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Applying Chemometrics to Evaluate Mine Tailings' Potential As Partial Cement Replacement

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Abstract

This study investigates the utilization of mine tailings, the by-product originating from metal- and mineral-based ore mining, as a new cement replacement material. This paper is based on the chemical and physical characteristics of 13 mine tailing samples. In this study, Chemometrics were applied to consider all parameters simultaneously and obtain a thorough screening of potential relations in the large data set. Hierarchical Cluster Analysis (HCA) groups samples according to (dis)similar features and Principal Component Analysis (PCA) visualizes predominating variables and relations to samples. The application of HCA highlighted a clear grouping between mine tailings according to characteristics. Meanwhile, PCA identified the predominant chemical and physical characteristics in the mine tailing samples. Chemometrics therefore provided a thorough overview of mine tailings' physical and chemical characteristics.

Keywords: mine tailings, chemometrics, cement replacement

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1. Introduction

The large generation of waste materials and industrial by-products constitute an increasing burden for industries due to potential environmental and health risks connected to the disposal of waste. As an alternative to disposal of the waste, several researchers have studied the utilization of various by-products as cement replacement in construction materials [e.g. [1, 2]]. Besides reducing environmental and economic costs connected to waste disposal, the utilization of waste and by-products has shown to improve the microstructure and consequently the mechanical and durability properties of concrete unachievable by Portland cement alone. It is therefore highly encouraged to find new applications to mine tailings [3], the by-product from ore-mineral treatment, which has resulted in investigations on high value uses. The potential of utilizing mine tailings as potential cement replacement relies on the physical and chemical properties, which vary greatly according to ore mineralogy and processing of mine tailings [4].

Diverse characteristics have resulted in contradictory findings from researchers due to limited focus on just one type of mine tailings [5–7]. The variation of mine tailing characteristics suggests a screening of several mine tailing samples to elucidate the potential valorization of mine tailings as constituents in cement-based building materials and ensure the concrete industry a high-quality substitution. The practice of studying a broad range of mine tailings samples generates large and complex data sets, which can be complicated to interpret by the use of uni- or bivariate statistics. During the last decades, the use of Chemometrics has been widely adopted in several fields of study to interpret large and complex data sets of multiple parameters [8]. However, the use of Chemometrics in the field of building materials are rather sparse despite several advantages of the methods [9, 10]. For the purpose of this study, the Chemometric tools of Hierarchical Cluster Analysis (HCA), which group samples according to (dis)similarity, and Principal Component Analysis (PCA), a data reduction and trend visualization tool, were suitable for the visualization of trends in the data set. Therefore, this study investigates the application of Chemometrics to be used in a study of mine tailings as partial cement replacement. This involves an evaluation of mine tailings characteristics' potential as partial cement replacement and an evaluation of the methods' suitability to this field of study.

2. Materials and Methods

2.1. Materials

This study investigated 13 mine tailings samples collected from the tailings disposal area or from the process outlet of 11 metal-based mines in China, Finland, Sweden, Norway, Greenland and Chile (Table 1). In addition, mine tailing samples were compared with characteristics of coal fly ash (CFA), cement (Basis Cement) and sand (Sea sand) commonly used for mortar mixtures.

2.2. Analyses

Testing of mine tailings' chemical and physical properties were performed on dried mine tailings samples (105°C, 24 hours). The analyses included *total chemical composition* of oxides measured by X-Ray Fluorescence (XRF) (SPECTRO Gmbh X-LAB 2000 fitted with a Pd-tube). Loss on Ignition was measured by weight loss on ignition at 550° for 1 hour (LOI550). pH was measured in KCl (1 M, 12.5 mL), shaken for 1 hour and measured by a pH-meter. Grain size distribution and Specific Surface Area (SSA) were measured by a laser diffraction analysis (Malvern Mastersizer 2000). Calcite content ($CaCO_3$) was measured by a volumetric calcimeter method (a Scheibler apparatus) which adds HCl (3 M, 20 mL) to the sample, and the developed CO_2 was measured and calibrated with $CaCO_3$. Particle density was determined by pycnometer which compares the weight difference of a pycnometer halfway filled, left overnight under vacuum suction and filled completely the next day.

2.3. Chemometrics

Chemometrics were performed in the SIMCA software version 14.1.0.2047 from MKS Umetrics AB. A *Hierarchical Cluster Analysis* (HCA) order data objects into groups of similar characteristics while separating data of dissimilar characteristics. The linkage method uses Ward D.'s method applied on Euclidean distances between data. This yields a dendrogram of clusters arranged according to (dis)similarity expressed in distance between clusters. A Principal Component Analysis (PCA) simplifies multivariable data by reducing variables into principal components. The practice visualizes trends as correlations between variables expressed by their position in a loading plot while the relation to data objects are expressed in score plots.

