UTILIZATION OF MINE TAILINGS AS PARTIAL CEMENT REPLACEMENT

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Abstract
Depositing mine tailings entail major economic costs and negative environmental impacts. Thus finding an alternative to depositing is of interest. This study focused on the use of mine tailings as partial cement replacement, thereby preventing depositing the mine tailings. At the same time, such use would reduce the CO_2 emission related to the production of cement. Mine tailings from two different mines Zinkgruvan (Sweden) and Nalunaq (Greenland) were both tested as 5 and 10 % cement replacement. All mortar specimens with mine tailings had lower compressive strength compared to a reference specimen at 7, 14 and 28 days of curing. Both mine tailings showed contributions to the pozzolanic activity. This tendency was more profound for Zinkgruvan. No evidence of either mine tailing containing minerals acting as nucleation sites was, however, seen. The specimens containing mine tailings were compared to a specimen containing a 10 % replacement of cement with coal fly ash, commonly used in Denmark. The compressive strength of specimens containing mine tailings exceeded the compressive strength of the specimen containing coal fly ash, indicating further the amorphous content of volcanic decent contained in the mine tailings to contribute to the pozzolanic activity and thus increase the compressive strength. Mine tailings have a high content of toxic chemical elements, but no significant amount of chemical elements was seen leaching from neither the pure mine tailings nor the mortar specimens containing mine tailings. Overall, the results show that these mine tailings have potential as a mineral admixture for substitution of cement in concrete.

Keywords:
Mine tailings; Mineral admixtures; Mortar; Compressive strength; Coal Fly Ash; Sustainability

1 INTRODUCTION

In recent years, an increasing focus has been on reduction of the anthropogenic CO_2 emissions. The production of cement for concrete production is responsible for at least 5-7% of the global, anthropogenic CO_2 emissions [IEA 2008, Allwood et al., 2010, Friedlingstein et al., 2010, UNSTATS, 2010]. This makes the use of secondary, raw materials as a replacement for cement of great interest.

Mine tailings are particulate waste materials originating from mineral processing in mining activities. As the mines are of different origin, they are of varying quality, composition etc. Today most mine tailings are deposited, but this leads to both occupation of land, costly constructions, maintenance, monitoring and potential environmental and ecological risks, such as air pollution and pollution of surface and underground water due to leaching of chemical elements [Ahmari and Zhang, 2013]. Therefore, alternatives to depositing of the mine tailings are necessary.

Replacement of cement with mineral admixtures, e.g. mine tailings, in a mortar or concrete mixture, can influence the properties of the final product, such as the compressive strength. The use of mine tailings as a mineral admixture in mortar and concrete has not been widely studied. Onuaguluchi and Eren, 2012 used mine tailings from a copper mine as an addition in mortar mixtures, showing the addition of copper tailings to have a positive impact on the compressive strength of mortar.

Mineral admixtures can behave differently depending on e.g. size, fineness and mineral content and can be divided into three groups; non-reactive minerals (inert fillers), pozzolans, and cementitious minerals, which possess different properties. Since mine tailings vary in composition, and as they have not been widely studied for cement replacement, it has not been possible to find literature describing to which of these category mine tailings can be attributed.

Non-reactive fine-grained minerals are referred to as fillers. They traditionally categorised as an inert material, which does not react itself but fills the intergranular voids between the cement grains in the mixture. This can contribute to a decrease in porosity and an increase in compressive strength, known as the filler effect [Deschner et al. 2012, Moosberg-Bustnes, Lagerblad & Forssberg 2004]. An inert filler can also have a heterogeneous nucleation effect, acting as nucleation sites for the hydrates in cement, accelerating the hydration reaction and thus improving the compressive strength [Lawrence, Cyr & Ringot 2005, Moosberg-Bustnes, Lagerblad & Forssberg 2004, Ye et al. 2007]. The mineral admixtures ability to act as nucleation sites depends on the fineness of the particles, the amount of mineral admixture and the affinity of the mineral powder to cement hydrates, related to the origin of the mineral admixture. This effect is developed at an early age and maintained over time [Lawrence, Cyr & Ringot 2005]. The addition of an inert material to a cement mixture results in a decreasing of the compressive strength when the replacement rate increases [Lawrence, Cyr & Ringot 2005].

