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Screening for key material parameters affecting early-age and mechanical properties of blended cementitious binders with mine tailings

Anne Mette T. Bagger *, Wolfgang Kunther, Nina M. Sigvardsen, Pernille E. Jensen

Department of Civil Engineering, Technical University of Denmark, Building 118, 2800, Lyngby, Denmark

A R T I C L E   I N F O

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Mine tailings
Supplementary cementitious materials
Partial cement clinker replacement
Ternary blend composite cement
Mortar
Mechanical performance
Early-age properties
Chemometrics

A B S T R A C T

Considering the vast amounts and wide variability of tailings available worldwide, means to assess the potential of tailings for cement clinker replacement based on their physical, chemical and mineralogical characteristics would be useful. This work studied the early-age properties and mechanical performance of mortar of Portland limestone cement (CEM II/A-LL) clinker in a ternary blend with partial clinker substitution by 13 metal and mineral mine tailings. The properties studied included workability, setting time, porosity and compressive strength. The effects of replacement level and mine tailing characteristics on the performance of mortar were assessed by chemometrics.

The results showed that most mine tailings reduced the workability of mortar (3–19 %) and that an increased replacement level reduced the workability further. For most mine tailings, the initial setting time was identical to the reference, while they reached the final setting faster. Tailings had a variable impact on the porosity at low replacement, while porosity generally increased at a higher replacement. The compressive strength decreased with increasing replacement in most cases, and a clear negative correlation was found between compressive strength and porosity. However, five mine tailings developed up to 10 % higher strength after 28 days with 20 % supplementary composite material compared to the reference.

Chemometric analyses showed that tailings with high specific surface area and silicon dioxide content influenced the mechanical properties of the mortar most positively. Conversely, larger grain sizes, high loss on ignition, calcium oxide and calcium carbonate content impacted compressive strength negatively.

The analyzed characteristics do, however, not fully explain the resulting early-age and mechanical properties, thus additional investigations are needed to understand the performance in detail.

1. Introduction

Supplementary Cementitious Materials (SCM) are widely used in combination with Ordinary Portland Cement (OPC) as they contribute positively to the properties of hardened concrete through hydraulic or pozzolanic activity. Incorporation of latent hydraulic SCMs such as blast furnace slag [1], pozzolanic SCMs such as coal fly ash [2], silica fume [3] and metakaolin [4] or filler materials such...
as limestone [5] has become an essential part of the cement and concrete industry [6–8]. Synergetic effects in ternary binders of e.g. limestone and Al-rich SCMs has also been documented [9]. The benefits of SCMs include improved mechanical properties [10], control of alkali-silica reactions [11] and enhancement of durability by e.g. chloride binding [12]. Another critical aspect of the replacement of cement by SCMs is the CO₂ reduction, as the cement industry contributes 5–8% of the anthropogenic CO₂ emissions [13,14]. However, several commercially available SCMs such as slag and coal fly ash are becoming increasingly scarce due to limited slag availability from steel production and the closing down of coal-fired power plants [15]. Alternative industrial by-products with potential as SCMs, which are produced in sufficiently large quantities and do not compromise the concrete quality, are therefore requested.

Mining of minerals and metals produces 20–25 billion ton of solid waste annually, and waste volumes are expected to increase due to decreasing concentrations of target minerals in the remaining ores [16]. In comparison, the total mass of cement produced in 2019 was estimated to be 4.1 billion ton globally [17]. One fraction of the mining waste is the mine tailings resulting from separating the target metal/mineral from the gangue material by chemical and physical processing. This fraction constitutes a sludge of fine-grained solids, which entails the risk of environmental and health hazards when deposited in on-land or underwater storage facilities. Currently, the utilization of mine tailings is limited, probably due to their frequent toxicity and the significant variations in mineralogy, often including reactive sulfide compounds. However, since each tailing is produced in large volumes, identifying few tailings with good performance could significantly contribute to filling the SCM availability gap [18].

