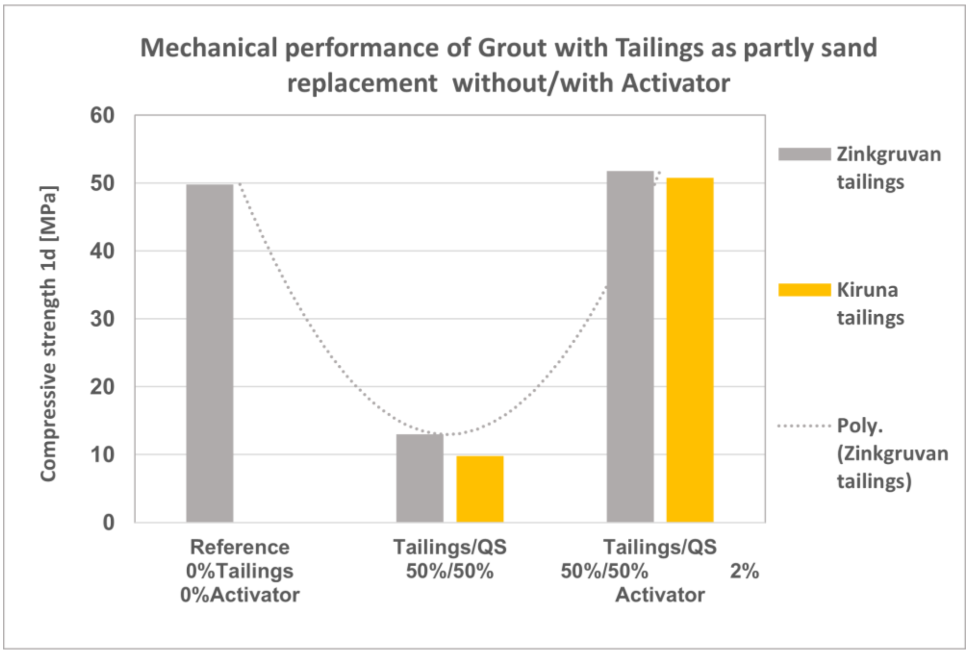

Figure 24: Mechanical performance of grout with Zinkgruvan or Kiruna tailings as partly sand replacement.

When the aggregates are partly replaced in the mortar formulation the compressive strengths (1d) are significantly decreased to, 13MPa when Zinkgruvan is used as the replacement, and to 9.8MPa when Kiruna is used as the aggregate's replacement. However, when the activator is added in the formulation surprisingly the first day's strength is increased to 51.8MPa (>50MPa reference) when Zinkgruvan is used as the replacement. When Kiruna is used in the formulation as the sand replacement, with the presence of the activator the first day's strength increases at 50.8MPa.

Some further investigation has taken place when Zinkgruvan or Kiruna tailings are used to replace sand in the presence of an activator and the results of the mechanical performance for 1, 7, and 28 days are presented in the Figure 25. below:

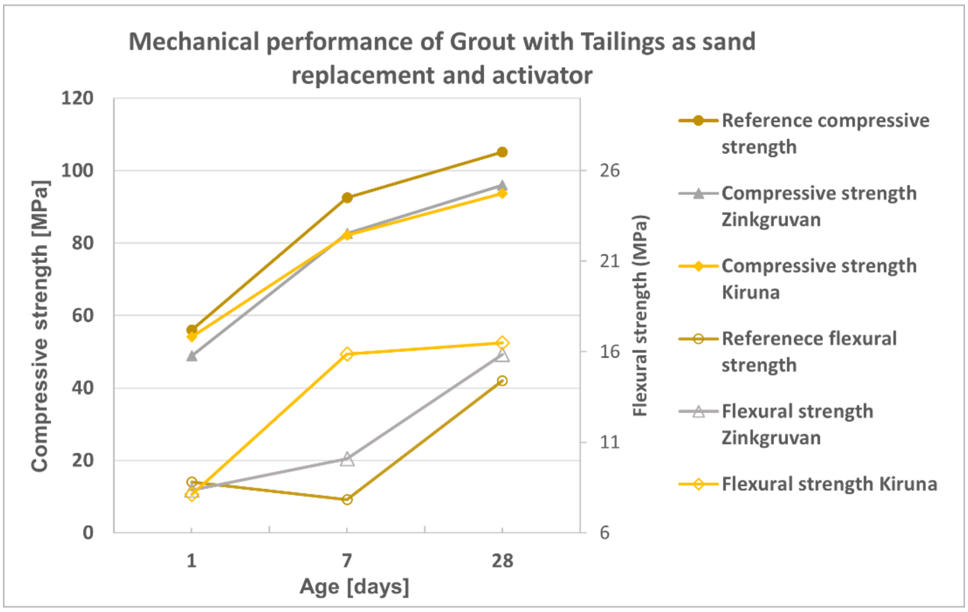

Figure 25: Mechanical performance of grout with Zinkgruvan or Kiruna tailings as sand replacement.

For the investigations of long term performance a mix size scale up was necessary. For the bigger mixes (> 4kg) a water reduction was indicated, what results in higher mechanical properties compared to smaller mixes of 2.5 kg.

The measurements of the compressive and flexural strength of the reference are as follows: 1d strength is 56MPa compressive, 8.8MPa flexural, 7d strength is 92.5MPa compressive, 7.8MPa flexural, and 28d strength is 105MPa compressive, and 14.3MPa flexural. When the sand is replaced partly by Zinkgruvan tailings then the measurements are as follows: 1d strength is 48.9MPa compressive, 8.3MPa flexural, 7d strength is 86MPa, 10.08MPa flexural, and 28d strength is 96MPa compressive, and 15.8MPa flexural. An increase in flexural strength measurements in comparison to the ones of the reference is observed. When the sand is replaced partly by Kiruna tailings then the measurements are as follows: 1d strength is 54MPa compressive, 8.1MPa flexural, 7d strength is 82.2MPa compressive, 15.8 flexural, and 28d strength is 93.7MPa compressive and 16.5MPa flexural. A more significant increase on the flexural strength of the grouts when sand is replaced by Kiruna tailings is observed.

Physical performance: For these formulations the investigation of physical performance has taken place with measurements of shrinkage and expansion. The results are presented in the Figure 26. below:

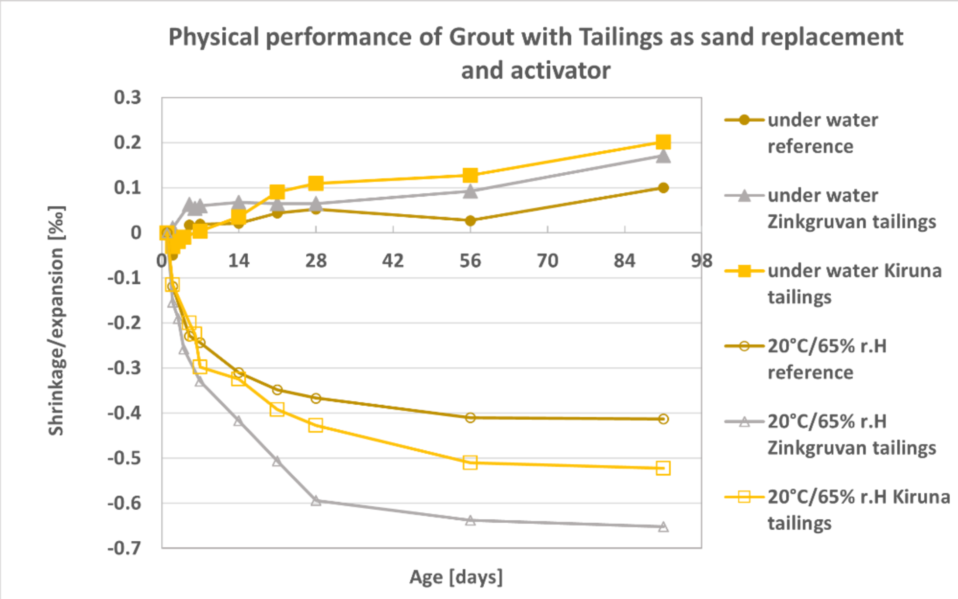

Figure 26: Shrinkage and expansion of grout with Zinkgruvan or Kiruna tailings as sand replacement.

From the graph above it is obvious that the mortars with Zinkgruvan or Kiruna tailings as sand replacement with an activator have higher values for expansion and for shrinkage. However, the measurements for shrinkage after 56 days seem to be stable and reaches a plateau.

Mercury Induced Porosimetry: The same mortar formulations that were used to measure the calorimetry measurements mentioned above were used to measure the porosity of the grouts after 28 days under water. The results obtained from the MIP measurement are presented in the Table 8. below:

Table 8: MIP measurement for grouts with Kiruna tailings as cement or sand replacement.

	Porosity	Pore volume	Pore fraction (pore diameter)						Middle pore diameter
Sample	Total %	Total mm^3/G	120-5µm		5µm-100nm		100-3.6nm		µm
			%	mm^3G	%	mm^3G	%	mm^3G	
Reference	7.9	41.5	8.6	3.6	18.4	7.6	73.0	30.3	14.9
Cem. Rep.	10.4	46.3	3.1	1.4	17.8	8.2	79.1	36.6	15.8
Cem. Rep+Act.	10.4	47.4	6.1	2.9	12.0	5.7	38.8	38.8	18.6
Agg. Rep	10.6	46.6	0.9	0.4	6.6	3.1	92.5	43.1	13.7
Agg. Rep + Act.	10.8	48.6	6.4	3.1	10.7	5.2	82.9	40.3	15.5

When cement is replaced by Kiruna tailings the total porosity is increased from 7.9% to 10.4% and the pore volume from 41.5mm^3/G to 46.3mm^3/G, this is mainly because the pore fraction from 100 to 3.6nm is increased from 73.0% to 79.1%, where the middle pore diameter is increased from 14.9 µm to 15.8µm. However, when an activator is added the total % porosity is the same and the pore volume increases a bit to 47.4mm^3/G, but that happens because even though the pore fractions are decreased the middle pore diameter is increased to 18.6µm.

When aggregates are replaced by Kiruna tailings the total porosity is increased from 7.9% to 10.6% and the pore volume from 41.5mm^3/G to 46.6mm^3/G, this is mainly because the pore fraction from 100 to 3.6nm is increased from 73.0% to 92.5%, where the middle pore diameter is decreased from 14.9 µm to 13.7µm. However, when an activator is added the total % porosity is 10.8% and the pore volume increases a bit to 48.6mm^3/G, that happens because the pore fractions are decreased to 82.9% the middle pore diameter is decreased to 15.5µm. From the measurements above there isn't as significant change in the porosity of the grouts with tailings in comparison with the reference.

SEM: From the SEM measurements of grouts with Zinkgruvan as sand replacement we obtain the following information:

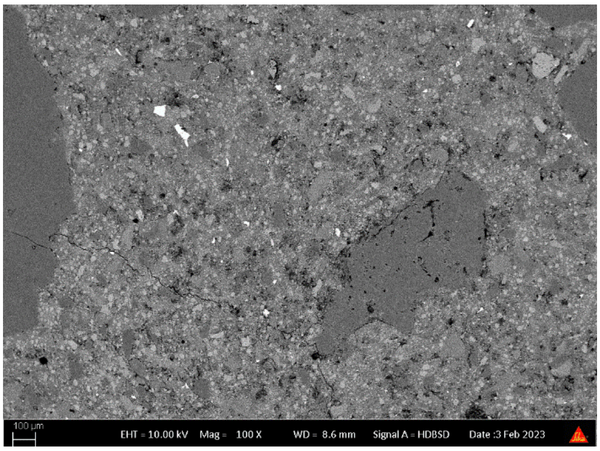

Figure 27: Magnification 100x

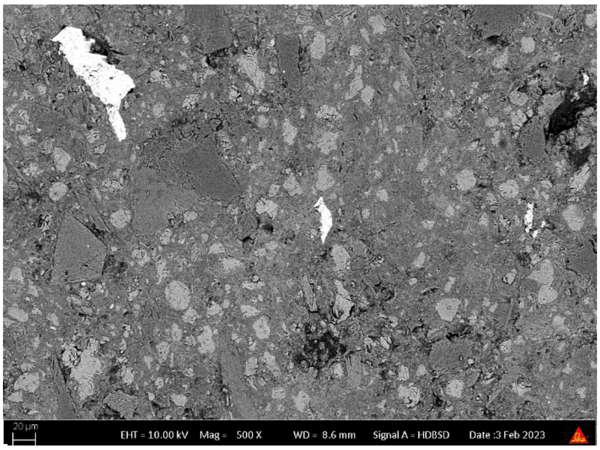

Figure 28: Magnification 500x

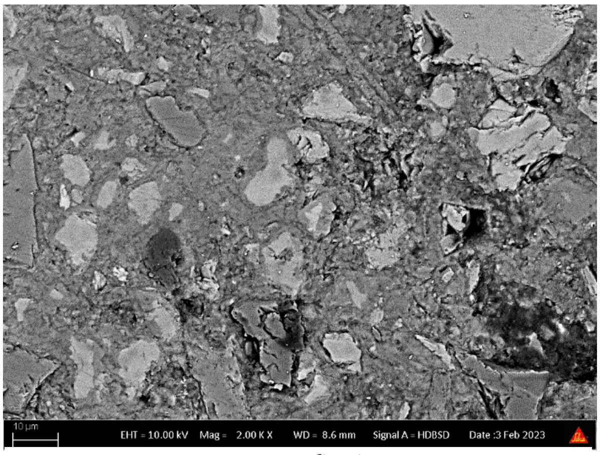

Figure 29: Magnification 2000x

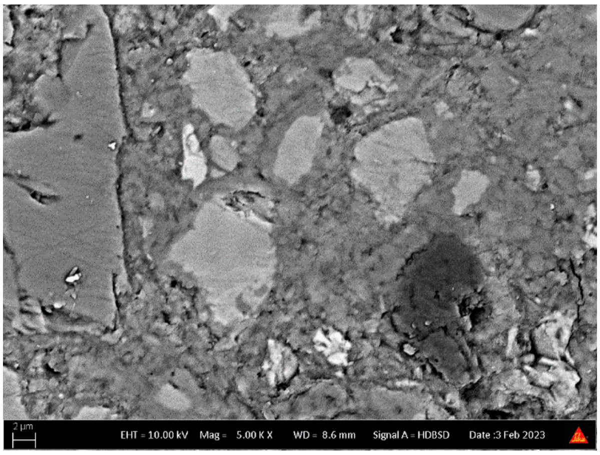

Figure 30: Magnification 5000x

From the pictures above we can see that the paste of Sample 4 doesn’t have a very dense paste. Most of the cement pastes seem to be hydrated. This can be easily observed in figures 28 and 29 where in some cases we can observe the hydration rim around the grains whereas in other cases it’s not so obvious. Also, in the Figures with the higher magnification it’s obvious that the paste was damaged during the process of the sample preparation, so this is another indication that the paste of the sample is not dense.