A pozzolan is defined as [ASTM International C125-15a 2003]: "*a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties*". Pozzolanic reactions contribute to the late development of the compressive strength and are mainly effective after 28 days [Lawrence, Cyr & Ringot 2005, Mehta 2006]. The pozzolanic activity further increases with the fineness of the particles, since smaller particles are more reactive [Davison, Natusch, Wallace & Evans 1974, Liu et al. 2004].

Cementitious minerals are minerals, which can contribute to the properties of mortar or cement, e.g. compressive strength, through hydraulic or pozzolanic activity, or both [ASTM International C125-15a 2003].

In addition to the influence on mortar properties of a mineral admixture, such use also calls for an evaluation of the leachability of toxic elements to prevent contamination in regards to the later demolition, depositing at landfills or possibility for recycling.

This study focuses on the compressive strength of mortar specimens with a partial cement replacement with two different mine tailings. Further, the leachability of toxic elements from the mine tailings and mortar specimens containing the two mine tailings was investigated. Coal fly ash (CFA) is a by-product of combustion of coal at the power plants, which are regularly used, in Denmark, as partial replacement of cement. CFA will be used in this study for comparison.

2 MATERIALS AND METHODS

2.1 Materials and characterisation

Two different types of mine tailings were investigated in this study.

Zinkgruvan (Z): From the zinc, copper and lead mine Zinkgruvan in Sweden. This deposit is a part of the Proterozoic aged Berslagen greenstone belt, which hosts massive Zn, Pb, Cu and Ag sulphides and banded iron formations in volcano-sedimentary complexes [Hedstroem, Simeonov & Malmstrom 1989]. The tailings mainly consist of quartz, feldspar and calcite [Forsberg and Ledin 2006].

Nalunaq (N): From the gold mine Nalunaq in the southern part of Greenland. This deposit is classified as an orogenic-type gold mineralisation and is hosted in amphibolite facies metavolcanic rocks [Secher, Stendal & Stensgaard 2008].

Further CFA from Avedøreværket in Demark, which is approved for the usage as a mineral admixture in mortar and concrete, was used. The cement used was Portland Basic Cement (CEM II).

The particle size distribution, mean particle size and specific surface area was found by laser diffraction. The pH was measured with a pH electrode and the conductivity with an electrical conductivity meter in a 1:2.5 solid to liquid ratio suspension in distilled water. The carbonate content was found by the use of Scheibler equipment. The water content was found by drying the samples in an oven for 24 hours at 105 ºC. For measuring of solubility a 1:5 solid to liquid ratio suspension with distilled water was prepared. The suspension was shaken for 1 min and decanted. Additional 500mL of distilled water was added. This procedure was repeated three times before the suspension was filtered, the sample dried and weighed. Loss on ignition (LoI) was measured in accordance with Danish Standard Euronorm (DS EN) 196, 2005a at 950ºC for 5 min with lid followed by 10 min without a lid. The mineral content was analysed by X-ray diffractions (XRD) measured with PanAlytical X-ray diffractometer.

Tab. 20: Mix compositions used for material testing. Mix composition for 10 % replacement were used for both specimens containing mine tailings and specimen containing CFA.

	CEM II (g)	Water (g)	Sand (g)	Mine tailing or ash (g)
REF	450	225	1350	0
5 % replacement	427.5	225	1350	22.5
10 % replacement	405	225	1350	45

Leaching was measured by placing a solution of 10 g of sample and 20 mL of distilled water at an agitating table for 23 hours. The solution was left to settle for 15 min and afterwards filtered. The content of As, Cd, Cu, Ni, Pb and Zn was measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). For measuring leaching of chemical elements from a mortar specimen

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containing mine tailings at 28 days of curing, the mortar specimens were pulverised using a hammer. The pulverised mortar specimen was dried at 105ºC before leaching of chemical elements were measured by duplicate determination.