Previous researchers mainly investigated the utilization of specific mine tailings for low-value purposes such as aggregates in construction materials [19–21], backfilling material in ceased mines [22] and the production of cement clinker among others [23]. Others have studied specific mine tailings' cementitious properties [24–29] and revealed reduced compressive strengths by addition of some mine tailings [25,28,30], while increased by others [24,26,27]. The impact on compressive strength were attributed to the grain properties of the tailings [28,30], while another found tailings to encounter pozzolanic characteristics [27]. Simonsen et al. [31] screened a wide variety of mine tailings with highly variable chemical, physical and mineralogical characteristics, and consequently very different performance potentials as SCMs.

Hypothesizing that a material’s performance as SCM is pre-determined by the material’s physical and chemical characteristics, new insight may be obtained by relating tailing characteristics and performance as SCM for multiple tailings. The purpose of this study was to correlate results of early-age properties and mechanical performance of multiple tailings used as SCMs in ternary binders with tailing characteristics.

### Table 1

<table>
<thead>
<tr>
<th>Tailing Code</th>
<th>Tailing Mine</th>
<th>Host rock</th>
<th>Ore mineral</th>
<th>Target metal/mineral</th>
<th>Mineral processing</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kemi A</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Pegmatite</td>
<td>Pegmatite</td>
<td>Quartz, alkali feldspar, REE</td>
<td>Crushed, ground, flotation with hydrofluoric acid</td>
<td>[33]</td>
</tr>
<tr>
<td>Kill A</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Karkortokite</td>
<td>Eudialyte</td>
<td>Ta, Nb, REE, Zr</td>
<td>Crushed (grain sizes &lt;600 μm, which are not applicable for magnetic separation).</td>
<td>[34]</td>
</tr>
<tr>
<td>Kill B</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Karkortokite</td>
<td>Eudialyte</td>
<td>Ta, Nb, REE, Zr</td>
<td>Crushed (grain sizes &gt;600 μm, non-magnetic)</td>
<td>[34]</td>
</tr>
<tr>
<td>Mata</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Mafic complex of gabbro, diabase, basalts and andesites</td>
<td>Chalcopyrite, pyrite, bornite</td>
<td>Cu, Mo</td>
<td>Crushed, milled, flotation</td>
<td>[21]</td>
</tr>
<tr>
<td>Kemi</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Skarn</td>
<td>Magnetite</td>
<td>Fe, Cu</td>
<td>Crushed, ground, gravimetric separation</td>
<td>[32]</td>
</tr>
<tr>
<td>Alteniando</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Pegmatite</td>
<td>Pegmatite</td>
<td>Quartz, alkali feldspar, REE</td>
<td>Crushed, ground, flotation with hydrofluoric acid</td>
<td>[33]</td>
</tr>
<tr>
<td>Kemi</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Karkortokite</td>
<td>Eudialyte</td>
<td>Ta, Nb, REE, Zr</td>
<td>Crushed (grain sizes &lt;600 μm, which are not applicable for magnetic separation).</td>
<td>[34]</td>
</tr>
<tr>
<td>Kill A</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Karkortokite</td>
<td>Eudialyte</td>
<td>Ta, Nb, REE, Zr</td>
<td>Crushed (grain sizes &gt;600 μm, non-magnetic)</td>
<td>[34]</td>
</tr>
<tr>
<td>Kill C</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Karkortokite</td>
<td>Eudialyte</td>
<td>Ta, Nb, REE, Zr</td>
<td>Crushed, magnetic separation (grain sizes &gt;600 μm)</td>
<td>[34]</td>
</tr>
<tr>
<td>Mata</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Mafic complex of gabbro, diabase, basalts and andesites</td>
<td>Chalcopyrite, pyrite, bornite</td>
<td>Cu, Mo</td>
<td>Crushed, ground, gravimetric separation</td>
<td>[32]</td>
</tr>
<tr>
<td>Alteniando</td>
<td>Killavaat Alangnut, Greenland</td>
<td>Skarn</td>
<td>Magnetite</td>
<td>Mo</td>
<td>Crushed, ground, gravimetric separation</td>
<td>[35]</td>
</tr>
<tr>
<td>Nalu</td>
<td>Nalu</td>
<td>Quartz-vein in metamorphosed pillow lavas</td>
<td>Quartz-vein</td>
<td>Au</td>
<td>Crushed, milled, treated with cyanide leaching</td>
<td>[36]</td>
</tr>
<tr>
<td>Raa</td>
<td>Raa</td>
<td>Magnetite</td>
<td>Magnetite</td>
<td>Fe</td>
<td>Crushed, ground, magnetic separation</td>
<td>[32]</td>
</tr>
<tr>
<td>Tian</td>
<td>Tianbao</td>
<td>Dolomitic limestone</td>
<td>Dolomitic marble</td>
<td>Pb, Zn, Al, Ge, Ga, Cu, Ag, Pd</td>
<td>Crushed, differential flotation separation method</td>
<td>[38]</td>
</tr>
<tr>
<td>WM</td>
<td>White Mountain, Greenland</td>
<td>Gneiss complex: Anorthosite</td>
<td>Anorthosite</td>
<td>Anorthosite</td>
<td>Crushed, ground, magnetic separation</td>
<td>[39]</td>
</tr>
<tr>
<td>Zink</td>
<td>Zink</td>
<td>Dolomitic marble</td>
<td>Dolomitic marble</td>
<td>Pb, Zn, Cu, Ag</td>
<td>Autogenous ground, bulk/selective flotation</td>
<td>[40]</td>
</tr>
</tbody>
</table>
2. Materials and methods