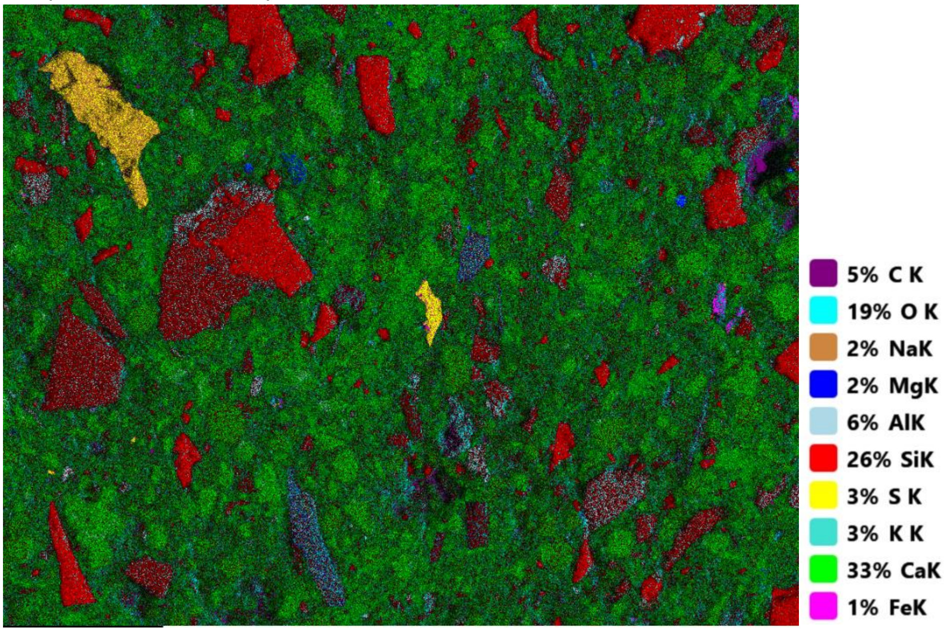

Figure 31: Mapping, magnification 500x

Figure 31. is the mapping of the sample, where the aggregates of the mortar are shown (red color particles), as well as the paste (dark green) and the cement grains (bright green). The yellow particles with the S content, might be existent due to the traces of Sphalerite ((Zn,Fe)S) or Pyrite present in Zinkgruvan (FeS_2). The blue particles with the Mg content, might be existent due to Diopside ($MgCaSi_2O_6$) and Dolomite ($CaMg(CO_3)_2$) present in Zinkgruvan. There are also particles where the presence of Fe and O can be observed (purple and light blue particles).

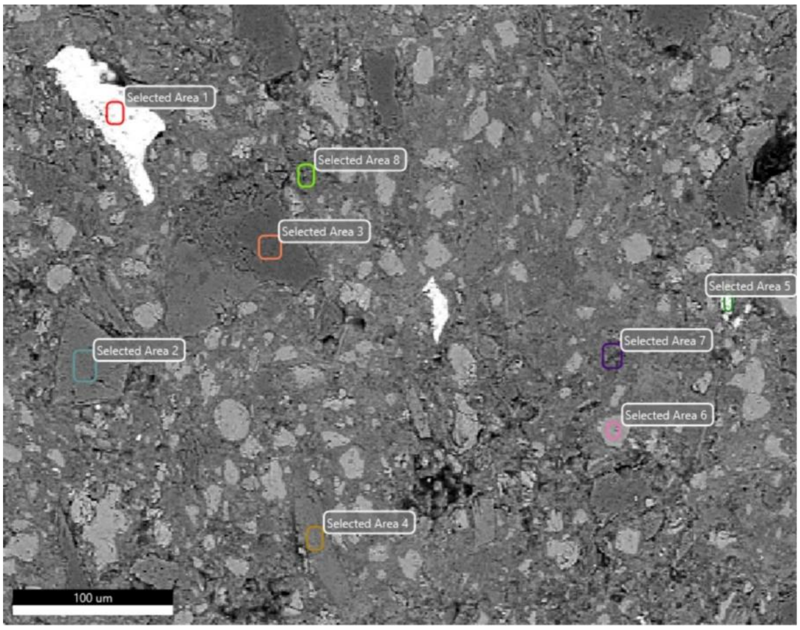

Figure 32: Spots for EDS spectra

Different spots shown in Figure 32., that seemed interesting from the mapping of the sample were analyzed and the results of the EDS spectrum are shown below, Figure 33.:

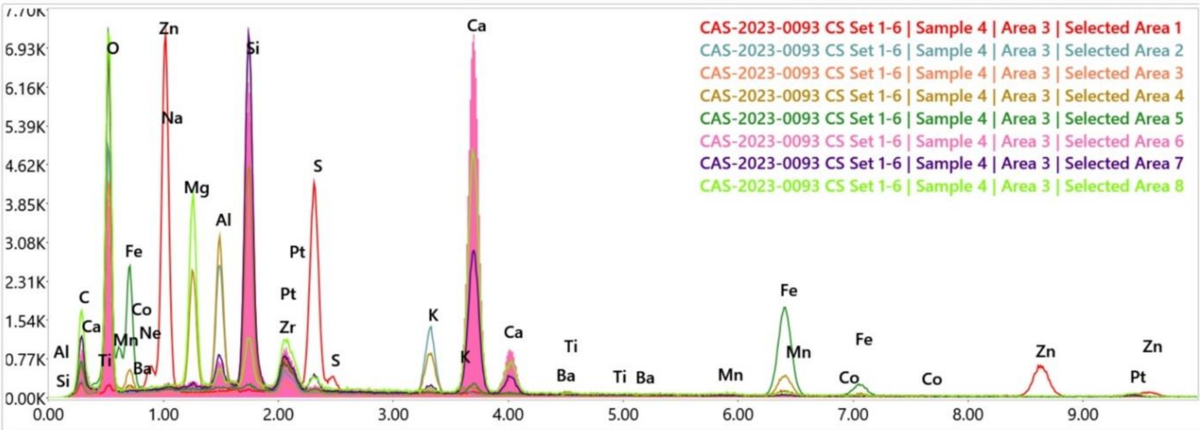

Figure 33: EDS spectrum

From the selected Area 1 of the EDS contains Zn and S, so this particle is Sphalerite as assumed previously from the mapping. Selected Area 2 contains Ca, Si and K so this particle might be Microcline or Orthoclase that are found in the Zinkgruvan mine tailings. Selected Area 3 contains Si and O from the quartz aggregates that are existent in the mortar. Selected Area 4 contains Mg, Al, Si and a little bit of Fe, so this particle might be Cordierite that is existent in the Zinkgruvan tailings. Selected Area 5 contains Ca, O and Fe. Selected Area 6 is a cement grain as it contains Ca, Si and O. Selected Area 7 is part of the paste and it contains Al, Si and Ca. Selected Area 8 contains Ca, O and Mg.

When the activator is added the results obtained are as follows:

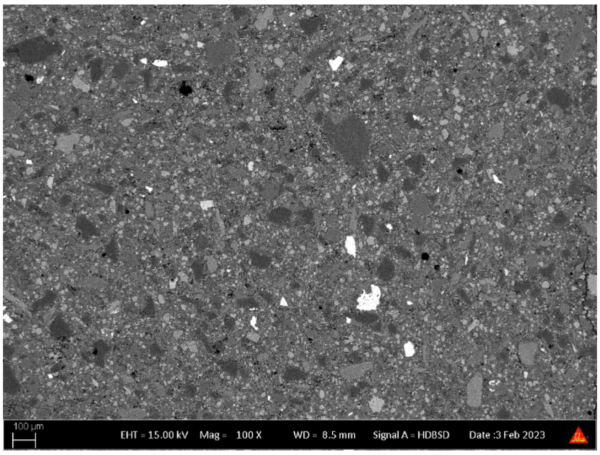

Figure 34: Magnification 100x

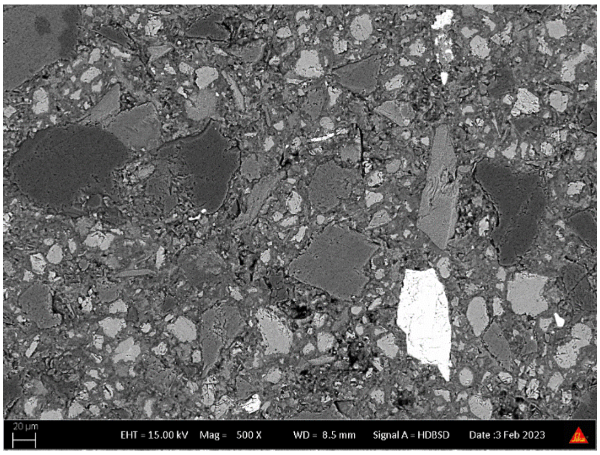

Figure 35: Magnification 500x

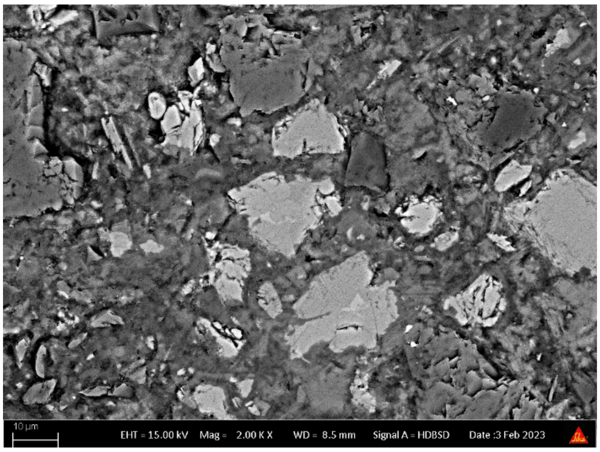

Figure 36: Magnification 2000x

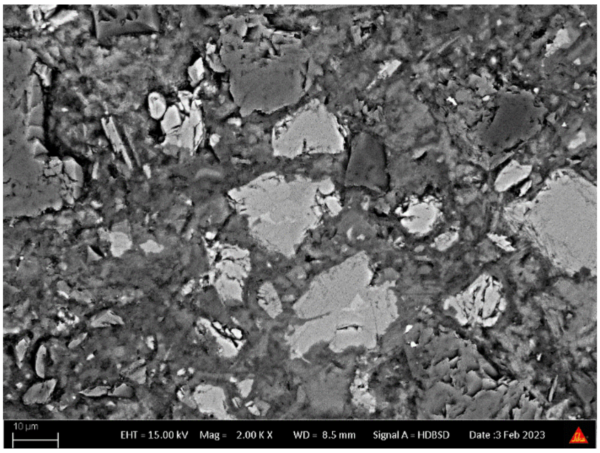

Figure 37: Magnification 5000x

From the pictures above we can see that the paste of this sample is not so dense. Most of the cement grains don’t have a hydration rim around them and that means that they are no hydrated enough.

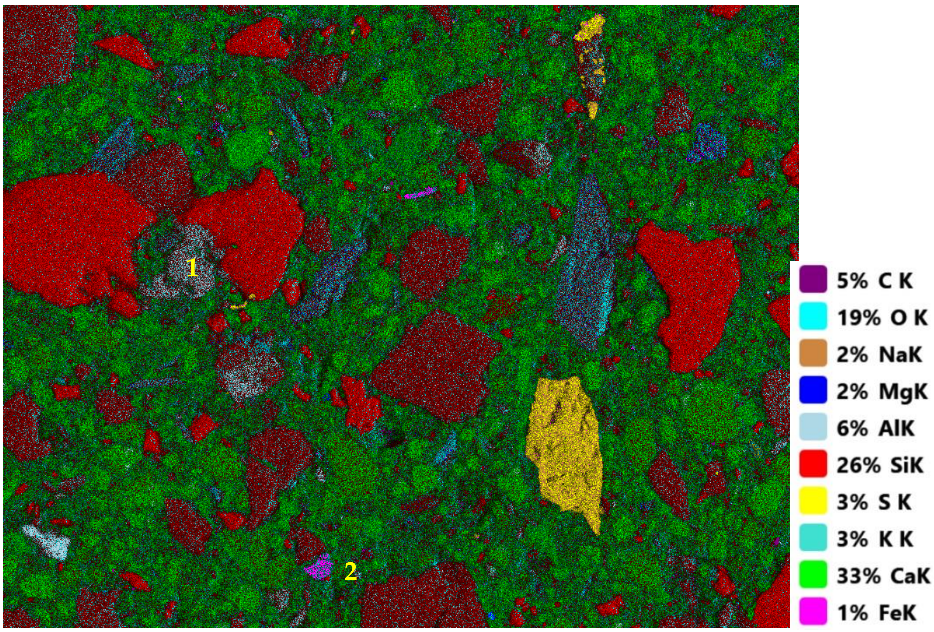

Figure 38: Mapping, magnification 500x

Figure 38- is the mapping of the sample where Zinkgruvan replaces aggregates, with activator. The aggregates of the mortar are shown (red color particles), as well as the paste (dark green) and the cement grains (bright green). The yellow particles with the S content, might be existent due to the traces of Sphalerite ($(Zn,Fe)S$) or Pyrite present in Zinkgruvan (FeS_2). The blue particles with the Mg and O content, might be existent due to Diopside ($MgCaSi_2O_6$) and Dolomite ($CaMg(CO_3)_2$) present in Zinkgruvan. The particle where spot 1 is contains Al and Si. The small particle where spot 2 is contains Fe and O.

