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Fingerprinting of South African ordinary Portland cements, cement blends and mortars for identification purposes — Discrimination with starplots and PCA

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Abstract

This investigation is an attempt to analyse some of the current commercial cements and cement blends in South Africa and mortars produced from them (1:3 mixtures of cementitious material with different sands) for a suite of minor and trace elements that will provide a unique fingerprint of the final product. It was found in both the case of the OPC and the blended cements that a suite of such elements can be successfully employed to uniquely characterise the materials. The contribution of such a fingerprint is that it can provide valuable information in the case of a forensic analysis for discrimination purposes.
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1. Introduction

The final composition of cement can significantly influence its behaviour in concrete. This composition depends heavily on the raw materials used, their geological origin, the kiln configuration, fuels used, burning conditions and mineral admixtures used in conjunction with clinker. Usually the chemical composition of cements has been and still is a topic that receives global attention [1–12]. However, these contributions are mainly limited to the characterisation of the major and some minor elements present in cement. The study to establish the role of minor and trace elements is important in order to better understand the behaviour of cement in concrete. Furthermore, minor and trace element profiles can potentially be used to pinpoint the source or origin of a specific cement employed in cases requiring forensic analyses of failures of application [4–12].

In South Africa, the composition of cement must conform to the requirements of the South African Bureau of Standards (SABS) specification EN 197 [13]. This specification is similar to the European norm and regulates cement according to its mechanical/physical performance. From a marketing perspective, as well as in the case of customer queries, it is often necessary and convenient to be able to distinguish between the cements from various producers. This matter is becoming increasingly important since the current specification allows one to produce a large number of blended cements from a variety of materials. In a number of countries, and also in South Africa, this has resulted in the manufacturing of several “new” cements by so-called third party blenders, who buy their raw materials (cement and secondary cementitious materials (SCM) such as fly ash and slag) from several sources and then produce their own mixtures and blends from it.

The most common cement and the one used most often in building applications, is ordinary Portland cement (OPC), or CEM I 42.5 MPa in the nomenclature of the EN197 specifications. Previous work on this topic of cement composition

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Table 1
List of materials used in the investigation

Material/product description	Strength class	Producer/ supplier	Comments
Duratech	42.5 MPa	Lafarge SA	OPC type cement
Powercrete	42.5 MPa	Lafarge SA	OPC with limestone
Buildcrete	32.5 MPa	Lafarge SA	OPC–fly ash blend
OPC	42.5 MPa	PPC Co. (Pty) Ltd	OPC type cement
Surebuild	32.5 MPa	PPC Co. (Pty) Ltd	OPC–fly ash blend
APC	32.5 MPa	Holcim SA	OPC–fly ash blend
IDM cement	32.5 MPa	IDM (Pty) Ltd.	OPC mineral admixture(s) blend
Castle cement	32.5 MPa	Castle (Pty) Ltd.	OPC mineral admixture(s) blend
Cemsure cement	32.5 MPa	Cemlock (Pty) Ltd.	OPC mineral admixture(s) blend
Drift sand	Not applicable	Drift	Washed building sand
Duarte sand	Not applicable	Duarte	Washed building sand
Multi sand	Not applicable	Multi	Washed building sand

concentrated mostly on the trace and minor element profiles of clinkers from selected countries or factories from a particular producer [4–11] to identify the origin of the material. However, when considering cement (OPC) and cement blends, one introduces a number of other materials into the mix with clinker that can significantly change and complicate the trace and minor element profiles of the resulting mixture. The situation is aggravated when these cements and cement-blends are used in mortars or concrete because of the chemical compositions of the various fine and coarse aggregates that can be used. Very limited work has been done [1–3,12] on fingerprinting of OPCs and only in one case in New Zealand [1,2] and another one in the Gulf of Mexico where oilwell cements were used [12], were trace elements in the cements considered. No record could be found in the literature where cement blends, or so-called CEM II 32.5 MPa cements, were involved in the investigation, nor cases where mortars were investigated. This paper is an early attempt to analyse different South African ordinary Portland cements and cement blends (CEM I 42.5 MPa and CEM II 32.5 MPa cements) as well as mortars made from them, with various sands, for different minor and trace elements to establish whether it provides a unique "fingerprint" that can be used to identify the source of the material. The ultimate goal of this work is to extend it to include concretes made from these cementitious materials with various sands in order to pinpoint the source of a cement used in concrete and masonry applications. If the proposed approach can be applied successfully to mortars, it should work for concretes also after the coarse aggregates (stones) have been removed. It is therefore a continuation of previous efforts by the same authors to develop the concept of fingerprinting from the initial clinkers produced to the final application of the manufactured cement in concrete.