2.1. Materials

In this study, 13 different mine tailings were used for partial cement clinker replacement in their untreated form. The samples were collected from 10 different metal, mineral and industrial mines located in Chile, China, Finland, Greenland, Norway and Sweden.
respectively (Table 1). When multiple samples were used from one mine, they originated from different processing steps or reservoirs. Samples were taken from either the process outlet or a waste storage facility. Apart from tailings, the mortar mixtures were prepared with sand as fine aggregate (Great Belt sea sand from Denmark, 0–4 mm), deionized water and blended cement as the binder (Basis Cement from Aalborg Portland, CEM II/A-LL 52.5). The cement contained 15 % limestone filler (see supplementary data) and represents an applicable industrial cement type for ternary blends, as the limestone content may be beneficial for synergetic effects [9] if mine tailings contain reactive alumino-silicate minerals.

2.2. Methods

2.2.1. Mortar preparation

Mine tailings were dried at 105 °C for 24 h to ensure moisture contents below 0.2 % but were besides that kept in their initial state. The water content of the mine tailings ranged between 0–25.5 %. Mortars were mixed according to EN 196-1 (2016) [41] with mortar proportions of cement, water and aggregates of 1:0.5:3. Two modified mortars with 5 % and 10 % Portland-limestone cement replaced by weight by each mine tailing were made. With the limestone filler content of 15 % (supplementary data), this corresponds to a ternary blended composite cement where approximately 20 % and 25 % was replaced by supplementary materials of mine tailings and limestone filler. A reference mortar consisted of the conventional mix design of identical materials (CEM II/A-LL) without mine tailings.

2.2.2. Mortar testing

The workability of fresh mortar was determined by flow table according to EN 1015-3 (1999) [42]. With this test, the consistency of the mortar denoted by the slump flow was measured in two perpendicular directions on a flow table. The test was performed in duplicate and results are given as the average with a standard deviation.

The setting time of fresh mortar was analyzed by Vicat according to EN 196-3 (2016) [43], except that the test was conducted on mortar instead of cement paste (apparatus Matest E044-03 N). According to the standard, the initial setting time is defined as the time when the distance between the needle and baseplate of the specimen is 6 ± 3 mm, while the final setting time is the time when the needle only penetrates 0.5 mm into the specimen. The test was performed as a single determination.