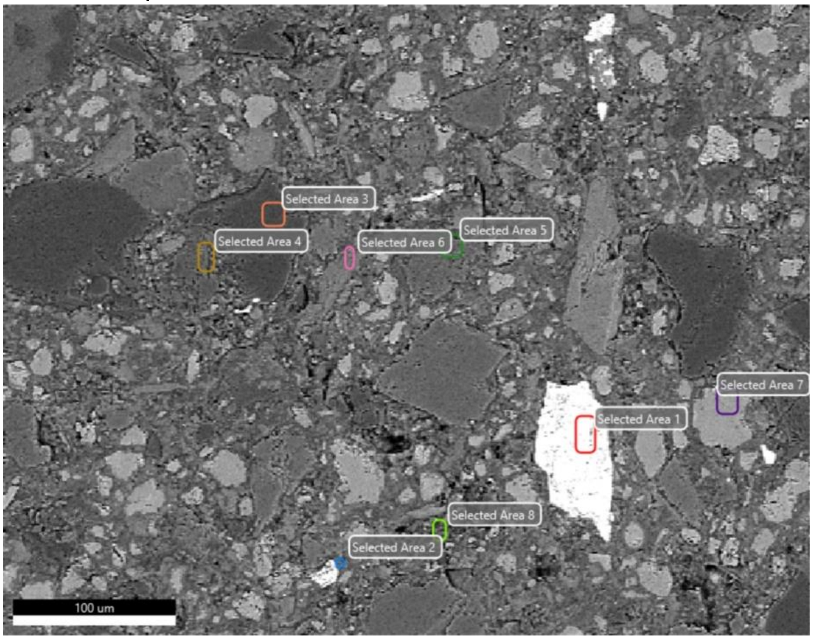

Figure 39: Spots for EDS spectra

Different spots shown in Figure 39., that seemed interesting from the mapping of Sample 5 were analyzed and the results of the EDS spectrum are shown below, Figure 40:

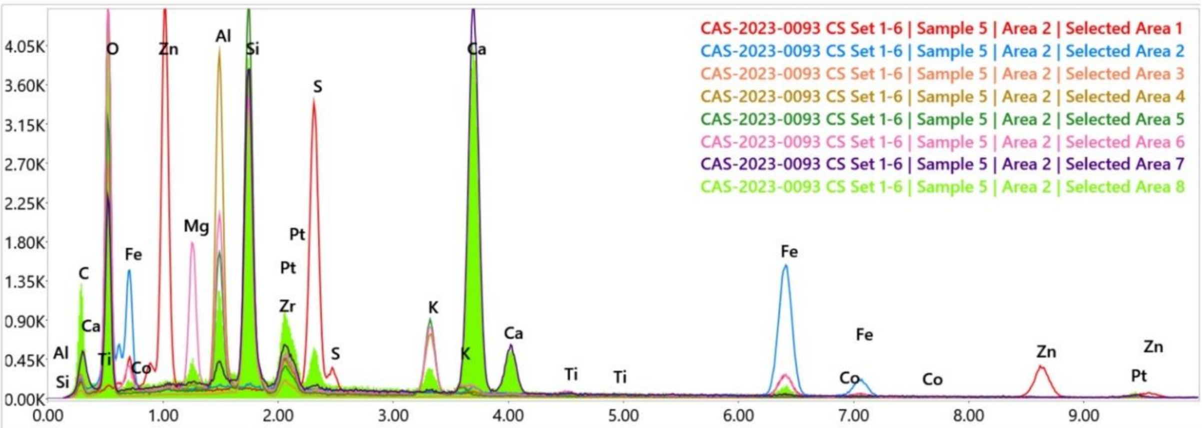

Figure 40: EDS spectrum

Selected Area 1 contains Zn and S from the Sphalerite that is present in Zinkgruvan tailings. Selected Area 2 contains Fe and O as shown in the mapping as well. Selected Area 3 contains O, Si and K and Selected Area 4 contains O, Si, Al and K maybe from the Microcline and

Orthoclase existent in the tailings. Selected Area 5 contains Si and O. Selected Area 6 contains O, Mg, Al, Si and K maybe because of the biotite existent in the Zinkgruvan tailings. Selected Area 7 contains Ca, O, Si and a small amount of Al so it must be a cement grain. Finally, Selected Area 8 contains Ca, O, Mg, Si and some smaller amounts of S, K and Fe and its part of the paste of the mortar.

When Kiruna is used as an aggregates replacement the SEM measurements obtained are as follows:

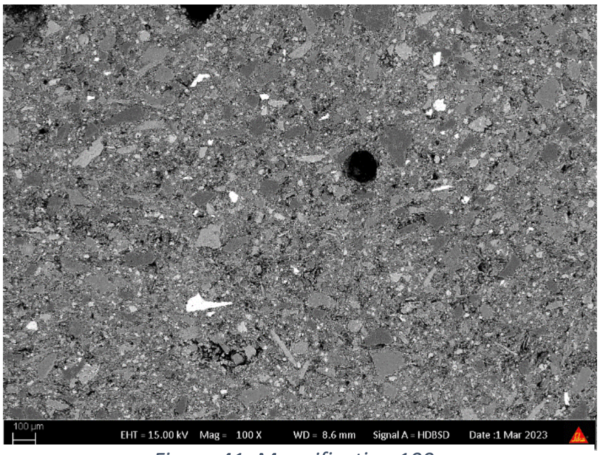

Figure 41: Magnification 100x

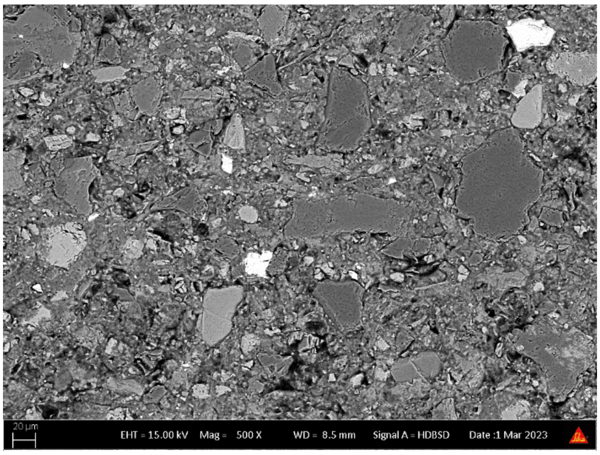

Figure 42: Magnification 500x

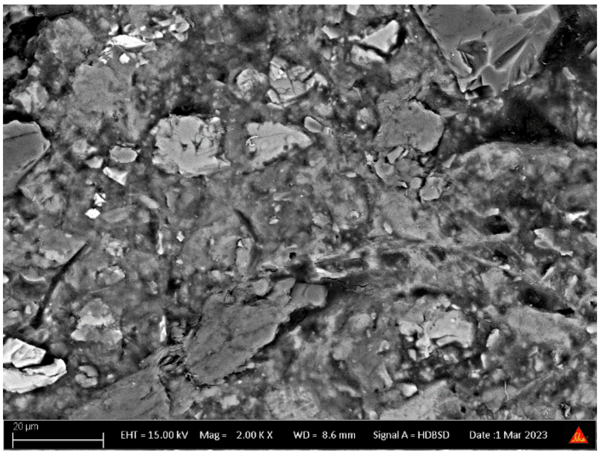

Figure 43: Magnification 2000x

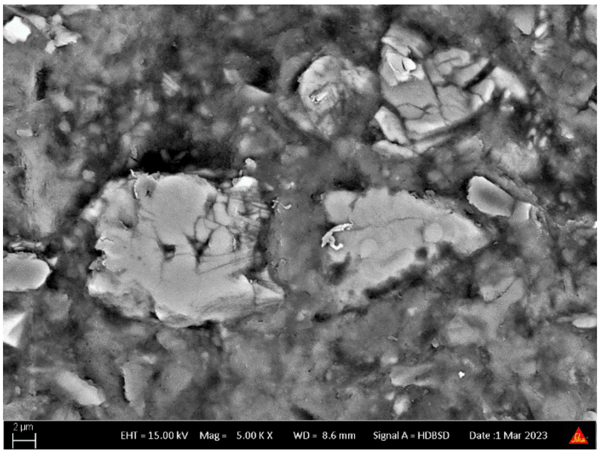

Figure 44: Magnification 5000x

From the pictures above we can see that the structure of the cement paste is not so dense but it's rather loose. It's not easy to observe cement grains that are well hydrated, that cement grains observed are big in size and without a hydration rim around them.

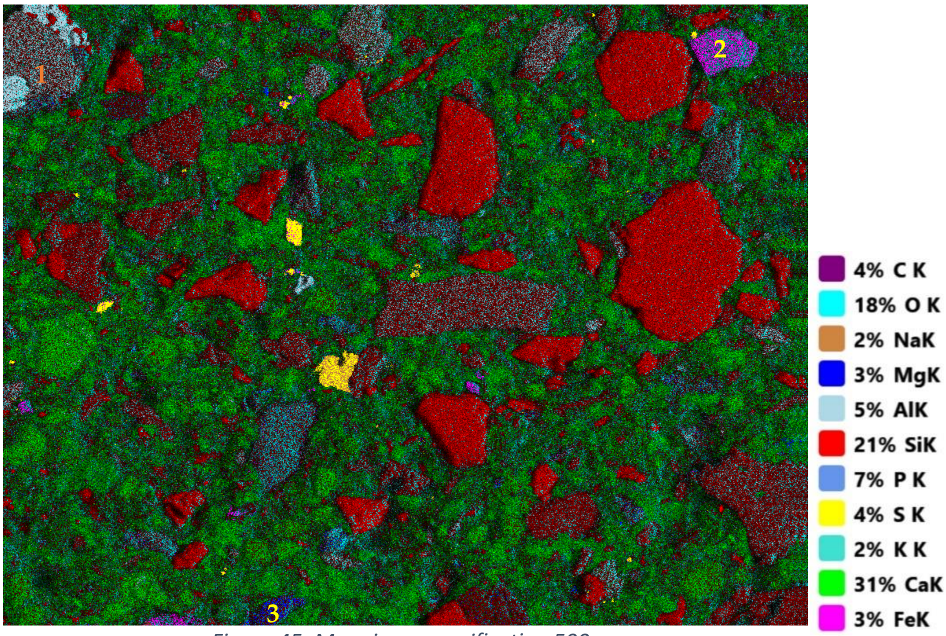

Figure 45: Mapping, magnification 500x

Figure 45. is the mapping of the sample, where the aggregates of the mortar are shown (red color particles), as well as the paste (dark green) and the cement grains (bright green). The small yellow particles observed have S content. The particles like the one where spot 1 is contain Al and Si. The particle where spot 2 is contains Fe and O. The blue particles like the one where spot 3 is, with the Mg content, might be existent due to Diopside ($MgCaSi_2O_6$) and Dolomite ($CaMg(CO_3)_2$) present in Kiruna tailings.

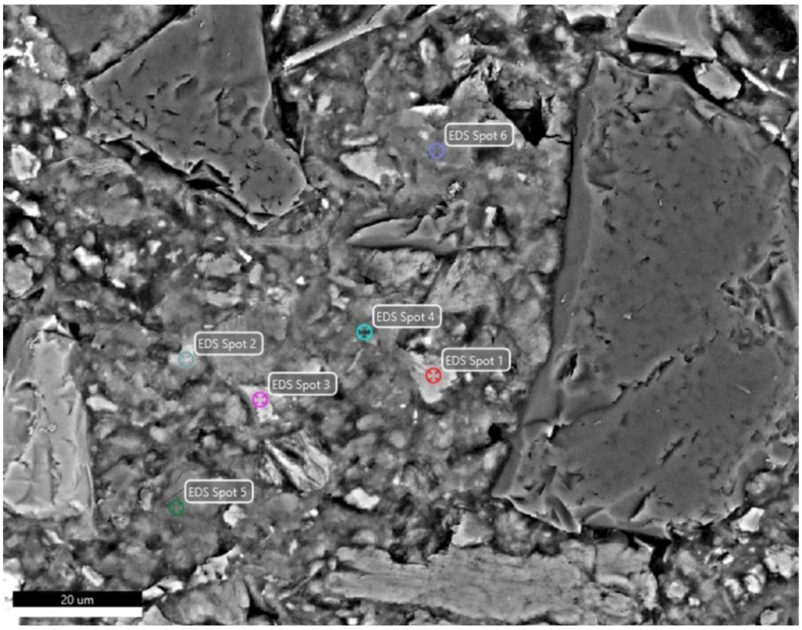

Figure 46: Spots for EDS spectra

Different spots shown in Figure 46, that seemed interesting from the mapping of the sample were analyzed and the results of the EDS spectrum are shown below, Figure 47.:

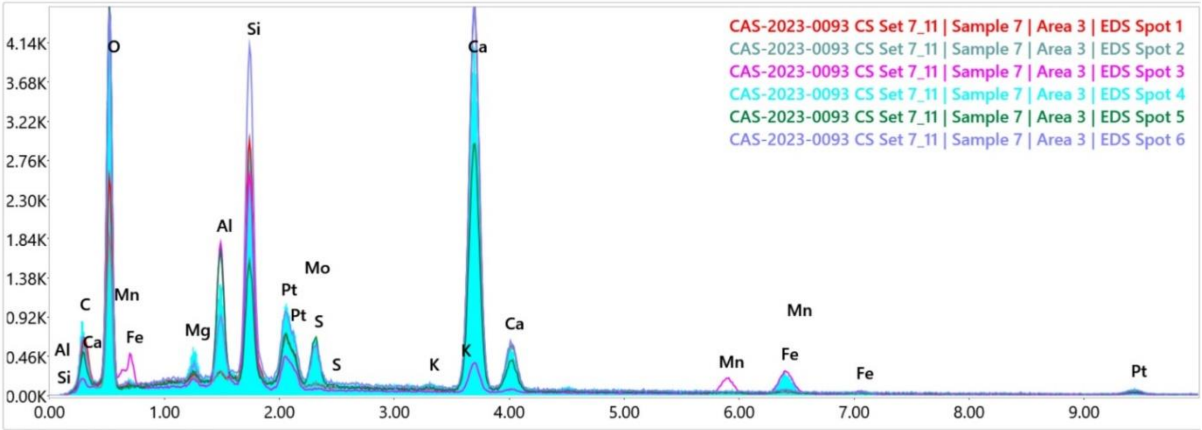

Figure 47: EDS spectrum

From the EDS spectrum above we can see that the selected areas 2 and 7 contain Ca, O, P, and a small amount of F, so those two particles might be the Fluorapatite ($Ca_5(PO_4)_3F$) that exists in the Kiruna tailings. The selected area 3 contains Al, Si and K, which might come from the Phlogopite or Annite phases that exist in the Kiruna tailings. The selected area 4 contains Fe and O, which we can also observe from the mapping of the same area, and it might be the Magnetite that is existent in the Kiruna tailings. The selected area 5 and 6, seems to be cement paste with Ca,O, Al, Si, S, and Pt from the platination of the cross section.