3. Results

Chemometrics were applied on the chemical and physical parameters of mine tailings presented in [11]. A HCA arranged data into five groups (Group 1-5), with a major division between group 1-3 (A) and 4-5 (B) (Fi1). In major division A, Group 1 was comprised of Cement, representing highly different characteristics to group 2 and 3 according to the high linkage distance. Group 2 contained the mine tailing sample of Kill A and Coal fly ash (CFA) and were connected to group 3 of Kill B, Nus, Code and Nalu at a low linkage point and are hence more similar in characteristics. Groups 4-5 are very different from group 1-3 since they represent their own major division (B). The mine tailings samples in Group 5 (Kemi, Kara, Mata, Sand, Zink, Kill C, Raa, WM) are nevertheless very similar to each other, due to the very low linkage point while Group 4 consists of mine tailing sample Tian alone. The clustering of samples showed mine tailing samples to exhibit highly different characteristics to cement, that Kill C is very similar to CFA, while a large number of mine tailings were similar to sand (Group 5). The HCA is not capable of identifying the particular characteristics that influence the grouping of mine tailing

TABLE 1: Information on mine tailing samples used.

Sample	Mine	Host rock	Ore mineral	Target metal
Code	El Teniente, Chile	Maffic complex	Sulphide	Cu, Mo
Kara	Kärväsvaara, Finland	Skarn	Magnetite	Fe, Cu
Kemi	Kemiö Island, Finland	Pegmatite	Pegmatite	Quartz
Kill A	Killavaat Alannguat, Greenland	Karkortokite	Eudialyte	Ta, Nb, REE, Zr
Kill B	Killavaat Alannguat, Greenland	Karkortokite	Eudialyte	Ta, Nb, REE, Zr
Kill C	Killavaat Alannguat, Greenland	Karkortokite	Eudialyte	Ta, Nb, REE, Zr
Mata	Mätäsvaara, Finland	Granitoids	Molybdenite	Mo
Nalu	Nalunaq, Greenland	Quartz-vein	Quartz-vein G13	Au
Nus	Nussir, Norway	Dolomite	Sulphide	Cu, Au, Ag, Pt
Raa	Raajärvi, Finland	Skarn	Magnetite	Fe
Tian	Tianbaoshan, China	Dolomitic limestone	Sulphide	Pb, Zn
WM	White Mountain, Greenland	Gneiss complex Dolomitic	Anorthosite	Anorthosite
Zink	Zinkgruvan, Sweden	marble	Sulphide	Pb, Zn, Cu, Ag

samples and is therefore only suitable for a preliminary analysis of the (dis)similarity in the dataset.

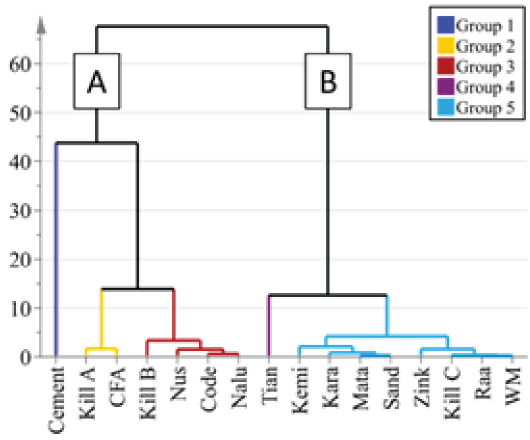

Figure 1: HCA illustrating the (dis)similarity of mine tailings according to physical and chemical characteristics.

In order to obtain information on predominating characteristics for the groups defined by the HCA and information about the relationship between parameters, a Principal Component Analysis (PCA) was performed (Table 2 and Fig. 2). The PCA yielded two PC's explaining 56% of the cumulative variation of the dataset (Table 2). The biplot in

TABLE 2: Parameters in PCA and related loadings on Principal Component (PC) 1 and 2. PC's below ±0.2 are retained to ease interpretation

Sample	**Mine**	**PC1**	**PC2**
SSA	Specific Surface Area (SSA)	0.93	
D10	The diameter where 10% of a sample's mass are comprised of smaller particles	-0.74	
D50	Mass median diameter	-0.87	
D90	The diameter where 90% of a sample's mass are comprised of smaller particles	-0.8	
∑Poz	Sum of Al_2O_3, Fe_2O_3, SiO_2 – pozzolanic indication		0.91
∑Hyd	Sum of Cao, SiO_2 – hydraulic indication	0.76	
Na_2O_Eq	Alkali content (Na_2O_{eq}=0.658×K_2O + Na_2O)		0.53
LOI	Loss on Ignition at 550°C	0.36	0.51
pH	pH	0.63	
Grain dens	Grain density	0.68	-0.47
GS range	Grain size range	-0.74	-0.39
Al_2O_3	Aluminium oxide – Al_2O_3	0.28	0.74
CaO	Calcium oxide – CaO	0.69	-0.65
Fe_2O_3	Iron oxide – Fe_2O_3		-0.67
MgO	Magnesium oxide – MgO		
SiO_2	Silicon dioxide – SiO_2	-0.35	-0.29
SO_3	Sulfur trioxide – SO_3	-0.21	0.8
Eigenvalue		5.33	3.62
% explained variation		33.3	22.7
% cum expl. variation		33.3	56