For (open) porosity measurements of mortar specimens, the test was adopted from EN 1936 (2007) [44]. Mortar samples were dried for three weeks at 50 °C to achieve stable weight. Samples were placed in a desiccator and the air was evacuated from the desiccator for 3 h. Then deionized water was led into the desiccator to cover the samples and the vacuum was kept for 1 h. For 12 h, the pressure was leveled out to reach atmospheric pressure. The water-saturated samples were weighted submerged in and above water after quick surface drying. The test was performed as a triple determination and the results are given as an average with standard deviation.

The compressive strength was measured on mortar prism specimens after 7, 14 and 28 days of curing according to EN 196-1 (2016) [41] on a Tony-300 apparatus (Toni Technik GmbH, Germany). All mortars were cast in triplicate. The prisms were halved in a flexural strength set up and tested on each segment to achieve a double determination. From this procedure, six results were obtained for each mine tailing and reference for 7, 14 and 28 days. The results are presented as an average with a standard deviation.

2.2.3. Statistical analyses

2.2.3.1. Chemometric tools. This study uses two chemometric methods for the analysis of the data set. The Principal Component Analysis (PCA) is a dimension reducing technique that produces principal components (PC) from linear combinations of the original variables of the data set [45]. The first PC (PC1) represents the maximum variance of the data set. The second principal component (PC2) is orthogonal to the first and contains maximum variance of the remaining data. The results are presented in a graphical representation, a biplot, which combines score and loading plots. A score plot illustrates the correlations between observations, e.g. mine tailing types, while a loading plot illustrates correlations between variables, e.g. variables on characterization and performance test results. A loading represents the correlation between the principal component and the original variable and is expressed by the angle between the principal component and variable.

The Partial Least Square (PLS) model examines the relationship between a descriptor matrix (X) and a response matrix (Y) in contrast to PCA, where only the individual X or Y value is considered [46]. The purpose of the PLS is to provide a predictive model where Y can be calculated by X. The method is based on the projection of X and Y onto latent variables (PCs) where the first principal
component is most predictive for \( Y \). The component is not determined by the direction of maximum variation, as was the case in PCA, but rather by maximizing the correlation between scores for both \( X \) and \( Y \). The fraction of explained variation in the \( X \)- and \( Y \)-matrix is termed \( R^2_X \) and \( R^2_Y \), respectively.

The software of SIMCA 14.1.0.2047 from MKS Umetrics AB was used for this analysis. The input variables used for chemometrics are shown in Table 2.

3. Results and discussion

3.1. Mortar performance testing of early-age properties, mechanical performance and porosity

The workability (Fig. 1) of mortar with 20 % and 25 % cement clinker replacement by mine tailings and limestone filler along with the reference (CEM II/A-LL with no replacement material) is shown in Fig. 1. Except for the mine tailings Code, Kemi and Nus, all other

Fig. 2. Initial and final setting time of mortar with 20 % and 25 % cement clinker replacement and a reference.

Fig. 3. The porosity of mortar with 20 % and 25 % cement clinker replacement and a reference.

Fig. 4. Compressive strength of mortar with 20 % (A) and 25 % (B) cement clinker replacement and a reference after 7, 14 and 28 days of curing.
mine tailings reduced their workability by 3–19% compared to the reference (124 mm). Code (20%: 125 mm and 25%: 127 mm), Kemi (20%: 128 mm) and Nus (20%: 132 mm) showed identical or slightly higher workability compared to the reference. The initial setting times (Fig. 2) were similar to that of the reference (159 min) for most mine tailings, while few tailings showed a slightly retarded (Kill C for 20% and WM for 25%) or accelerated (Kill A and B for 20% and Kill B, Kill C, Nalu and Zink for 25%) initial setting time. In general, the cement clinker replacement caused a shortening of the final setting time compared to the reference (450 min), except for the mortar mixes with Code, which was significantly delayed (610 min). The increase of replacement did, however, not show any clear effect. The porosity (Fig. 3) was higher or similar to the reference (0.20 m³/m³) for most of the mine tailings (Kara, Kill C, Mata, Nalu, Nus, Tian, WM, Zink), while lower for some (Code, Kemi, Kill A, Kill B, Raa). Porosity increased slightly with increasing cement clinker replacement except for mortar containing the mine tailings Kara, Kemi, Kill B, Nalu and WM for which it remained constant or decreased slightly. The results of compressive strengths after 7, 14 and 28 days are shown in Fig. 4. Early-age strength at 20% cement clinker replacement was generally reduced compared to the reference, while strengths after 28 days of curing for tailings Code (50 MPa), Kemi (49 MPa), Kill A (52 MPa), Kill C (50 MPa) and Nalu (53 MPa) was similar to or slightly higher than that of the reference (48 MPa). The remaining mine tailings (Kara, Kill B, Mata, Nus, Raa, Tian, WM and Zink) showed a decreased compressive