When Kiruna is substituting aggregates with the presence of an activator the results obtained are as follows:

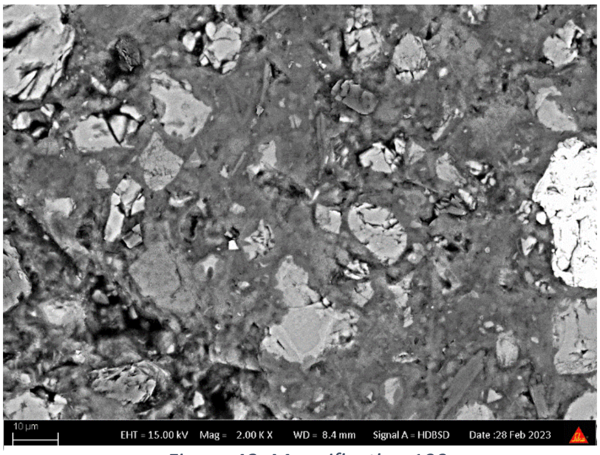

Figure 48: Magnification 100x

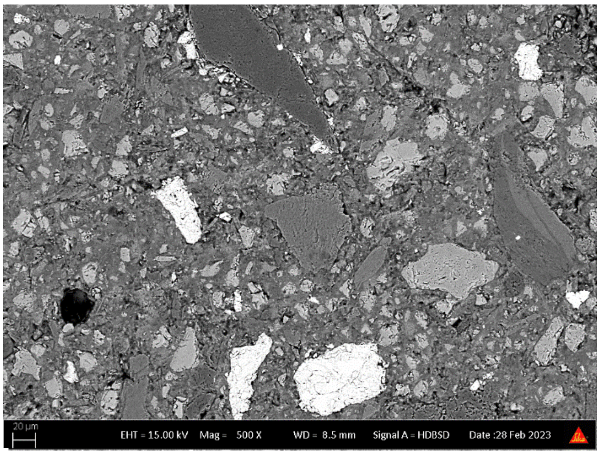

Figure 49: Magnification 500x

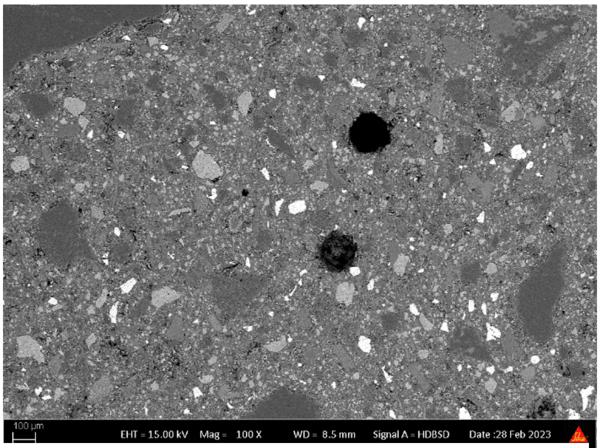

Figure 50: Magnification 2000x

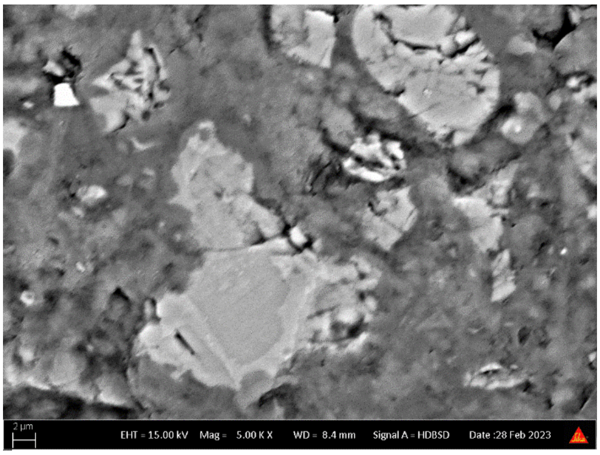

Figure 51: Magnification 5000x

From the pictures above we can see that the paste of the sample where Kiruna tailings are used as an aggregate's replacement, with the presence of activator is dense. The cement grains seem to be well hydrated, as we observe the hydration rim around most of them.

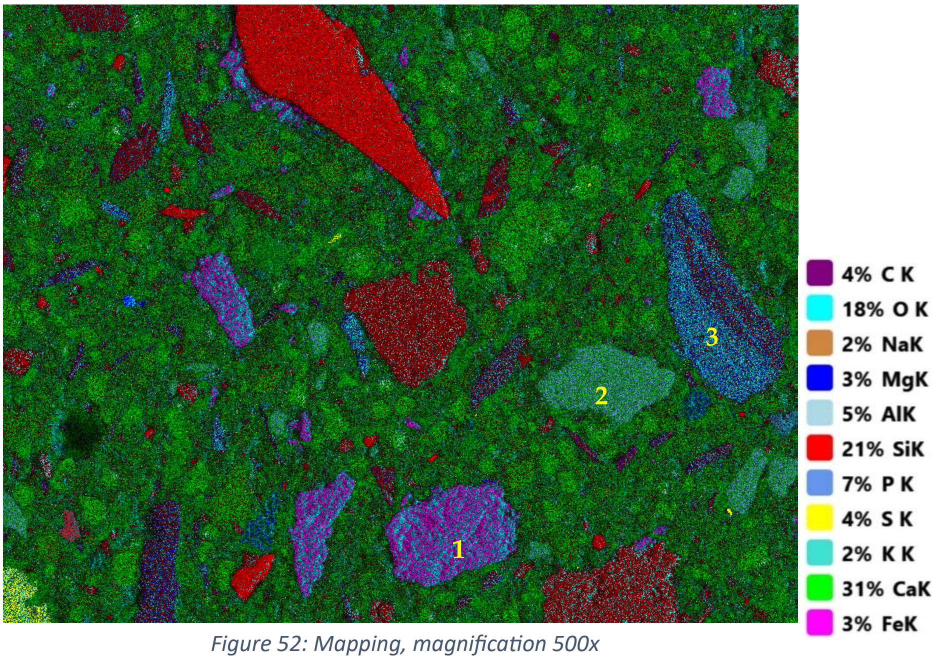

Figure 52: Mapping, magnification 500x

Figure 52. is the mapping the sample with Kiruna tailings used as an aggregate's replacement, with the presence of activator. The aggregates of the mortar are shown (red color particles), as well as the paste (dark green) and the cement grains (bright green). The purple particles like where spot 1 is located contain Fe and O, maybe coming from the magnetite that is existent in the Kiruna tailings. The particles like in spot 2, look like they contain P and Ca, so maybe they are the Apatite that is existent in the Kiruna tailings. The particles like in spot 3, contain Mg, O and maybe carbon or Si and this can be like this because of the Talc that is existent in the Kiruna tailings.

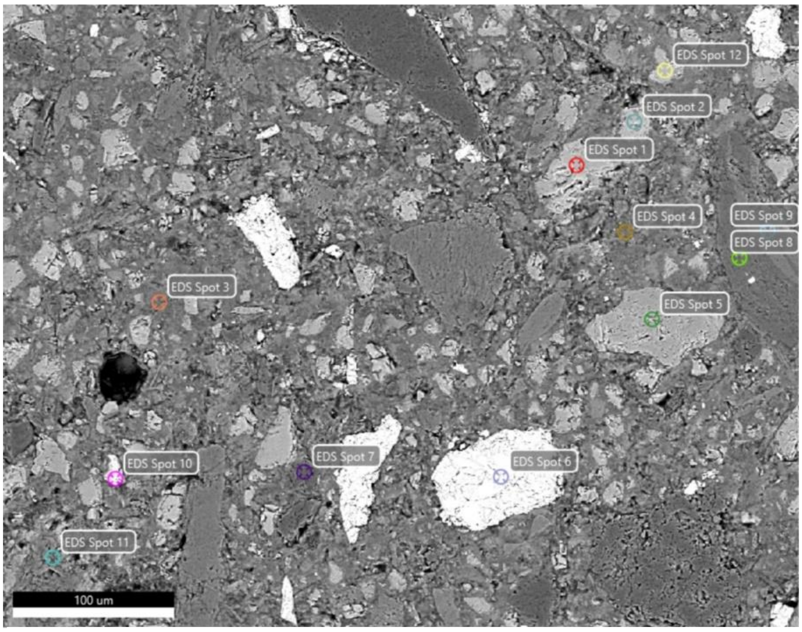

Figure 53: Spots for EDS spectra

Different spots shown in Figure 53., that seemed interesting from the mapping of the sample were analyzed and the results of the EDS spectrum are shown below, Figure 54.:

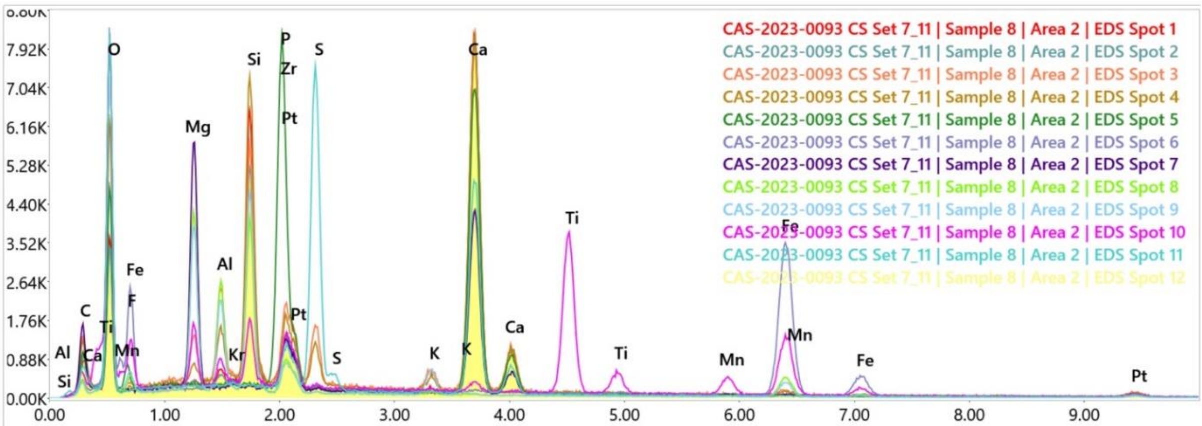
Figure 54: EDS spectrum

From the EDS spectrum above we can observe that selected areas 1, 2 and 12 contain Ca, O, Si and in some case very small amounts of Al, so these particles are cement grains. The selected areas 3, 4, and 11 are part of the paste of the mortar and they contain Ca, O, Si and S. Because of the existent of S throughout the paste we can assume the formation of Ettringite. The selected area 5 contains Ca, O and P, so this particle is Apatite that is existent in the Kiruna tailings, also shown in the mapping above. The selected area 6 contains Fe and O, so this particle is coming from the Magnetite that is existent in the Kiruna tailings. The selected area 7 contains Ca, Mg and Pt. The selected area 8 contains Mg and O, Si, Al, and Ca and it may be coming from the Talc that is existent in the Kiruna tailings. Spot 9 contains Mg, and O. Whereas, selected area 10 contains O, Fe, Mg, Ti, a small amount of Al, Mn and Pt and could be coming from the titanite existent in the Kiruna tailings.

From the fractures of the above mortars, it is possible to obtain more information about the microstructure of the mortars containing Zinkgruvan or Kiruna tailings as sand replacement with and without activator.

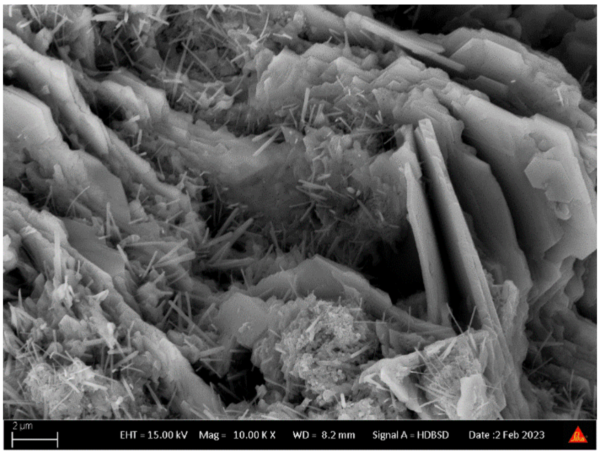

Figure 55: Magnification 10.000x (platelets)

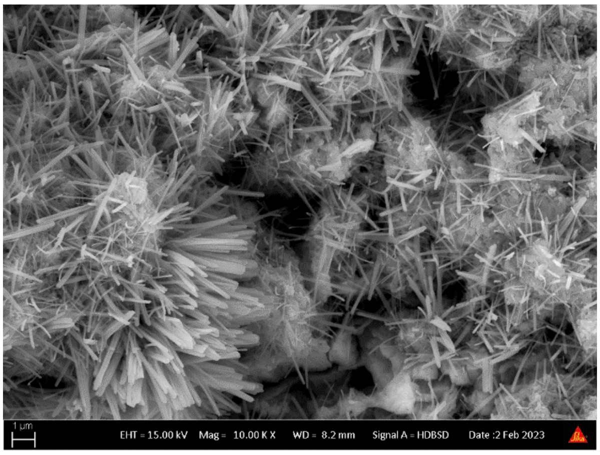

Figure 56 : Magnification 10.000x (ettringite needles)

From the pictures above it is observed that when Zinkgruvan is substituting aggregates in grout formulation the formation of ettringite needles takes place, but in some places of the paste there are also some platelets that might be portlandite incorporated with the ettringite needles.