2. Experimental procedure

2.1. Materials collection

Selected cements representing different strength classes were collected from different South African cement producers, blenders and sand suppliers with plants in the northern parts (Gauteng and North West provinces) of the country. A weekly composite sample of cement was collected in each case at the various plants and reduced to a final mass of 100 g. At the end of a twelve-week period, all these composite samples were combined and homogenised into a single sample of approximately 1.2 kg. In the case of sands, a composite sample compiled from weekly grab samples over a period of one month, was collected from each supplier. Table 1 lists the materials used in this investigation. Mortars of the various cementitious materials were prepared by mixing three parts of sand with one part of cementitious material and a constant volume of water.

2.2. Sample preparation and analysis

A 30 g sample of each sample material was crushed in a swing mill for 3 min, or until it passed a 75 μm sieve. Approximately 1–2 g of the final sample was fused with lithium tetraborate to produce a glass bead suitable for bulk component analysis by XRF. A Philips 2400 XRF spectrometer with Cu (Kα) radiation was employed for the analysis at a voltage of 30 kV and a current of 40 mA. Table 2 summarises the bulk chemical composition of each material used in the investigation. Similar beads were dissolved in nitric acid and the insoluble

Table 2
Chemical composition of the materials investigated

Element	Elemental concentration as the oxide (% m/m)											
	Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	SO_3	LOI
LSA Duratech	1.35	0.13	0.34	66.5	0.21	0.06	21.8	4.7	<0.1	0.4	2.17	2.79
LSA Powercrete	1.32	0.14	0.32	63.7	<0.01	0.02	21.1	4.2	1.3	0.3	2.02	4.93
LSA Buildcrete	1.61	0.08	0.80	50.1	0.24	0.16	29.1	11.0	1.1	0.4	1.63	3.23
PPC OPC	1.37	0.46	0.21	64.1	0.26	0.01	20.7	4.1	1.9	0.4	1.67	5.90
PPC Surebuild	1.32	0.44	0.19	50.7	0.25	0.01	27.6	11.5	1.8	0.3	1.48	3.48
Holcim APC	1.56	0.37	0.77	47.5	0.62	0.16	31.1	12.1	1.2	0.3	2.02	3.36
Castle	1.28	0.46	0.71	40.1	0.73	0.11	35.2	14.2	3.8	0.4	1.41	2.04
Cemlock	1.37	0.50	0.77	39.0	0.58	0.16	35.2	14.2	4.7	0.4	1.69	2.47
IDM	1.44	0.35	0.89	42.1	0.59	0.31	31.7	13.5	2.6	0.5	1.58	3.25
Duate	1.54	0.01	0.20	0.19	1.12	<0.01	92.6	3.2	<0.1	0.5	<0.01	0.95
Drift	1.11	<0.01	0.16	0.02	0.09	<0.01	95.6	2.1	<0.1	0.1	<0.01	1.01
Multi sand	1.55	<0.01	0.13	0.12	0.99	<0.01	93.1	3.3	<0.1	0.2	<0.01	0.89

Table 3
Wavelengths used for the analysis of elements by ICP-OES

Element	Wavelength (nm)
Mn	257.610
Mg	279.553
Sr	407.771
Ba	455.403
Ti	336.121
K	766.490