Fig. 5. Principal Component Analysis (PCA) biplot with scores of mine tailings (20 % and 25 %) and the reference (0 %) along with loadings (Y) of mortar performance tests of workability (Work), initial setting time (Initial ST), final setting time (Final ST), porosity (Porosity) and compressive strength after 7, 14 and 28 days (CS 7, CS 14, CS 28) presented in Figs. 1–4. Variables, abbreviations and value ranges are presented in Table 2. The colored arrows illustrate the change in score of mortar with a specific mine tailing at an increased replacement level.
strength compared to the reference. Decreasing compressive strength was observed for increasing cement clinker replacement to 25 %, except for the tailings Mata, Raa, Tian and WM. For the 25 % replacement level, no mine tailing exceeded the compressive strength of the reference.

### 3.2. The relation between cement clinker replacement level and mortar performance

A Principal Component Analysis of Y-variables (PCA-Y) was performed to investigate the relation between the cement clinker replacement levels (0 %: reference, 20 % and 25 % cement clinker replacement with mine tailings and limestone filler) and the mortar performance (early-age properties, mechanical performance and porosity) presented in Figs. 1–4. Fig. 5 shows the calculated PCA-Y in a biplot, which combines scores of mine tailings and loadings of Y-variables (mortar performance tests). The biplot shows PC1 and PC2 to explain 61 % of the cumulated variation (PC1: 40.6 % and PC2: 20.6 %). PC1 could therefore be interpreted to represent variables involving mechanical performance. PC2 is dominated by negative variables of final setting time (Final ST: 0.5) and workability (Work: 0.6) and by the positive variable of initial setting time (Initial ST: 0.7). Therefore, this component could be interpreted to relate to the early-age properties of workability and hardening of mortar mixes.

The close location between variables of compressive strengths (CS 7, CS 14, CS 28) illustrates a strong positive correlation. Furthermore, the model reflects a strong negative correlation between compressive strength variables and porosity illustrated by the Y-variables' opposite location to each other. In this data set, mine tailings located closer to variables of compressive strength encounter high strength and low porosity. These mine tailings include Kill A, Raa, Kill C and Code, which also showed some of the highest compressive strengths in Fig. 4. On the opposite side of the plot (in the negative direction of PC1), WM and Tian tailings are characterized by high porosity and low compressive strengths. Regarding PC2, the biplot shows a strong positive correlation between workability (Work) and final setting time (Final ST). Conversely, these two variables are negatively correlated with initial setting time (Initial ST).

The replacement levels (20 % and 25 %) of certain mine tailings are located geometrically close to each other (e.g. Zink, Kara, Mata), which indicates minor effects of increased replacement level on the mortar tests. Other mine tailings display greater distances between the replacement levels (e.g. Code, Kill A, WM), which suggest more significant property changes with the increased replacement. Besides highlighting the distance of the scores, which represent the magnitude of change, it is equally important to notice the direction of change of the scores as they reflect the actual changes in mortar properties. The colored arrows illustrate the direction on the biplot in Fig. 5. Ten mine tailings showed decreased compressive strengths at increased replacement (Yellow, purple and blue arrow) since the 25 % replacement moves away from the variables of compressive strength. On the contrary, the mine tailings Tian, Raa and Mata showed an increase in strength with an increase in replacement. Workability and hardening properties changed inconsistently with the replacement level.