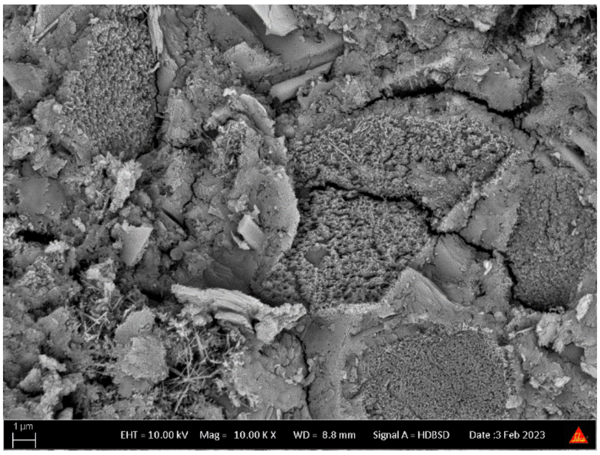

Figure 57: Magnification 10.000x (paste)

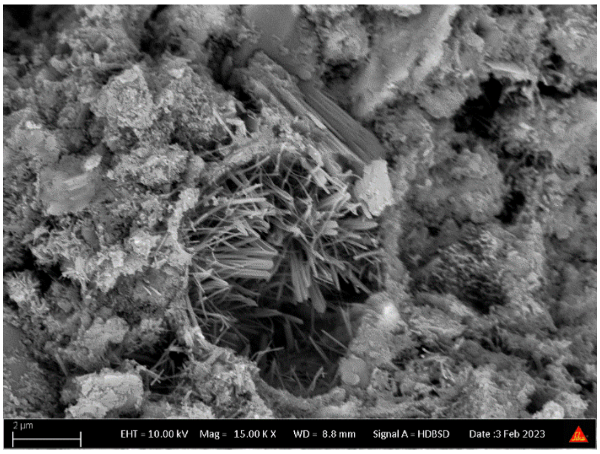

Figure 58 : Magnification 15.000x (ettringite needles).

When the activator is added in the formulation the paste of the mortar is denser and the ettringite needles forming are lesser and smaller than before.

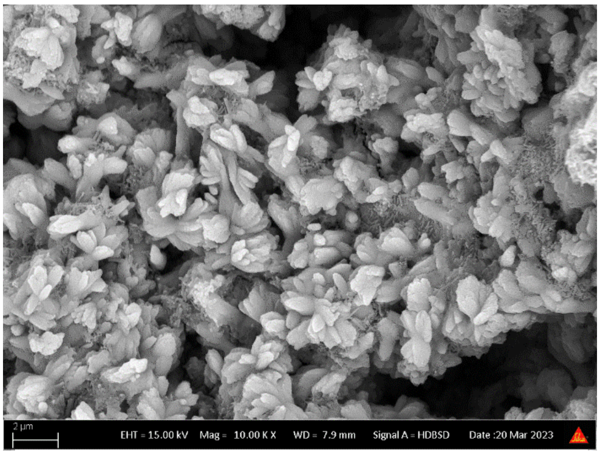

Figure 59: Magnification 10.000x.

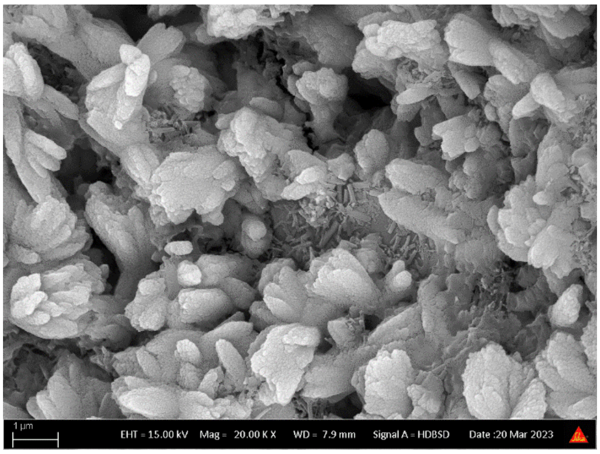

Figure 60: Magnification 20.000x.

From the pictures above we are able to observe that when Kiruna tailings are used as an aggregates replacement there is the formation of this structure as shown and, in some areas, there might be the formation of ettringite needles but in much lesser percentage than the cases mentioned before.

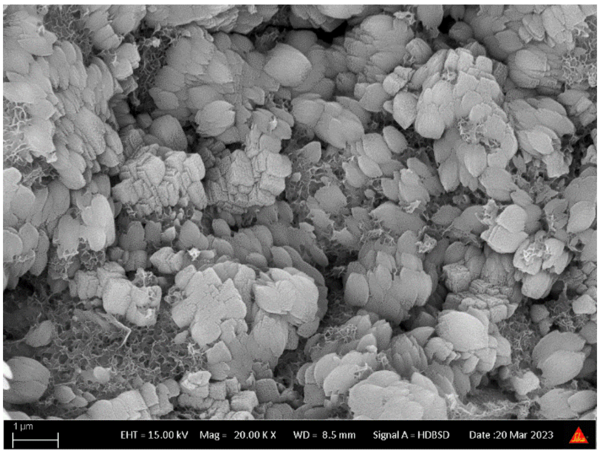

Figure 61: Magnification 10.000x

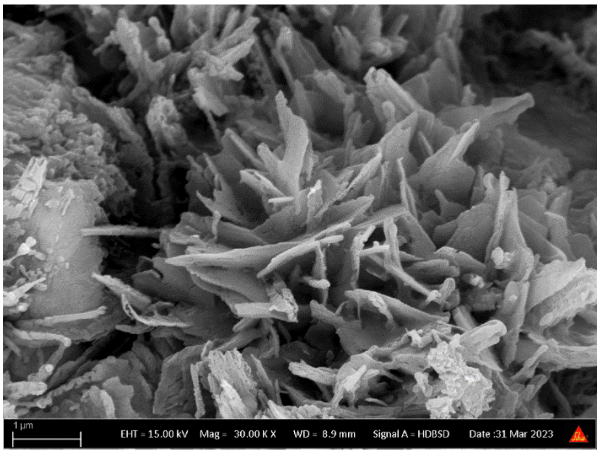

Figure 62: Magnification 30.000x.

When an activator is added in the mortar formulation the paste becomes much denser and there are some plates produced that could be portlandite.

Rheology of the repair mortar: The workability of the repair mortar when replacing partly the cement and/or the aggregates with Vale tailings is shown below:

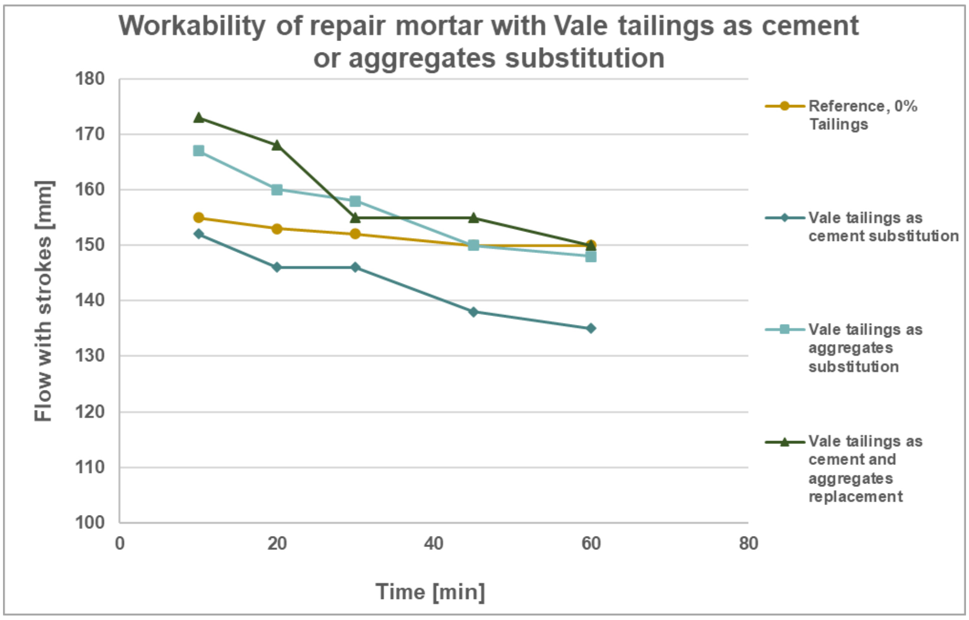

Figure 63: Workability of repair mortar with Vale tailings.

The flow of the repair mortar when substituting partly the cement with Vale tailings is lower than the reference. However, the flow of the repair mortar when substituting partly the aggregates in the formulation or partly the aggregates and the cement at the beginning is higher than the reference but after 30minutes it decreases significantly. In all the situations the addition of superplasticizer to adjust the flow wasn't needed.

Calorimetry: The Calorimetry of the same formulations is presented in the Figures below.

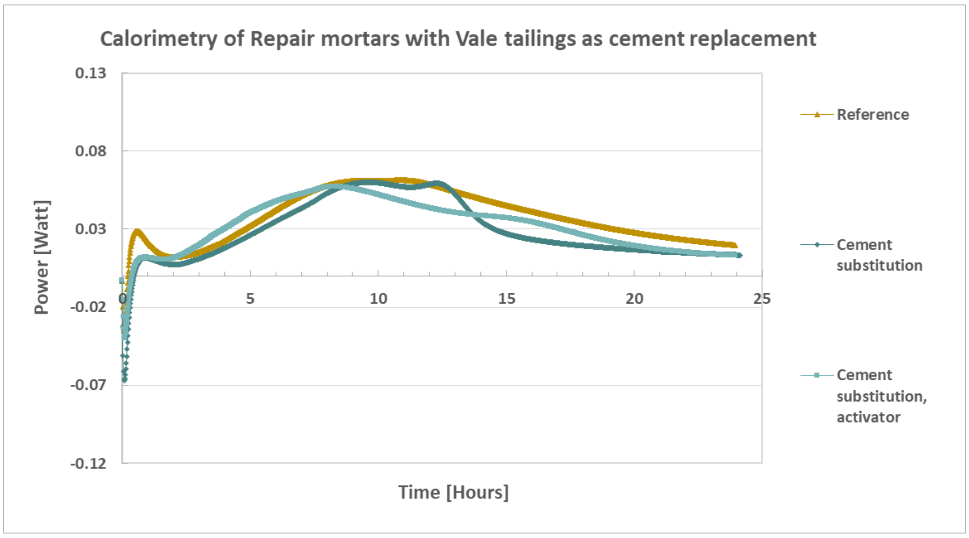

Figure 64: Calorimetry of repair mortar with Vale tailings as cement replacement.

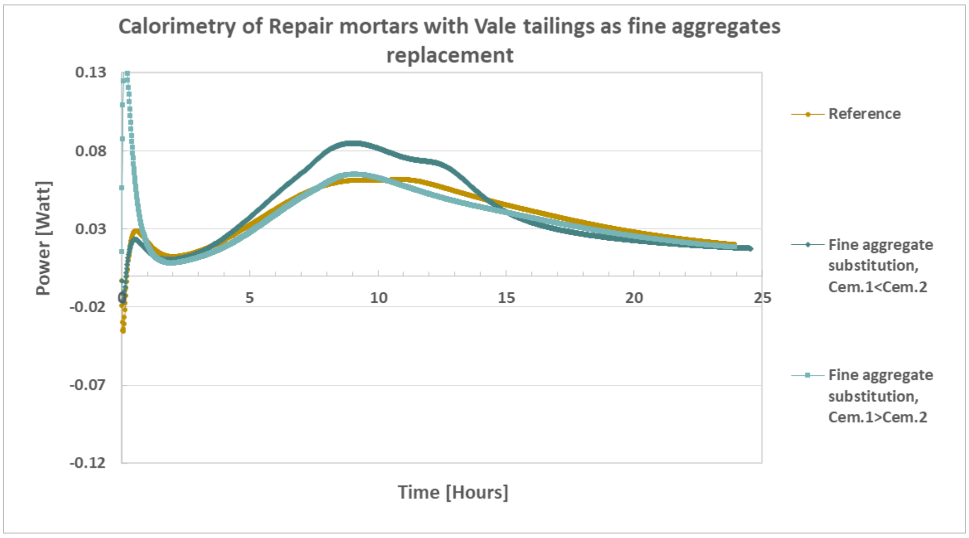

Figure 65: Calorimetry of repair mortar with Vale tailings as fine aggregates replacement.

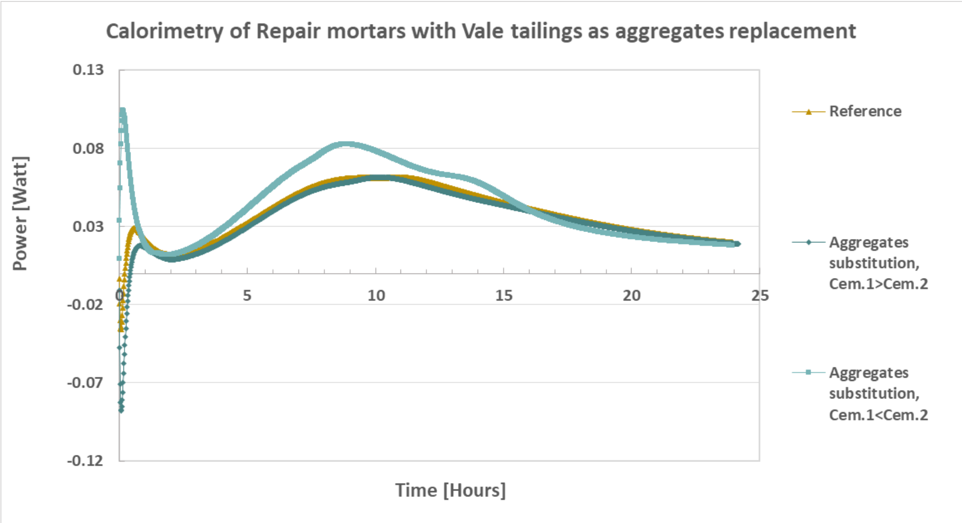

Figure 66: Calorimetry of repair mortar with Vale tailings as aggregates replacement.