2.2 Material testing

Mortar specimens (40x40x160mm) were cast with all three recipes displayed in Tab. 1 in accordance with Danish Standard Euronorm (DS EN) 196, 2005b. The specimens were de-moulded after 24 hours and submerged in water to cure. Table 2 gives an overview of curing ages of the mortar specimens.

The notation in Tab. 2 is as follows:

REF is a reference specimen without addition of any mineral admixture

5 Z and 5 N are 5 % replacements of cement with mine tailings from Zinkgruvan and Nalunaq respectively.

10 Z and 10 N are 10 % replacements of cement with mine tailings from Zinkgruvan and Nalunaq respectively.

10 CFA is 10 % replacement of cement with CFA.

The compressive strength of the mortar specimens was tested according to the Danish Standard Euronorm (DS EN) 196, 2005b.

Tab. 21: Curing ages of mortar specimens

	7 days	14 days	28 days
REF	x	x	x
5 Z	x	x	x
10 Z	x	x	x
5 N	x	x	x
10 N	x	x	x
10 CFA			x

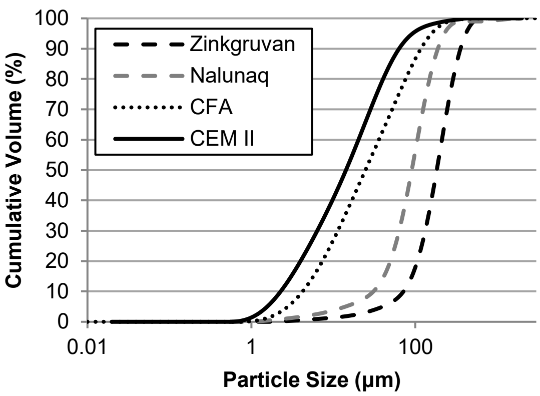

Fig. 18: Cumulative particle size distribution of test materials.

3 RESULTS AND DISCUSSION

3.1 Characteristics of investigated mine tailings

The particle size distribution is shown in Fig. 1, and the morphology are shown by SEM images Fig. 2.

Mine tailings are not approved as a mineral admixture in concrete. The Danish Standard Euronorm (DS EN) 450, 2012 includes definition, specification and conformity criteria for fly ash for use as a mineral admixture in concrete and will be used for comparison. According to this standard, 40% of the particles must be retained when sieved on a 45 µm sieve. CFA conforms with this limit and Zinkgruvan and Nalunaq does not. Moosberg Bustnes, Lagerblad and Forssberg 2004 describes particles smaller than 125 µm to contribute to the filler effect. 70% of Nalunaq conforms with this limit and only 25% of Zinkgruvan. 100% of CFA conforms with this limit.