The reference (Ref) is located in the positive direction of PC1 towards variables of compressive strengths. Mine tailings Code, Kemi, Kill A, Kill B, Kill C, Nalu, Nus and Raa arrange closest to the reference, suggesting relatively similar properties to the reference.
3.3. The relation between mine tailing characteristics and mechanical performance

A Partial Least Square (PLS) model investigated the relationship between mine tailing characteristics (presented in supplementary materials) and the resulting performance tests of mortar bars with 20 and 25 % cement clinker replacement by mine tailings and limestone filler (presented in Figs. 1–4). The amount of the X-matrix variance described by the PLS in Fig. 6 is 42.2 % ($R^2_X$) and 34.6 % for the Y-matrix ($R^2_Y$).

Regarding Principal Component 1 (PC1), the Y-variables of compressive strength tests (CS 7, CS 14, CS 28) correlated positively with especially the X-variable of Specific Surface Area (SSA) illustrated by their close geometrical location. This relation between X- and Y-variables is emphasized by box A in Fig. 6. Furthermore, a strong positive correlation is found between the variables of silicon dioxide (SiO$_2$) and compressive strengths due to the variable’s strong loading on PC1. In contrast, the Y-variables of compressive strengths correlated negatively with X-variables of grain sizes and grain size range (D10, D50 and D90, GS Range) along with Loss on Ignition (LOI), which are located in the negative direction of PC1 (Box B). This negative correlation means that the compressive strength decreases with increasing grain sizes and LOI content.

Compressive strength variables also correlated negatively with calcium-bearing mineral compounds (CaO, CaCO$_3$). The negative correlation demonstrates that CaO or CaCO$_3$ do not contribute to the strength development of the mortar samples. Instead, CaO and CaCO$_3$ relate closely to porosity, as emphasized in Box C, as well as to grain size (D10, D50 and D90) (Box B). The positive correlation between calcium-bearing minerals, higher grain sizes, and LOI suggests that these characteristics contribute to a higher porosity in mortar. The positive correlation to coarse grain sizes suggests that most CaO could exist as grains in the mine tailings.

PC2 was dominated by a strong correlation between workability (Work) and final setting time (Final ST), which links high workability to long final setting time. This correlation is emphasized by box D. The early-age properties correlate positively with the content of Fe$_2$O$_3$, K$_2$O and SO$_3$. SO$_3$ usually represents an indirect measure of the amount of gypsum. In mine tailings, the sulfur can, however, originate from other mineralogical forms, including sulfides. If gypsum dominated the tailings, SO$_3$ would arrange closely to CaO (CaSO$_4$·2H$_2$O). Instead, the two oxides are located almost diagonal, which illustrates variables with no relation.

Workability and final setting time correlated negatively with the oppositely located X-variables of Al$_2$O$_3$ and pH. This negative correlation suggests a relation between a longer final setting time and a lower Al$_2$O$_3$ content, supporting a retarded setting by the lack of Al$_2$O$_3$. Initial setting time (Initial ST) is less associated with PC2, illustrated by the central location in the loading plot. Variables located in the center of the plot illustrate a limited contribution to the principal components and hence less importance for the variation in the data set.

Since PC2 is orthogonal to PC1, their variables are uncorrelated. Early-age properties (workability and setting time) of PC2 and grain size properties (D10, D50, D90, GS Range) of PC1 are thereby not correlated. This lack of correlation could indicate that the grain size distribution is not affecting the properties of the fresh concrete within the range investigated. Compressive strength and pH were also orthogonal, visualizing that the tailings’ pH did not influence the compressive strength.

3.4. Classification of mine tailings according to the key parameters affecting their performance in mortar

A PLS investigated the relationship between the studied mine tailings, their characteristics and performance in mortar (Fig. 7). The model scores include both 20 % and 25 % cement clinker replacement due to an insignificant difference between results. The X-matrix...
explains 44.2 % (R2X) and the Y-matrix explains 34.5 % (R2Y) of the variance in the data set. The model supplements the main findings of previous plots by emphasizing the critical parameters of mine tailings that affect their performance in mortar. A summarized classification of mine tailings is shown in Table 3.