Fig. 2 represents a combined score and loading plot and illustrates a clear clustering of groups defined by the HCA (Fig. 1). Table 2 and Fig. 2 showed the variables of SSA (0.93) and ∑Hyd (0.76) to be responsible for the highest positive loadings while D50 (-0.87) and D90 (-0.80) were shown to have the highest negative loadings on PC1. These variables were hence most defining for the grouping of samples. From the location of scores (mine tailing samples) relative to the variables it could be seen that Group 1 was highly characterized by high fractions of especially CaO and grain density. Group 5 was distributed opposite to Group 1 and was hence mostly characterized by larger (D10, D50, D90) and wider grain size distributions (GS range). Group 2 was distributed in the positive direction of PC2 and was hence mostly characterized by high organic matter-content (LOI550), Al_2O_3 and ∑Hyd among others. PC2 is however less significant for the dataset, as PC2 (22.7% explained variation) explained less variation of the data set than PC1 (33.3% explained variation). The isolated location of Group 4 in the negative direction of PC2 illustrates the reason why the HCA arranged Tian in its own group. Tian is characterized by a higher calcite-content ($CaCO_3$) than Group 5, but is still located in the negative direction of PC1 and may therefore still have characteristics in common with Group 5. Group 3 was distributed centrally in the plot, which demonstrated less significant characteristics according to the PCA.

4. Discussion

The application of Chemometrics to mine tailing samples contributed with a grouping of mine tailings according to their chemical and physical properties. It is evident that PC1 contains grain size (D10, D50, D90, GS range, SSA, density) and CaO (CaO, $\sum$Hyd) information while PC2 is related to pozzolanic indications ($\sum$Poz, SiO_2, Al_2O_3), alkalies (Na_2Oeq) and calcite ($CaCO_3$). The connection between CaO and smaller grain sizes could be related to the easy degradability and hence is found in lower grain sizes (connected to the high SSA and grain density). Based on the preferred properties according to cement chemistry, samples located in positive direction of PC1 are considered most suitable for cement replacement, mostly concerning samples from group 2 and 3. This relates to a higher pH (to prevent a corrosive environment), smaller grain sizes (to enable a higher reaction potential), higher Hydraulic indications (related to direct cement replacement). In addition, scores located in the positive direction of PC2 may also seem more suitable for replacement due to a higher pozzolanic indication necessary for hydration reactions to occur. A visible discrimination was found between the binder, cement, located in the positive direction of PC1 and the constituent, sand, located in the negative direction of PC1. Sand was closely connected by the HCA with mine tailing's samples of group 4 and 5, indicative of a close similarity in characteristics, and hence presumably a weak potential for cement replacement with these mine tailings in their original form. However, certain samples of group 4 and 5 were also composed of a high SiO2 content, which, along with other oxides, enable mineral additives to react in cement- based building materials.It is therefore possible, that these mine tailings samples could be exposed to a suitable pre-treatment to unlock proper replacement characteristics.

The above-mentioned results were achieved through one of the advantages of PCA; the visual presentation of a multivariate data set. However, the method in practice can be complicated. As such, mistakes can easily be made, if axes scales in score plots are incomparable or if different amounts of variance of PC's are not considered. A variable with a high loading on a PC with low explained variance can therefore be considered unimportant for the interpretation of results. In this study, two PC's explained 56% of the total variance, where the horizontal distribution (PC1: 33.3% explained variation) of the score and loading plots was more explaining than the vertical distribution (PC2: 22.7% explained variation).