residue together with the precipitated silica filtered off. The resulting solution was made up to a standard volume with distilled water and analysed for Mn, Mg, Sr, Ba, K and Ti with an inductively coupled plasma spectrometer (ICP-OES). A GBC-Integra-XM type ICP spectrometer with a mini-plasma torch was used at a radio frequency of 40 MHz and a power output of 2 kW. The spectral range utilised varied from 165–800 nm, and data computation was done with EPIC (Evolutionary Program for Instrument Control) software, which is proprietary to the company that manufactured the instrument. Table 3 summarises the wavelengths used in this study in nm. Duplicate samples were prepared of all cements, cement blends, mortars and sands, and if the results differed more than 10% relatively, sample preparation and analysis was repeated. The concentrations of the various minor and trace elements varied substantially across the range of samples analysed. This means that one cannot use the absolute concentrations as determined, but that it is necessary to calculate an average value for each of the different elements measured and ratio each individual determination for all the trace elements against their respective average values. In this way one can graphically depict the large variations that occur among the different samples in each particular element of analysis in an easily distinguishable way. A detailed description of the approach used, can be found in other work published earlier in this regard [3,7,9,10]. Tables 4–7 represent the ratios of the different minor and trace elements in the different cementitious materials and their respective mortars with different sands.

3. Results and discussion

For the graphical representation of the results, so-called "Star Plots" were used. For this purpose one has to resort to using averages of the different trace element concentrations. Averages of the concentrations of each one of the respective trace elements have been calculated using data of the analysis of all the various materials analysed in this investigation. The real average of each trace element in anyone particular sample was then ratioed against the general average and this ratio was plotted on a 60° radial axes system. In order to reduce the number of variables (dimension reduction) and to detect structure in the relationships between variables PCA (Principal Component Analysis) was applied to the data matrix. The PCA calculations were carried out using the SIMCA-P software package (Umetri AB and Ericsson Erisoft AB, Sweden), based on the covariance matrix of the different raw data. The star plot results will be dealt with first, and then a description will be given on the PCA approach to evaluate the same data.

From the bulk chemical analyses one can observe substantial differences between the CaO, MgO, SiO_2 and Al_2O_3 contents of these various classes or groups of materials investigated. Potgieter [3] indicated previously that these differences, together with the alkali and Sr contents can be used to discriminate between various CEM I 42.5 MPa or OPC cements produced in South Africa by various cement factories. However, the previous work did not extend to mortars, which are also covered in this investigation.

The star plots constructed from the ratioed values for six trace elements present in the cementitious and mortar samples from the various producers are graphically represented in Figs. 1–12.

The plots of the different cements in Fig. 1 indicate that one can easily distinguish between the products of one producer. The slight difference between the ratios of the various minor and trace elements between the Lafarge products can probably be ascribed to a slight dilution of the Powercrete with limestone compared to the Duratech. However, both of them differ substantially from the Buildcrete material containing fly ash, especially as far as the ratios of Ti, Mg, K and even Mn are concerned. A similar pattern emerges from Fig. 2 depicting the mortars of these three cements with one of the sands (Drift).

When considering the second group of cements and blends as shown in Fig. 3, it can be seen that one can once again distinguish between the different products from one producer (PPC) and the two similar CEM 32.5 MPa strength ones from Holcim (APC) and PPC (Surebuild) that both contain fly ash as mineral extenders. As was the case with the Lafarge products,

Table 4
The calculated ratios of trace elements in various cement samples

Ratios of elements						
Sample ID	Ba	Sr	Mn	Ti	K	Mg
LSA Duratech	0.70±0.01	0.47±0.01	0.66±0.01	0.74±0.02	0.70±0.24	0.87±0.01
LSA Powercrete	0.46±0.01	0.35±0.01	0.51±0.01	0.58±0.02	0.26±0.24	0.47±0.01
LSA Buildcrete	0.78±0.01	0.47±0.01	0.43±0.01	1.16±0.02	0.36±0.24	0.62±0.01
PPC OPC	0.85±0.01	0.24±0.01	1.23±0.01	0.39±0.02	0.83±0.24	0.95±0.01
PPC Surebuild	1.03±0.01	0.25±0.01	1.33±0.01	0.45±0.02	1.34±0.24	0.19±0.01
Holcim APC	0.95±0.01	1.55±0.01	0.65±0.01	1.48±0.02	1.06±0.24	0.61±0.01
IDM best build	1.47±0.01	2.54±0.01	1.10±0.01	1.43±0.02	1.69±0.24	1.98±0.01
Cemlock Cemsure	1.47±0.01	1.57±0.01	1.61±0.01	1.37±0.02	1.54±0.24	1.77±0.01
Castle cement	1.28±0.01	1.56±0.01	1.48±0.01	1.41±0.02	1.20±0.24	1.54±0.01