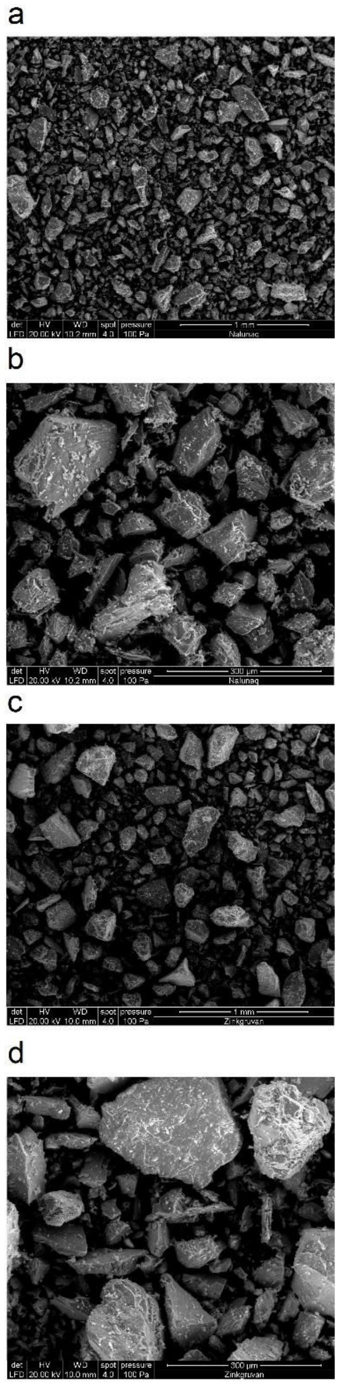

Fig. 2: SEM analysis of Nalunaq magnified 50 times (a), Nalunaq magnified 200 times (b), Zinkgruvan magnified 50 times (c) and Zinkgruvan magnified 200 times (d)

The physical characteristics, LoI and mineralogy of the investigated mine tailings and CFA are summarised in Tab. 3. The mineralogy is analysed qualitatively and "X" in Tab 3. marks a detected mineral. All three mineral admixtures contain quartz, which can contribute to the pozzolanic activity. Nalunaq further contains kaolinite, which also can contribute to the pozzolanic activity [Kurdowski 2014]. Both types of mine tailings are of volcanic origin. This can lead to a further contribution to the pozzolanic activity from the amorphous material (detected, not quantified) contained in the mine tailings since volcanic rocks are categorised as a natural pozzolan [Kurdowski 2014]. Mullite are present in CFA, which further can contribute to the pozzolanic activity.

Contribution to the pozzolanic activity is further dependent on the reactivity of the mineral admixture [Kurdowski 2014]. The conductivity gives an indication of the amount of soluble ions present in the mineral admixture and thus the reactivity. Further, [Davison et al.1974] and [Liu et al. 2004] described a decreasing reactivity, when the particle size increases due to the lower specific surface area. As displayed in Tab. 3 and Fig. 1 CFA has the highest conductivity and the smallest particle size, thus the highest expected reactivity. Zinkgruvan contains the largest particles, thus expected to be the least reactive, but Zinkgruvan also has a higher conductivity compared to Nalunaq.

Compressive strength

Fig. 3 displays the compressive strength at 7, 14 and 28 days of curing of REF, 5 Z, 10 Z, 5 N, 10 N and the compressive strength at 28 days of curing for 10 CFA. All specimens containing mine tailings had a lower 7 days compressive strength compared to REF. The difference becomes more pronounced at 14 and 28 days of curing, except for 5 Z at 28 days, which obtained 95% of compressive strength of the REF. For 10 Z and 10 N, the compressive strength decreased slightly from 7 to 14 days. This is a reflection of the workability of fresh mortar decreasing with an increase in the replacement rate, making it dry and difficult to place and compact at high replacement rates.

Mortar 5 Z had a lower compressive strength at both 7 and 14 days of curing compared to N 5. Mortar 10 Z and 10 N obtained the same compressive strength at every curing duration. No increase of the compressive strength from increasing the replacement rate was seen for either Zinkgruvan or Nalunaq, indicating that no heterogeneous nucleation took place, as, thus the mineral content of the mine tailings does not contain minerals acting as nucleation sites. The increase in the compressive strength of 5 N at 7 and 14 days of curing compared to 5 Z are attributed to the filler effect.

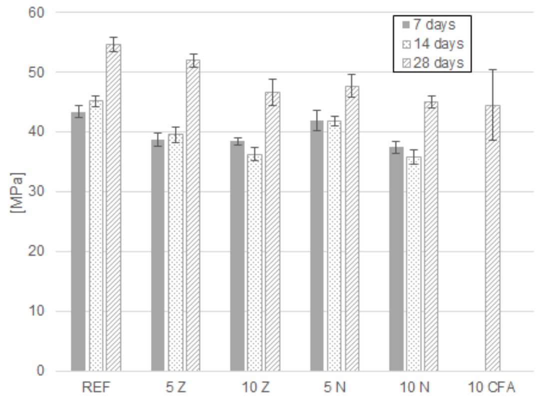

Fig. 3: Compressive strength of REF, 5 Z, 10 Z, 5 N and 10 N at 7, 14 and 28 days of curing and 10 CFA at 28 days of curing.