Box I includes the mine tailing Kill A, which shows high compressive strength related to SSA and SiO2 content and hence encounters potential as cement clinker replacement. The positive correlation between SSA (hence fine grain sizes) and compressive strength found in the PLS agrees with Lawrence et al. [48], who showed small particle sizes of inert mineral admixtures to enhance cement hydration due to the physical effects of heterogeneous nucleation. Due to the finer grain sizes and high SSA, the tailings Code, Kill A and Nus were thus expected to contribute physically to cement hydration [47]. Unexpectedly, Nus, though, showed lower compressive strength than the reference, which indicates that not all decisive characteristics have been elucidated. The decrease in compressive strength with the increasing replacement level found in this study is in accordance with the results of similar studies [25,26,28,29]. The decrease indicates a non-reactive behavior [28,49] and that limits for the benefit of filler additives are exceeded at the highest replacement level [25]. Box II and III include the mine tailings Nalu, Kemi and Kill C, which all developed high strength (Fig. 4) and hence may be considered potentially useful as cement clinker replacement. They are all placed in the middle of the diagram and thus performance is linked to having average characteristics among the investigated tailings rather than having extraordinary characteristics. Box IV includes Code which is characterized by high SiO2 content and high compressive strength, which also characterize it as potentially useful for cement clinker replacement. The high content of primary oxides and an amorphous phase found in Code, Kill A and Nus [47] was expected to contribute to strength as found in similar studies [25]. However, no relation was found between Al2O3 content and strength development, suggesting that the mine tailings tested do not contain enough reactive aluminosilicates to react with the limestone and display synergetic effects resulting in higher strengths [9]. Together with the fact that strength correlated negatively with the lime content suggests that the performance of tailings may be improved if combined with CEM(I) rather than CEM(II). Box V and VI include mine tailings WM, Kara, Tian and Zink, for which the performance was affected by high grain size, high LOI and Ca contents. These characteristics may have imposed high porosity (Figs. 3 and 6), which again may have affected the strength development, in agreement with the findings of Almeida et al. [28], who found porosity to influence mechanical performance negatively. The negative correlation between compressive strength and CaO (and CaCO3) agrees with the findings of Sigvardsen et al. [25], who proposed the calcium content to inhibit mechanical properties of the mortar. The mine tailings Mata, Raa, Tian and WM

<table>
<thead>
<tr>
<th>Box</th>
<th>Mine tailings</th>
<th>Key characterization parameters</th>
<th>Influence on mortar performance</th>
<th>Expected results based on characteristics [47]</th>
<th>Pretreatment and potential for optimization based on the chemometrics analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Kill A</td>
<td>High SiO2 and SSA</td>
<td>High strength</td>
<td>Kill A is fine-grained and silicon-rich with a minor amorphous phase. It meets the minimum content of primary oxides. It was therefore expected to contribute to hydration/development.</td>
<td>Fine-grained and silicon-rich mine tailings were considered the optimal characteristics for use as SCM and should be investigated further.</td>
</tr>
<tr>
<td>II and III</td>
<td>Nalu, Kemi and Kill C</td>
<td>No significant characteristics according to the PLS</td>
<td>High strength</td>
<td>Nalu, Kemi and Kill C are all medium to coarse-grained but unexpectedly perform high strength. The tailings do not contain significant oxide content. Kill C contained minor amorphous. Nalu met hydraulic requirements for oxide content. Both were expected to contribute to strength development.</td>
<td>A grinding of coarse tailings can improve their performance or make them contribute as fillers.</td>
</tr>
<tr>
<td>IV</td>
<td>Code</td>
<td>High SiO2 content</td>
<td>High strength</td>
<td>Code is fine-grained and silicon-rich with a minor amorphous phase. It meets the minimum content of primary oxides expected to contribute to hydration/development.</td>
<td>Fine-grained and silicon-rich mine tailings were considered the optimal characteristics for use as SCM and should be investigated further.</td>
</tr>
<tr>
<td>V</td>
<td>Zink, Mata and Kara WM and Tian</td>
<td>High grain size, LOI content and wide grain size range High CaO2 and CaO</td>
<td>High porosity, Low strength</td>
<td>Zink, Mata and Kara are all coarse-grained and not expected to contribute to hydration/development.</td>
<td>A grinding of coarse tailings can make them contribute as fillers.</td>
</tr>
<tr>
<td>VI</td>
<td>Remaining Nalu, Kill B</td>
<td>No significant characteristics according to the PLS</td>
<td>Low strength</td>
<td>Nus is one of the most fine-grained mine tailings and met the hydraulic requirements for oxide content. Kill B contained similar oxide content as Kill A besides a slightly lower silicon dioxide content. Also, Kill B was coarser than Kill A and was more spherical and round-shaped. Kill B was expected to contribute due to the oxide content. Raa is located next to Kill C in the PLS but performs differently.</td>
<td>Fine-grained mine tailing can be used as filler or be purposed for low-strength material.</td>
</tr>
</tbody>
</table>