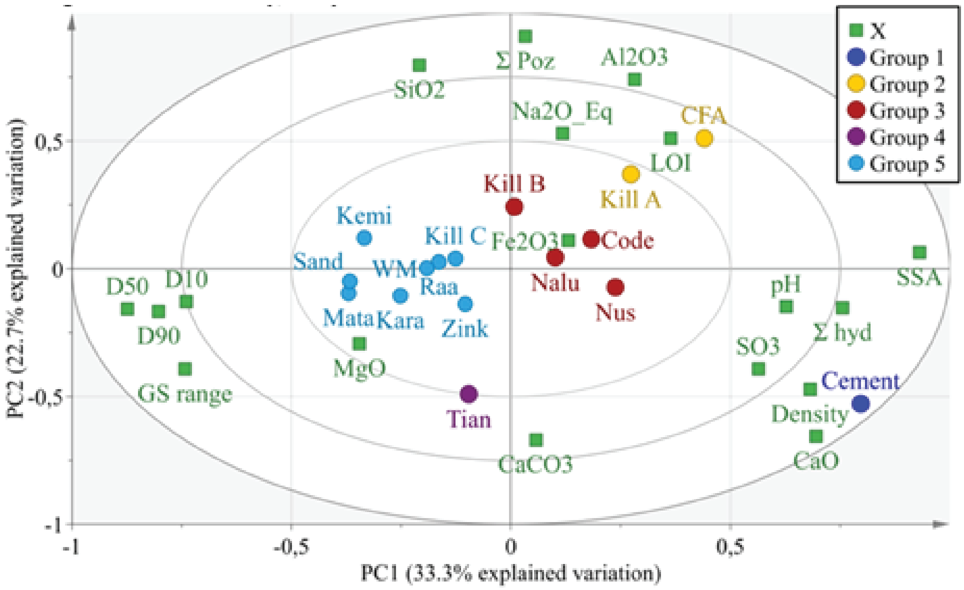

Figure 2: Principal Component Analysis (PCA) of mine tailing samples (scores) in relation to chemical and phsyical variables' loading (X). Mine tailing samples are coloured according to the grouping by HCA (Fig.1).

Even though the two PC's explained nearly an equal amount of variance, the variables with low loading on PC1 and scores located centrally should still be considered less significant. This could concern the score of group 4, which is located far from the center of the plot in the negative direction of PC2 but at the same time is located centrally according to PC1. This could generate the interpretation of group 4 being more connected to group 1. As illustrated by the HCA (Figure 1), the samples of group 1-3 are more similar in characteristics, which supports the importance of PC1. On the contrary, group 2 appears to be positioned orthogonal on the score plot in the positive direction of PC2, indicating that these are uncorrelated even though the HCA connects them in same subgroup. Instead of focusing on group 4's location far from the centre (according to PC2), it is more significant for the data set to focus on this groups' location in the negative direction of PC1. It is noteworthy, that several samples from group 3 and 5 are centrally located in the score plot, which underestimate their importance. Centrally located samples are characterized by parameters located closely to these i.e. Fe_2O_3, and are hence dominated by other variables than prevailing for PC1 and PC2.

Parameter's relation to samples are not detectable by the HCA, as this method clusters samples independent on connection. These examples demonstrate the advantage of combining more Chemometric tools to aid the interpretation. It is evident that all Chemometric tools possess positive and negative attributes and are after all highly subjective and dependent on the interpreter's intentions and expectations to the results. The HCA is based on arbitrary decisions such as the choice of the distance calculation method, group clustering algorithm and final number of groups, which rarely rely on any strong theoretical basis as seen in several studies [12, 13]. Thus, it is important to emphasize, that the outcome of the Chemometric tools are non-universal and depend not only on the methods employed but also on the interpreter's judgement and expertise.

In order to avoid misinterpretations or to investigate the data set further, i.e. the samples located centrally in the score plot, the PCA offers the opportunity to extract additional information from all PC's obtained, thus capable of explaining the entire data variance. In the application of Chemometric tools in scientific and technological studies it is often sufficient to retrieve 2 or 3 PC's to achieve a thorough understanding of the data set as the studies usually compromise on the depth of the analysis in favour of simplicity and obvious trends recognition [14–16]. However, if Chemometrics is used for modelling or predictions, a significant number of PC's should be obtained. Several component significance tests exist to retrieve the sufficient number of PC's where the rule of "keeping eigenvalues larger than 1" often occurs [9]. If this was applied, the PCA would render five PC's, in total explaining 82.8% of the variance in the data set. A large amount of the variance in the data set can hence become neglected if the prober amount of PC's are ignored in the analysis. The chemical properties of waste products are often complex and can be affected by several interacting factors, and should hence be analysed in depth to avoid misinterpretations. This novel method of categorizing samples according to cement replacement potential should therefore be taken with caution due to the parameters' relative connection. An evaluation of mine tailings' characteristics should be performed in combination with the exact parameter values, as parameters are generated on the basis of the data set. Presenting high or low characteristics are hence relative to the data set.

5. Conclusion

This study demonstrated that Chemometrics serves as a highly suitable method to obtain an overview of mine tailings samples' potential to be used as cement replacement in cement-based building materials. Despite the fact that all mine tailings samples deviated from cement characteristics, certain samples of group 2 and 3 encountered potential characteristics to be used as partial cement replacement based especially on finer grain sizes and content of oxides. As Chemometric tools exhibit both advantages and disadvantages, it is recommendable to combine more chemometric tools instead of relying on one alone in order to gain better information and prevent misinterpretations.

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