From the Calorimetry measurements shown above we can observe that when substituting cement by Vale tailings in repair mortars the hydration of cement is happening around 10-15 hours, when an activator is present in the formulation it is obvious that the rection will take place earlier, and faster. When fine aggregates are substituted by Vale tailings and Cem.1 < Cem.2 the reaction is more intense, whereas when a part of the aggregates is substituted the and Cem.1 > Cem.2 the reaction is more intense.

Mechanical performance: The mechanical performance of repair mortars (compressive and flexural strengths) when using Vale tailings as partly cement and/or aggregates replacement is shown in the Figure 67. below:

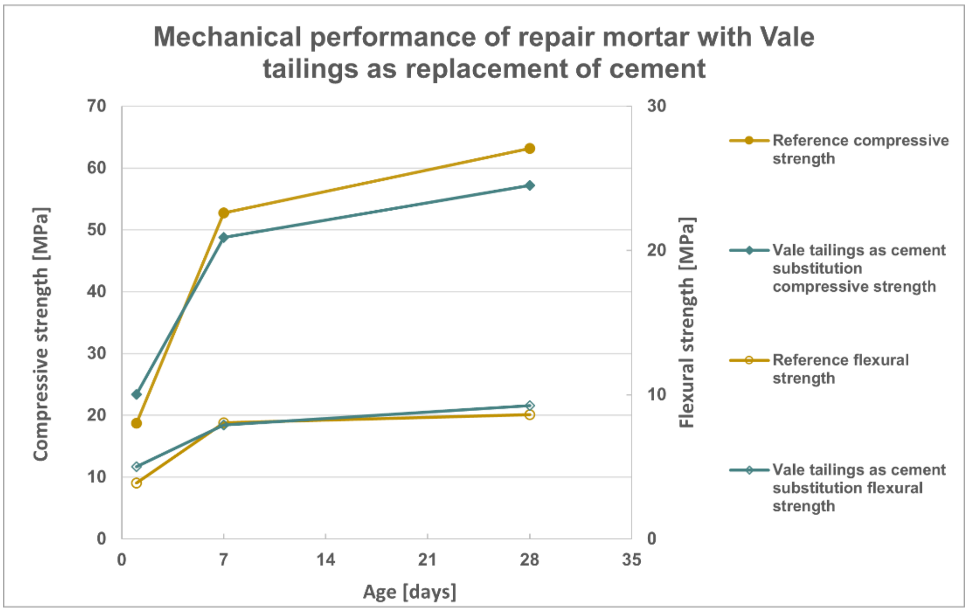

Figure 67: Mechanical performance of repair mortar with Vale tailings as replacement of cement.

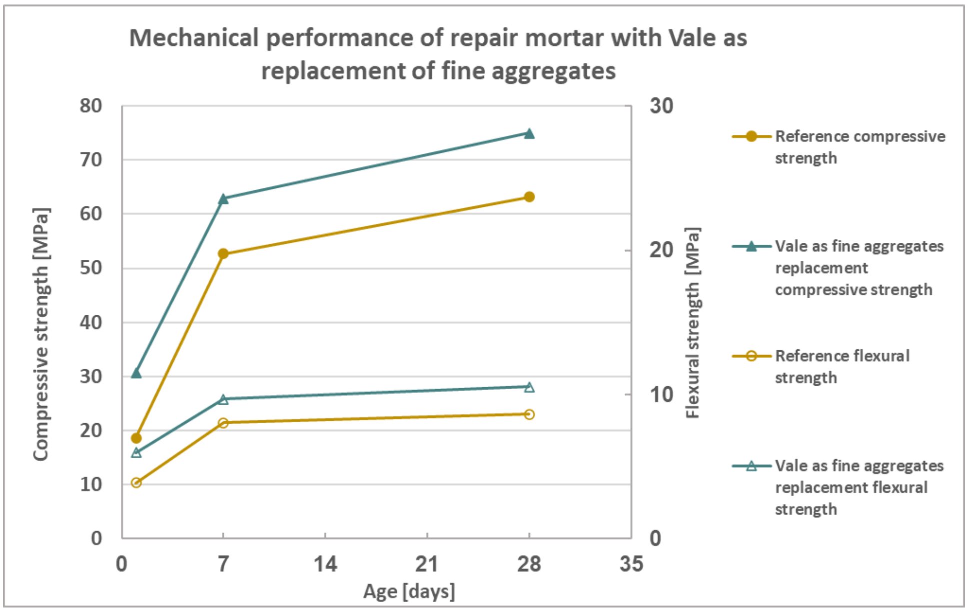

Figure 68: Mechanical performance of repair mortar with Vale tailings as replacement of fine aggregates.

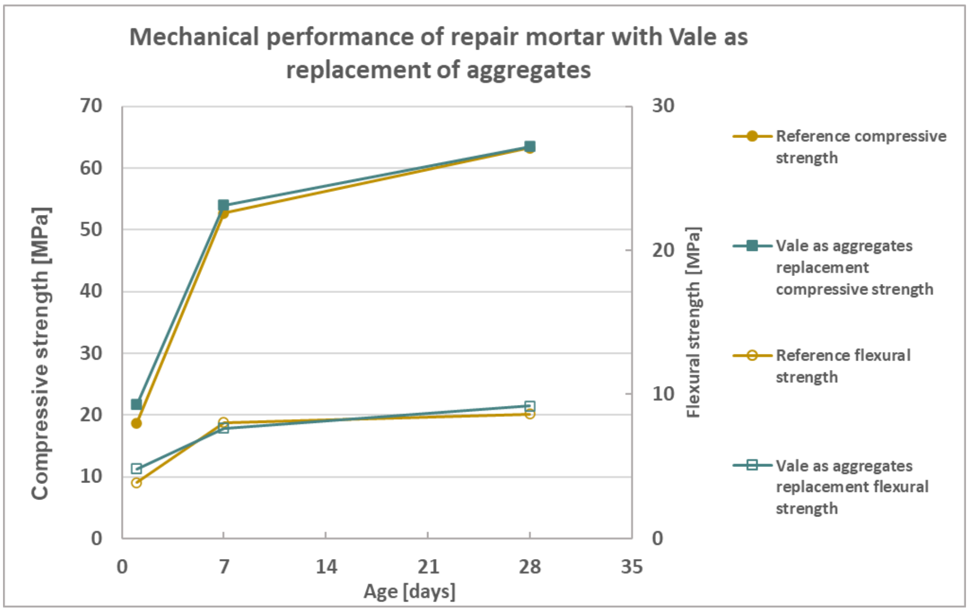

Figure 69: Mechanical performance of repair mortar with Vale tailings as replacement of aggregates.

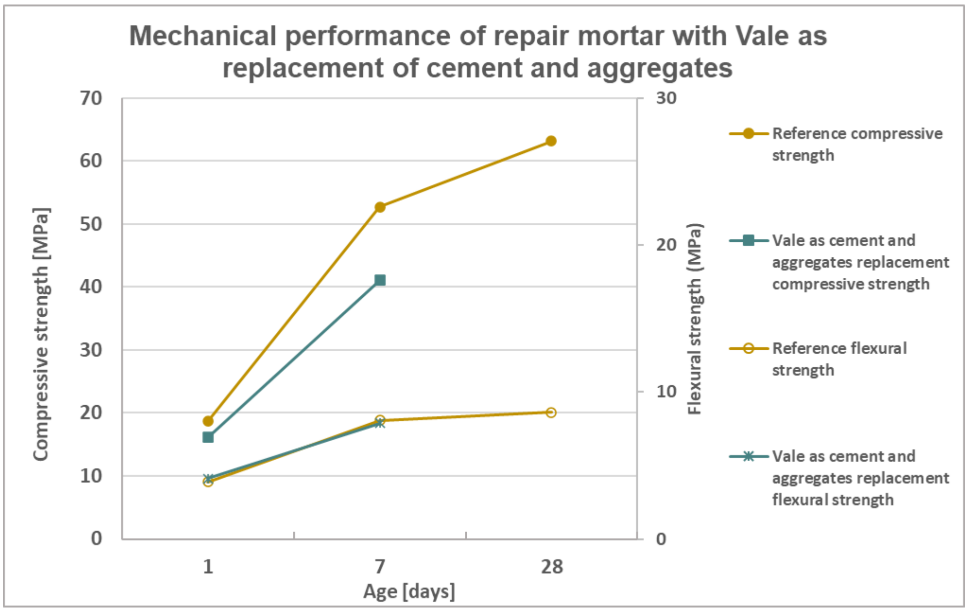

Figure 70: Mechanical performance of repair mortar with Vale tailings as replacement of cement and aggregates.

From the graphs above it is obvious that the compressive strength of the repair mortar when substituting cement with Vale tailings is lower in comparison to the reference mortar (1d strength 18.7MPa, 7d strength 52.7MPa, 28d strength 63.2MPa for the reference, and 1d strength 23.4MPa, 7d strength 48.8MPa, 28d strength 57.2MPa when substituting cement) whereas for the flexural strength slightly higher values are obtained (1d strength 3.88MPa, 7d strength 8.06MPa, 28d strength 8.63MPa for the reference, and 1d strength 5MPa, 7d strength 7.89MPa, 28d strength 9.23MPa when substituting cement).

When substituting the finer fractions of aggregates with Vale tailings the mechanical performance of the repair mortar is better than the one of the reference's (1d strength 30.7MPa compressive, 5.97MPa flexural, 7d strength 62.9MPa compressive, 9.7MPa flexural 28d strength 75MPa compressive, 10.55MPa flexural.

When substituting a part of the aggregates with Vale tailings the mechanical performance of the repair mortar is very similar to the reference's as shown in the Figure 69. above.

Finally, when substituting part of the cement and the aggregates in the repair mortar with the Vale tailings then the compressive strength is much lower than the reference, but the flexural strength remains the same.

Physical performance: The physical performance of the same mortars is shown in the Figures below, where the shrinkage and the expansion of these mortars is measured.

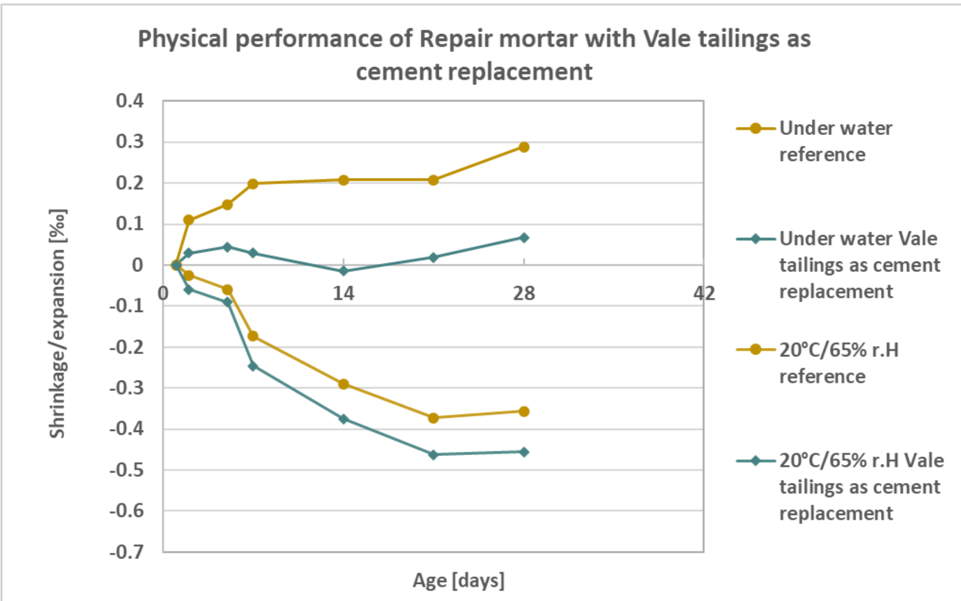

Figure 71: Shrinkage and expansion of repair mortar with Vale tailings as cement replacement.

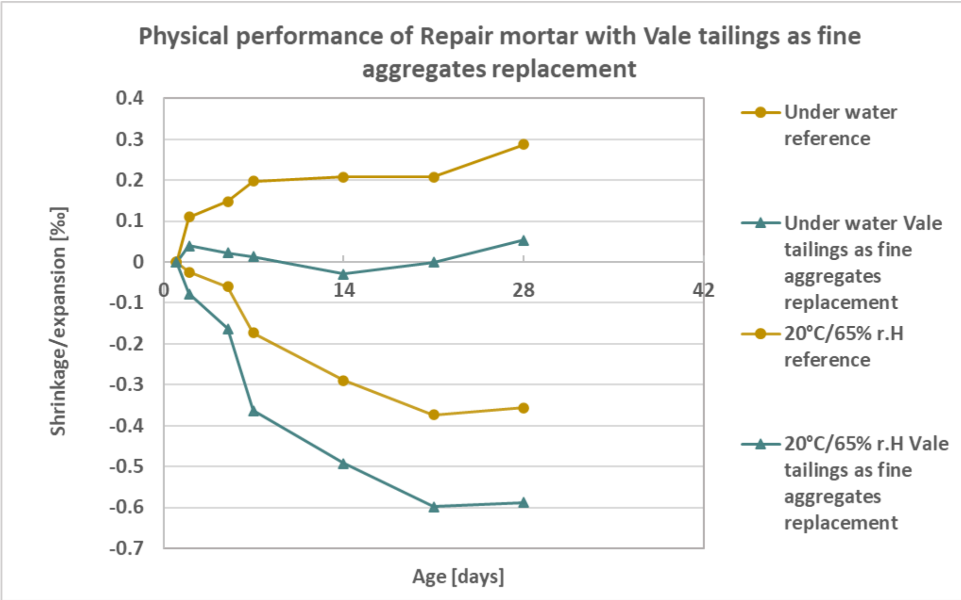

Figure 72: Shrinkage and expansion of repair mortar with Vale tailings as fine sand replacement.