Tab. 22: Physical characteristics, LoI and mineralogy as found by the XRD analysis of investigated mine tailings and CFA. ± defines the standard deviation

	Zinkgruvan	Nalunaq	CFA
Mean particle size (µm)	183.1	90.7	24.7
Specific surface area (m^2/kg)	67	131	553
pH	7.7 ± 0.03	8.2 ± 0.07	12.0 ± 0.01
Conductivity (mS cm^{-1})	1.2 ± 0.06	0.6 ± 0.01	2.5 ± 0.15
Volumetric content of carbonate (%)	10.6 ± 0.75	1.7 ± 0.11	1.5 ± 0.01
Water content (%)	9.0 ± 0.67	15.5 ± 1.01	0.1 ± 0.01
Solubility (%)	0.92 ± 0.19	0.75 ± 0.13	1.2 ± 0.015
LoI	5.06 ± 0.43	1.40 ± 0.03	2.59 ± 0.07
Quartz (SiO_2)	x	x	x
Microline ($KAlSi_3O_8$)	x	x	
Amphibole ($Ca_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$)	x	x	
Kaolinite ($Al_2Si_2O_5(OH)_4$)		x	
Calcite ($CaCO_3$)	x		
Plagioclase feldspar ($CaAl_2Si_2O_8$)	x	x	
Dolomite ($MgCa(CO_3)_2$	x		
Mullite ($3Al_2O_3 \cdot 2SiO_2$)			x
Lime (CaO)			x

Tab. 23: Initial content of selected elements in mine tailings (mg/kg ± standard deviation), (Jensen et al., 2016). Limit according to (Miljøstyrelsen, 2010) (mg/kg)

	As	Cd	Cu	Ni	Pb	Zn
Limit	20	0.5	500	30	40	500
Zinkgruvan	21 ± 2	11 ± 0.2	372 ± 28	24 ± 3	3,700 ± 233	7,331 ± 322
Nalunaq	122 ± 35	2.8 ± 0.9	105 ± 28	48 ± 13	59 ± 14	45 ± 22

The compressive strength of all specimens is seen to increase from 14 days to 28 days of curing. Specimens containing Zinkgruvan obtained the highest compressive strength of the two at both 5 and 10 % replacement at 28 days of curing. This indicates a higher contribution from the pozzolanic activity to the compressive strength for specimens containing Zinkgruvan. Nalunaq has a higher specific surface area compared to Zinkgruvan, thus expected to be more reactive and contribute more to the development of the compressive strength through pozzolanic reactions, if the mineralogy had been the same. Had the mineralogy contributing to the pozzolanic activity been the same for the tailings, the compressive strength for both 5 N and 10 N would be expected to exceed the compressive strength of 5 Z and 10 Z. Since this is not the case, this observation indicates that Zinkgruvan contains a larger quantity of minerals contributing to the pozzolanic activity than Nalunaq.

The compressive strength of 10 CFA at 28 days of curing is also seen in Fig. 3. All specimens containing mine tailings cured for 28 days exceeded compressive strength for 10 CFA, 5 Z more evident than 5 N, 10 Z and 10 N. From the analysis of the mineralogy, CFA is seen to contain several minerals, which could contribute to the pozzolanic activity, as well as indications of a high reactivity, e.g. high specific surface and conductivity, compared to Zinkgruvan and Nalunaq. The exceeding of the compressive strength of 10 CFA by all mortars containing mine tailings might be explained by the amorphous content of the mine tailings. The amorphous content in the mine tailings is considered to consist mainly of volcanic rocks, which is a natural pozzolan [Kurdowski 2014]. The amorphous content of CFA is however not determined but known not to be of volcanic origin. The determined content of minerals, alongside the amorphous content of Zinkgruvan and Nalunaq, might constitute to a higher amount of minerals contributing to the pozzolanic activity, thus achieving a higher compressive strength than the mortar with CFA at 28 days of curing.