Table 3
Interpretation of critical parameters of mine tailings affecting the performance as cement clinker replacement in ternary composite binders based on the separation of tailings in Box I-VI in Fig. 7.
nevertheless showed a slightly increasing strength after 28 days with a higher replacement level, even though strength levels did not correspond to the reference. This indicates potential for use at higher replacement levels. The remaining tailings Raa, Nus and Kill B showed no significant characteristics and performance according to the PLS and additionally they showed low compressive strength (Fig. 4).

In addition to the summary of tailing classification given in Table 3, suitable pretreatments to increase their performance are given. Tailings Kill A and Code exhibited optimal performance and should be explored further for their potential for use as SCM. The tailings Nalu, Kemi and Kill C also showed good potential despite their coarse-grained nature, thus the potential to increase their performance even more by grinding should be investigated. Grinding was shown to improve the performance of other coarse-grained tailings [50, 51] due to the reduced grain size. Tailings Zink, Mata and Kara all may benefit from grinding before potential use as their coarse-grained nature inhibited their performance. The tailings WM and Tian may benefit from pretreatment by thermal activation due to their high CaO content. Such treatment was shown by Vargas et al. [50] to increase performance. The use of thermal treatment, however, depends on the mineralogy of the waste. Crystalline waste may improve reactivity as seen for Andesite-material [52], while materials containing high CaO may benefit from thermal treatment as if reactive phases are being formed, such as observed in hydraulic materials (e.g. Ground Granulated Blast furnace slag). Tailings Raa, Nus and Kill B performed non-optimal despite their fine-grained nature, which leaves them for use as potential fillers only. Finally, utilization of the investigated tailings should be preceded by investigations of their long-term performance, including durability and environmental performance.

4. Conclusion

This study evaluated the potential of 13 mine tailings as partial cement clinker replacement in a ternary blend on early-age properties and mechanical performance in mortar. The study revealed five mine tailings (Kill A, Code, Nalu, Kemi and Kill C) to have potential as SCM based on their high strength after 28 days. The application of chemometrics linked the high strength to high specific surface area and silicon dioxide content. On the contrary, high contents of calcium oxide, loss on ignition and coarse-grained tailings were related to high porosity of mortar, resulting in reduced compressive strength. Based on the results, five of the mine tailings (Zink, Mata, Kara, WM and Tian) were evaluated as unfeasible as SCM in their current state, but pretreatment by grinding or thermal activation is rendered likely to improve their performance, while needing testing. A higher replacement generally affected mortar negatively for most tailings. However, the strength increased with increasing replacement level for four mine tailings (Mata, Raa, Tian and WM), thus investigations of even higher cement clinker replacement fractions for these tailings could be interesting. The general performance of the tailings as SCM was only partially explained by the characteristics included in the study, despite the fact these include all characteristics typically mentioned in the literature to be decisive. Identification of further determining characteristics is therefore necessary to be able to pre-determine tailings performance based on their characteristics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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