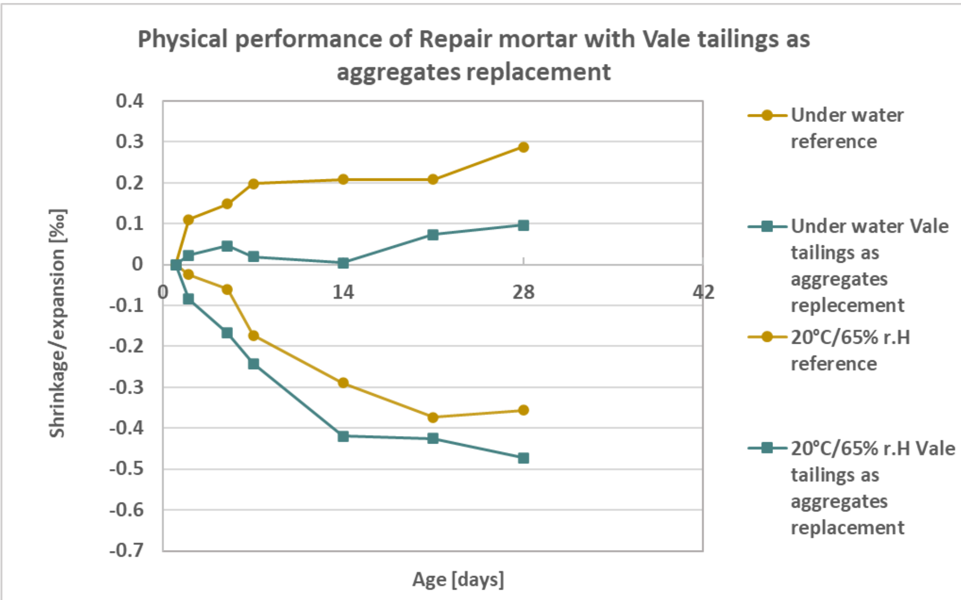

Figure 73: Shrinkage and expansion of repair mortar with Vale tailings as aggregates replacement.

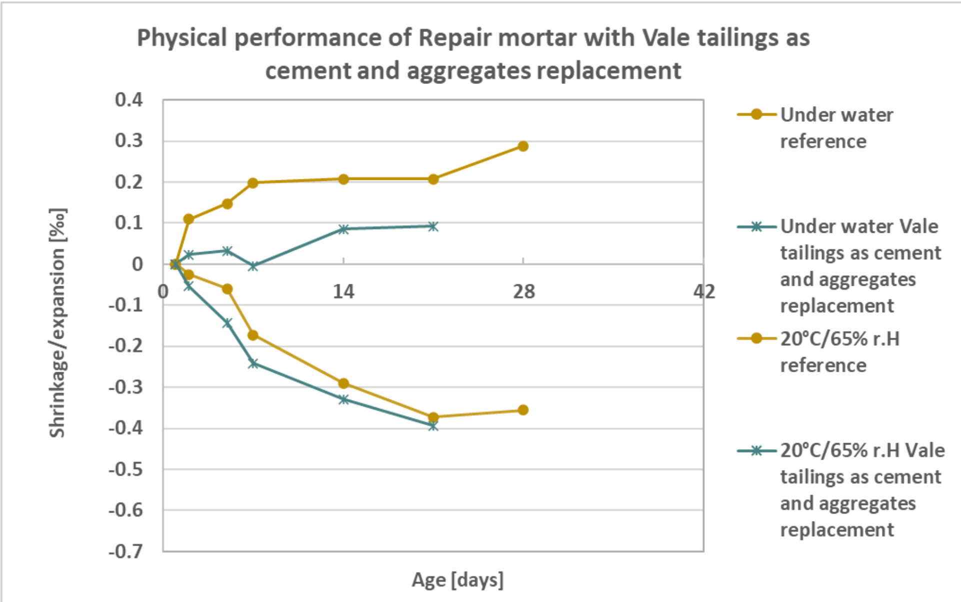

Figure 74: Shrinkage and expansion of repair mortar with Vale tailings as cement and aggregates replacement.

The results shown above are for the shrinkage and expansion of repair mortars for 28days of measurement. It is observed in all the cases that the expansion of the repair mortars containing Vale tailings is lower than that of the reference. However, the shrinkage in all the cases seems like it has higher values than those of the reference.

Application on concrete substrate: The repair mortars mentioned above were applied on prewetted concrete substrates, to evaluate the possible formation of cracks. Those applications are presented in the pictures below where no crack formation has been observed:

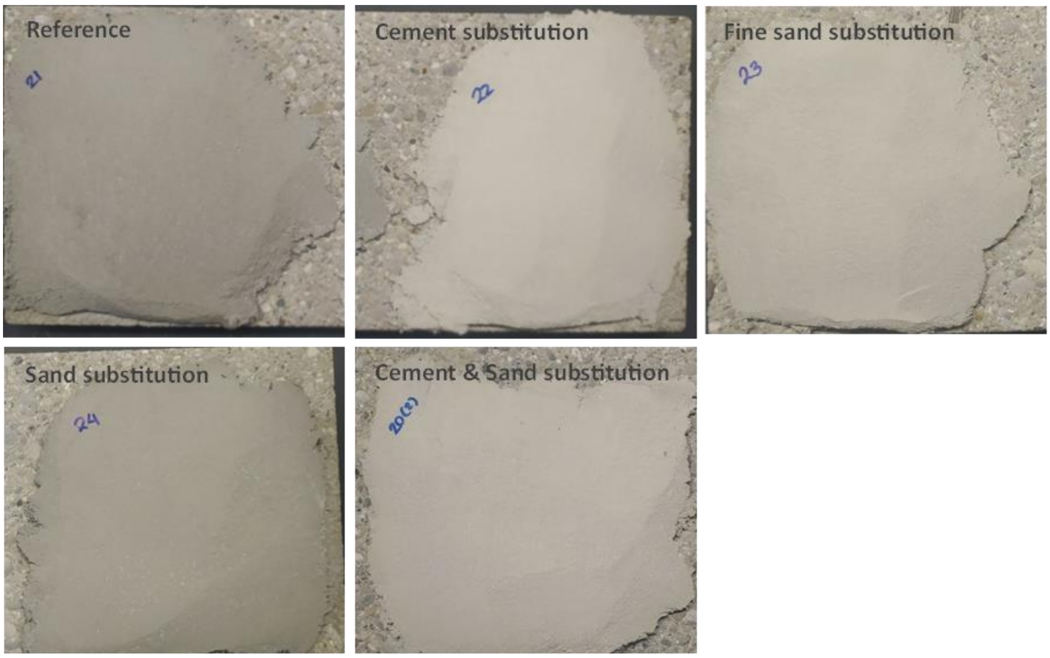

Figure 75: Application of repair mortars on concrete substrate.

5 Examples of monuments where these materials can be applied.

The fundamental goal of safeguarding cultural landmarks is rooted in the scientific endeavor to perpetuate the embodiment of cultural heritage. Restoration constitutes a meticulously orchestrated array of measures devised to preclude subsequent deterioration and to cultivate optimal conditions for the enduring safeguarding of cultural relics. These relics encompass a spectrum of entities, including individual architectural edifices, artistic creations, archaeological discoveries, and various material conduits of cultural expression. In contradistinction to conventional reparative undertakings, the restoration of architectural heritage is predicated upon a comprehensive evaluation grounded in scholarly inquiry. This evaluative foundation is further buttressed by the utilization of specialized methodologies derived from contemporary construction practices.

In the present epoch, the process of restoring architectural heritage demands assiduous dedication and meticulous adherence to established legal frameworks. Article 47 of the Federal Law governing "Cultural Heritage of the People of the Russian Federation" [59]designates architectural monument restoration as a mode of reconstruction, underscoring the significance of this endeavor. Complementing this, Article 43 mandates the execution of exhaustive research, evaluations, design, and implementation activities, all conceived with the overarching objective of ensuring the preservation of structures bearing historical significance. This meticulous preservation effort pertains to architectural heritage, as it strives to resuscitate and reinforce structures. To achieve this, restoration interventions invariably employ materials reminiscent of the originals, deploying techniques that safeguard the structural authenticity while ensuring optimal longevity.

Embedded within this meticulous restoration process is a commitment to restoring damaged elements, purifying tarnished segments, and excising subsequent alterations that detract from the monument's original essence. Within the prevailing context, GOST R 56891.2-2016 "Preservation of Cultural Heritage Objects. Terminology and Definitions. Part 2. Monuments of Historical and Cultural Significance" serves as a beacon, defining the term "restoration of a monument or ensemble" as a multidisciplinary endeavor encompassing research, design, and implementation activities, all driven by the imperative to unearth and conserve the historical and cultural worth of a given heritage object.

At the crux of scholarly restoration practices lies the foundational principle of minimal intrusion into historical materials. This principle is intrinsic to the scientific approach and aligns seamlessly with the essence of the Venice Charter, a seminal document endorsed during the May 1964 International Congress of Architects and Technical Specialists in Historical Monuments. Commonly referred to as the "Venice Charter," this proclamation conveys the wisdom that "for the monument, the most correct approach involves the study, restoration, and utilization of historical technologies."

Integral to this discourse is the concept of historicism—a pivotal facet that guides the meticulous restoration of heritage entities. Historicism, grounded in a deep-seated appreciation for historical context, serves as the lodestar illuminating the path toward meticulous restoration. It underscores the imperative to encapsulate the essence of a bygone era while adhering to the ethos of authenticity, thus engendering a more profound connection between the present and the past.

Furthermore, a crucial dimension of the discourse encompasses the legal scaffolding enveloping restoration pursuits. Legal frameworks serve as the bulwark, outlining the parameters within which restoration activities unfold. This legal architecture harmonizes with the scholarly and scientific endeavors, dictating the parameters within which restoration interventions may transpire. A synergy between legal edicts and academic prudence forms the cornerstone of a holistic approach to restoration, fostering the enduring conservation of our cultural legacy.

In summation, the pursuit of safeguarding cultural heritage, particularly architectural monuments, is a multifaceted endeavor rooted in meticulous scientific exploration. This exploration is characterized by adherence to principles such as minimal intrusion, historicism, and legal compliance, all of which collectively constitute the fulcrum upon which restoration activities pivot. Through the application of scholarly rigor and legal diligence, the preservation and restoration of cultural heritage materials are elevated to an endeavor that bridges temporal chasms, nurturing a profound connection between the past, present, and future.

Based on this the new materials that are proposed to be applied for the restoration of monumental structures should be compatible chemically with the authentic ones. The grouts developed in this thesis with the Zinkgruvan or Kiruna tailings used as cement or aggregates replacement could be used for the rehabilitation of a building consisted of concrete. For example, they could be used in the building of the Mills of Crete, which is located in Souda, Chania to strengthen possible defect areas.

Mills of Crete is a very big concrete structure located in the port of Souda in Chania and it was built in 1953. These buildings of the factory are some places have damages. In order to preserve their integrity strengthening of the structure is important. This could be achieved by the application of the grouts with Zinkgruvan or Kiruna tailings for reconstructing the damaged areas.

Figure 76: The Mills of Crete.

The repair mortars that are developed in this thesis with Vale tailings used as cement and/or aggregates replacement could be used for the restoration of cementitious monuments of the nineteenth century, like for example the neoclassical buildings that already incorporated cement into their materials. One example of a neoclassical building in the city of Chania is the Government building that was the Judicial and Administrative Palace, initially of the Cretan State and then of the Prefecture of Chania. This building is still existent in the city of Chania it’s been almost 125 years since it was built, and its restoration for its preservation could become needed. In these types of building the repair mortars developed in this thesis can be applied after the scientific evaluation of the authentic material.

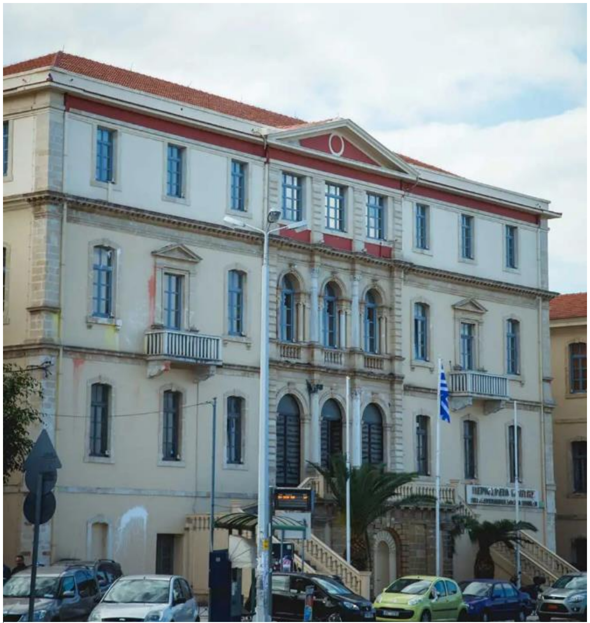

Figure 77: The Government building in Chania.

6 Conclusions

In conclusion, the incorporation of mine tailings into construction materials offers a promising approach for mitigating CO_2 emissions coming from cement manufacturing. This innovative approach not only addresses environmental concerns by repurposing waste-hazardous materials, which are detrimental to both ecosystems and human health, but also has the potential to alleviate the escalating costs associated with importing raw materials. By utilizing nearby tailings facilities, the expenses linked to material transportation can be curtailed significantly.

The mineralogical and chemical composition of mine tailings makes them well-suited for serving as partial substitutes for cement in mortar formulations. Their particle size distribution, positioned between that of cement and fine sand, renders them suitable for replacing either cement or aggregates due to their optimal “packing” properties. The feasibility of substituting both cement and aggregates are viable, although the incorporation of certain additives, such as superplasticizers, may be necessary to achieve desired performance characteristics. Although the particle size distribution of tailings can substantially influence the workability of fresh mortar, its impact is generally controllable.