3.2 Leaching characteristics

Tab. 4 shows the initial content of selected chemical elements in the mine tailings and the limit for the content of chemical elements of residues and soils for building and construction according to note number 1662/2010 [Environmental Protection Agency of Denmark 2010]. The initial content of the selected chemical elements As, Cd, Cu, Ni, Pb and Zn does not comply with this set of limits.

The leaching characteristics of pure mine tailings and specimens containing 5 and 10 % replacements are shown in Tab. 5. The concentrations of chemical elements in the leachate from the mortar specimens containing 5 and 10 % replacements are significantly lower than from the mine tailings themselves. Ahmari and Zhang 2013 describes a possible stabilisation of deposited mine tailings with cement, due to mine tailings reacting with the calcium content in cement. The mine tailings are thus chemically stabilised by a hardened surface, which isolates the underlying tailings from the environment reducing the amount of chemical elements leaching, corresponding well with the obtained results in Tab. 5. Also, the high pH in mortar causes precipitation of heavy metals and lowers the leachable fraction.

Tab. 5: Leaching of selected elements in mine tailings (µg/kg ± standard deviation).

	As	Cd	Cu	Ni	Pb	Zn
Zinkgruvan	51.6 ± 2.7	< 20	23.4 ± 5.8	23.6 ± 0.9	403.2 ± 32.8	361.5 ± 313.2
Z 5	< 20	< 20	21.6 ± 4.7	< 20	< 20	< 20
Z 10	< 20	< 20	< 20	< 20	< 20	< 20
Nalunaq	286.2 ± 20.6	114.3 ± 95.4	539.5 ± 174.2	47 ± 3.5	134.7 ± 39.8	15002.4 ± 10872.2
N 5	< 20	< 20	< 20	< 20	< 20	< 20
N 10	< 20	< 20	< 20	< 20	< 20	< 20

The reaction between the mine tailings and the calcium content in the cement might lead to some limitations in the use, as this may influence the mechanical properties of a mortar specimen when used as a partial cement replacement [Ahmari and Zhang 2013]. The impact of the reactions between calcium and the mine tailings might also be reflected in Fig. 3., contributing to a reduction of the compressive strength, but are not separately identified.

4 CONCLUSION

The use of two different mine tailings as a partial cement replacement has been studied in this paper. The main focus was on the influence on compressive strength and leaching of chemical elements. The major conclusions are:

Specimens with partial cement replacement with mine tailings from Nalunaq and Zinkgruvan obtain a lower compressive strength compared to the reference specimen without mine tailings.
The mine tailings do probably not act as nucleation sites accelerating the hydration reactions.
Zinkgruvan contributes more to the compressive strength, probably due to a larger quantity of minerals contributing to the pozzolanic activity compared to Nalunaq.
The compressive strength of specimens with a partial cement replacement with mine tailings exceeds the compressive strength of a specimen with a partial cement replacement with coal fly ash, which is most likely attributed to the volcanic origin of the mine tailings, leading to a contribution to the pozzolanic activity from the amorphous content in the mine tailings.
The initial content of chemical elements in the mine tailings exceed the limits allowed in residues and soils for building and construction according to note number 1662/2010 [Miljøstyrelsen 2010].
Leaching of chemical elements from mortars with mine tailing is significantly reduced compared to the leaching from the mine tailings themselves.

In conclusion, both Zinkgruvan and Nalunaq seems to be a possible substitute for cement based on the compressive strength when comparing with CFA, which is already used today. However, further studies are needed and the issue on leaching needs to be addressed.

5 ACKNOWLEDGMENTS

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