An intriguing aspect of mine tailings lies in their potential reactivity. While further investigation could provide insights from Luxan tests, FTIR, TGA, XRD, and mineralogical performance assessments were corroborated, particularly when $Ca(OH)_2$ is introduced, suggesting the pozzolanic activity of certain mine tailings. This pozzolanic activity can enhance mortar performance by increasing mechanical resistance, even surpassing reference values.

In conclusion, mine tailings hold great promise as a sustainable resource in construction materials, with the potential to not only reduce environmental impact but also maintain or even enhance the mechanical properties of mortar formulations. The workability of the grout can be affected when tailings are in the system because of their fineness, the grout becomes stickier but with the addition of superplasticizer in the formulation this problem is overcome. In grouts when the cement is replaced partly by Zinkgruvan or Kiruna tailings in the presence of an activator, it was observed that the 1d strengths increased from 24.5MPa to 40MPa, and from 21.4MPa to 39MPa respectively (reference 50MPa). When the aggregates are replaced in the formulation of grouts by Zinkgruvan or Kiruna tailings in the presence of an activator the mechanical performance is notably increased. If the sand is replaced partly by Zinkgruvan tailings then the measurements are as follows: 1d strength is 48.9MPa compressive, 8.3MPa flexural, 7d strength is 86MPa, 10.08MPa flexural, and 28d strength is 96MPa compressive, and 15.8MPa flexural, where an increase of flexural strength is observed in comparison with that of the reference. When the sand is replaced partly by Kiruna tailings then the measurements are as follows: 1d strength is 54MPa compressive, 8.1MPa flexural, 7d strength is 82.2MPa compressive, 15.8 flexural, and 28d strength is 93.7MPa compressive and

16.5MPa flexural. A more significant increase on the flexural strength of the grouts when sand is replaced by Kiruna tailings is observed.

This increase in mechanical performance when an activator is incorporated in the formulation in comparison with the grout formulation without the activator reveals that the tailings can be activated. This conclusion could also be derived by the calorimetry results presented in Figure 22. where the peaks of the reactions of the grout formulations when tailings are used with an activator are taking place earlier than the reference and much earlier than the formulations without activator.

The exploration of alternative construction materials has unveiled a field of possibilities for addressing the repair and preservation needs of diverse architectural structures. The incorporation of Zinkgruvan or Kiruna tailings into grout formulations, serving as either partial cement substitutes or aggregates, has demonstrated a remarkable potential. These specialized grouts, when activated, exhibit properties that render them well-suited for repairing and rehabilitating contemporary structures. Interestingly, their porosity levels are close to those of established reference materials, a vital consideration in achieving structural integrity.

In parallel, the formulations of repair mortars that use Vale tailings as replacement for cement and/or aggregates introduce a distinct avenue for restoring historical landmarks, especially those coming from the twentieth century. An important issue is the compatibility between the materials, a pivotal aspect when dealing with structures of historical significance. This approach not only promises effective restoration but respects the style of architectural heritage.

Embracing these innovative material solutions an effective restoration practice is proposed and a sustainable approach to construction practices is adopted. By turning towards these unconventional materials, we not only strengthen the longevity of modern buildings but also ensure the survival of historical treasures for generations to come. This dual-pronged strategy, marked by its adaptability and eco-consciousness, stands as a testament to human ingenuity in the fields of architecture and conservation.

Continued research and development in this area will undoubtedly shed more light on the specific applications and benefits of incorporating mine tailings into the construction industry.

7 Future Work

Further research must take place for incorporating mine tailings into mortars, and especially repair mortars that are going to be applied for the restoration of monumental structures. Some of the research that needs to be investigated in more detail is presented below:

- **Further Reactivity Investigation:** While initial indications suggest the pozzolanic nature of certain mine tailings, a comprehensive study focused on understanding the extent and mechanisms of their reactivity is essential. This could involve more rigorous testing with various activators, extended time frames, calculation of the amorphous content and a deeper exploration of the underlying chemical reactions.
- **Optimal Tailings Formulation:** To effectively harness the potential of mine tailings, it is imperative to determine the optimal ratio of tailings to other constituents in mortar formulations. This would involve a systematic investigation into how different combinations influence mechanical properties, workability, and durability, while considering potential drawbacks such as increased setting times or changes in color.
- **Long-Term Durability Studies:** Understanding the long-term performance and durability of mortar containing mine tailings is crucial. This can involve accelerated aging studies, exposure to extreme weather conditions, and assessing their resistance to chemical attacks. These investigations would provide insight into the suitability of such formulations for real-world construction scenarios.
- **Environmental Impact Assessment:** As part of a sustainable approach, evaluating the environmental impact of using mine tailings in construction materials is necessary. This could encompass a life cycle assessment to a analyze the overall environmental benefits and potential drawbacks of the approach compared to traditional materials.
- **Tailings Sourcing and Processing:** Investigating different sources of mine tailings and their processing methods can lead to tailings with varied compositions. Understanding how different processing techniques impact the chemical and physical properties of tailings is crucial for tailoring their incorporation into construction materials.
- **Regulatory Considerations:** Since the use of mine tailings involves repurposing waste materials, it's important to navigate any regulatory hurdles. Collaborating with regulatory bodies to establish guidelines and standards for the incorporation of mine tailings in construction materials would be beneficial.
- **Toxicity leaching of heavy metals:** Investigating the heavy metal content of the tailings is very important. There are indications that the heavy metals are incorporated into the cementitious matrix when used in mortar formulations, in this case toxicity characteristic leaching procedure has to take place to determine the amount of heavy metals leaching in the environment. Further investigation using SEM in specific mortar formulations with tailings and obtaining EDS spectra from the cementitious paste to quantify the amount of heavy metals existent in the paste.
- **Economic Viability:** Conducting a cost-benefit analysis of utilizing mine tailings in construction materials is essential. This would involve evaluating the economic

feasibility of large-scale implementation, considering factors such as transportation costs, material processing, and potential savings in cement production.

- **Comparative Studies:** Comparing the performance of mortar containing mine tailings with other sustainable construction materials, such as fly ash or slag, can provide valuable insights into the overall efficacy and advantages of this approach.
- **Scale-Up and Field Trials:** Transitioning form laboratory-scale experiments to field trials is a crucial step in validating the practicality and performance of mine tailings in real-world construction projects. Collaborating with construction companies for pilot projects would provide valuable feedback and real-world data. After the field trials the grouts and repair mortars that are obtained by this thesis could be proposed more easily for the rehabilitation and restoration of modern buildings and cementitious monuments respectively.

8 References

(1) M. Gou, L. Zhou, N. Wie Ying Then.: Utilization of tailings in cement and concrete: A review. Sci Eng Compos Mater 26:449-464 (2019).

(2) D. Kossof, W.E. Dubbin, M. Alfredsson, S.J. Edwards2, M.G. Macklin, K.A. Hudson-Edwards.: Mine tailings dams: Characteristics, failure, environmental impacts, and remediation. Applied Geochemistry 51, 229-245 (2014).

(3) B.G. Lottermoser.: Characterization, Treatment and Environmental Impacts. Mine Wastes 3rd edition, Springer ISBN 978-3-642-12418-1 (2010).

(4) A. Kontopoulos, K. Komnitsas, A. Xenidis, P.Passiopi.: Environmental Characterization of The Sulfidic Tailings In Lavrion. Minerals Engineering 8(10), 1209-1219 (1995).

(5) B. Cox, S. Innis, A. Mortaza, N.C. Kunz, J. Steen.: A unified metric for costing tailings dams and the consequences for tailings management. Resources Policy 78 (2022).

(6) N. Sivakugan, R. Veenstra, N. Naguleswaran.: Underground Mine Backfilling in Australia Using Paste Fills and Hydraulic Fills. Int. J. of Geosynth. And Ground Eng. Springer (2015).

(7) C. Qi, A. Fourie.: Cemented paste backfill for mineral tailings management: Review and future perspectives. Minerals Engineering 144 (2019).

(8) Kundu, S. Aggarwal, A. Mazumdar, S. Dutt, B.: Stabilization characteristics of copper mine tailings through its utilization as a partial substitute for cement in concrete: preliminary investigations. Environmental Earth Sciences 75, 1-9 (2016).

(9) M.M. Arbili, M. Alqurashi, A. Majdi, J. Ahmad, A.F. Deifalla.: Concrete Made with Iron Ore Tailings as a Fine Aggregate: A Step towards Sustainable Concrete. Materials 15, 6236 (2022).

(10) G. Li, Y.J. Chen, H. Di.: The Study on used Properties of Mine Tailings Sand. Advanced Materials Research 859, 87-90 (2014).

(11) Peys, A. Snellings, R. Peeraer, B. Vayghan, A.G. Sand, A. Horckmans, L. Quaghebeur, M.: Transformation of mine tailings into cement-bound aggregates for use in concrete by granulation in high intensity mixer. Journal of Cleaner Production 366(132989), 1-10 (2022).

(12) P. Segui, A. M. Safhi, M. Amrani, M. Benzaazoua. Mining Wastes as Road Construction Material: A Review. Minerals 13, 90 (2023).

(13) H. Paiva, F. Simoes, H. Maljaee, J. Yliniemi, M. Illikainen, V.M. Ferreira.: Production of ceramic construction materials as an environmental management solution for sulfidic mine tailings. SN Applied Sciences 3:751 (2021).

(14) Sigvardsen, N.M. Nielsen, M.R. Ottosen, L.M. Jensen, P.E.: Utilization of mine tailings as partial cement replacement. In: 2nd International Conference on Bio based building materials & 1st Conference on ECOlogical valorisation of GRAnular and FIbrous materials, pp. 272-277. Clermont-Ferrand, France (2017).

(15) J. Esmaeili, H. Aslani, O. Onuaguluchi.: Reuse Potentials of Copper Mine Tailings in Mortar and Concrete Composites. Journal of Materials in Civil Engineering 0899-1561 (2020).

(16) S. Siddique, J.G. Jang. : Assessment of molybdenum mine tailings as filler in cement mortar. Journal of Building Engineering 31-101322 (2020).

(17) S. Vignesh, B.M. Ramalinga Reddy, S.S. Nachiar.: Effect of Partial Replacement of Natural Sand With Gold Mine Tailings on Some Properties of Masonry Mortars. International Journal of Engineering & Technology 4 (2015).

(18) A. Bakolas, E. Aggelakopoulou, A. Moropoulou, S. Anagnostopoulou.: Evaluation of pozzolanic activity and physico-mechanical characteristics in metakaolin-lime pastes. Journal of Thermal Analysis and Calorimetry 84, 157-163 (2006).

(19) A. Saedi, A.J. Zanjani, A.K. Darban.: A review on different methods of activating tailings to improve their cementitious property as cemented paste and reusability. Journal of Environmental Management 270-110881 (2020).

(20) B.L. Dutrow, C.M. Clark.: X-ray Powder Diffraction. Geochemical Instrumentation and Analysis. X-ray Powder Diffraction (XRD) (carleton.edu).

(21) K. Wirth, A. Barth.: X-ray Fluorescence. Geochemical Instrumentation and Analysis. X-Ray Fluorescence (XRF) (carleton.edu).

(22) Particle Size Distribution Measurement by the Laser Diffraction/Scattering Method Part 1. Shimadzu Excellence in Science. Particle Size Distribution Measurement by the Laser Diffraction/Scattering Method Part1 : SHIMADZU (Shimadzu Corporation).

(23) What is FTIR Spectroscopy? Merck. What is FTIR Spectroscopy? (sigmaaldrich.com).

(24) D. Harvey.: Thermogravimetry. LibreTexts Chemistry. 31.1: Thermogravimetry - Chemistry LibreTexts.

(25) M.P. Luxan, F. Madruga, J. Saavedra.: Rapid evaluation of pozzolanic activity of natural products by conductivity measurement. Cement and Concrete Research 19, 63-68 (1989).

(26) Ministry of Public Works, Spain (1977). Determination of Carbonates in Soils by the Bernard Calcimeter Method, UNE 7-367, Madrid.

(27) Committee 046 Cement used in construction industry (2015). Methods of testing cement- Part 1: determination of strength, EN 196-1, Austrian Standards Institute, Vienna.

(28) European committee for Standardization (1999). Methods of testing for mortar for masonry-Part 3: determination of consistence of fresh mortar (by flow table), EN 1015-3, Comité Européen de Normalisation, Brussels.

(29) European committee for Standardization (1999). Products and systems for protection and repair of concrete structures- Test methods- Determination of compressive strength of repair mortar. EN 12 190, Comité Européen de Normalisation, Brussels.

(30) Calorimetry. LibreTexts Chemistry. Calorimetry - Chemistry LibreTexts.

(31) M. Pavan, V. Raja, A.R. Barron. : ICP-MS for Trace Metal Analysis. LibreTexts Chemistry. 1.6: ICP-MS for Trace Metal Analysis - Chemistry LibreTexts.

(32) Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) Spectroscopy. Surface Science Western. Scanning Electron Microscopy (SEM) - Surface Science Western.
(33) Borges de Castro, N.L. Fajardo, A.A. Oliviera, C.A. dos Santos, W.J.: Influence of Addition Contents of Iron Ore Tailings on Structural Mortar. Journal of Management and Sustainability 11, 74-87 (2021).
(34) Moropoulou, A. Bakolas, A. Bisbikou, K.: Characterization of ancient, byzantine and later historic mortars by thermal and X-ray diffraction techniques. Thermochimica Acta 269/270, 779-795 (1995).
(35) K. Zamanian, J. Zhou. Y. Kuzyakov. : Soil carbonates : The unaccounted, irrecoverable carbon source. Geoderma 384-114817 (2021).
(36) Lu, C.C. Hsu, M.H. Lin, Y.P.: Evaluation of heavy metals leachability of incinerating recycled aggregate and solidification/stabilization products for construction reuse using TCLP, multifinal pH and EDTA mediated TCLP leaching tests. Journal of Hazardous Materials 368, 336-344 (2019).
(37) Federal Law governing. Cultural Heritage of the People of the Russian Federation. Article 47.
(38) GOST R 56891.2-2016. Preservation of Cultural Heritage Objects. Terminology and Definitions. Part 2. Monuments of Historical and Cultural Significance.