Table 5
The calculated ratios of trace elements in mortars made with Multi sand and different cements

Ratios of elements						
Sample ID	Ba	Sr	Mn	Ti	K	Mg
LSA Duratech	0.75±0.00	0.72±0.00	0.64±0.01	0.79±0.02	0.59±0.24	0.26±0.01
LSA Powercrete	0.67±0.01	1.30±0.01	0.61±0.01	0.70±0.02	0.09±0.24	0.24±0.01
LSA Buildcrete	1.65±0.01	0.59±0.01	0.86±0.01	1.83±0.02	2.29±0.24	0.93±0.01
PPC OPC	1.79±0.01	0.87±0.01	2.9±0.01	1.42±0.02	2.53±0.24	2.72±0.01
PPC Surebuild	0.72±0.01	0.51±0.01	0.87±0.01	0.46±0.02	0.25±0.24	0.06±0.01
Holcim APC	0.81±0.01	1.07±0.01	0.61±0.01	1.02±0.02	0.62±0.24	0.03±0.01
IDM best build	0.98±0.01	1.67±0.01	0.96±0.01	1.02±0.02	1.22±0.24	1.79±0.01
Cemlock Cemsure	0.72±0.01	1.04±0.01	1.03±0.01	0.82±0.02	0.47±0.24	1.40±0.01
Castle cement	0.92±0.01	1.23±0.01	1.15±0.01	0.96±0.02	0.93±0.24	1.57±0.01

the ratioed Mg and K content, and to a lesser degree the Ti and Mn ratios made the discrimination between the various materials obvious. An almost identical picture is obtained in the case of the star plots of the mortars of these cements with Drift sand. One would expect it to be so in the mortars, because the cements are diluted by the same factor (the fraction of cement is the same in all mortars) and then a constant fraction of sand is added contributing with its trace element concentration to the overall composition.

Even in the case of the products of the third party blenders, one can fingerprint a specific cement from the different star plots displayed in Fig. 5 and their respective mortars with Drift sand depicted in Fig. 6. In this particular case, the elemental ratios proving to be the most dissimilar are Mg, Mn and K.

The star plots of the three cement-blends with fly ash extenders produced by the three cement producers (Lafarge, Holcim and PPC) are shown in Fig. 7. One can clearly distinguish between these three products on the basis of differences in their K, Ti, Mn and Sr contents. It is remarkable that Sr that always differed substantially for one of the cementitious materials now becomes a distinguishing feature between the various products. The strong discriminating appearance of Ti in the fly ash blended cements can be ascribed to the fly ash additions to the cements.

A fairly similar picture can be distinguished in Fig. 8 from the star plots of the mortars made from the blended cements with Drift sand. However, K and Mn are now no longer differing sufficiently for discriminating purposes, only Ti and Sr with, surprisingly, Ba in addition. When compared with the mortars made from blended cements produced by the third party blenders (IDM, Castle and Cemlock) as shown in Fig. 6, two completely different visual patterns can be seen. Furthermore, in the latter case Mg and K were the elements with the most discriminating features, while in the mortars with the blended cements from the recognised cement producers Ti, Sr and Ba are the ones possessing the largest differences between the various mortars. This implies that it might be very feasible and possible to distinguish even the blended cements between the various producers.

However, one should be careful to generalise. This is emphasized when considering the star plots of the mortars made from the fly ash blended cements produced by the cement producers when two other different sands, Multi sand and Duarte sand, are considered. As can be seen from Figs. 9 and 10 displaying these star plots, not only do completely different visual patterns emerge when compared to Fig. 8, the discriminating elements in both cases changed to K and Ti from Ti, Sr and Ba in the case when Drift sand was used in the mortars.

The current work indicates that Mg, K and to a lesser degree Mn and even sometimes Ti can be used to discriminate between the different cement products from the three different cement manufacturers and various third party blenders, regardless of the strength class or type of cement (OPC or blended cement). This correlates with earlier work by Potgieter [3] on South African OPC cements from various producers and regions in the country, in which it was found that Mg, alkalis and Sr can be used to discriminate between the various products. Work by Tamas [4] and Tamas et al. [6,9,10] indicated that Mn is a very strong indicator of cement origin between various factories from

Table 6
The calculated ratios of trace elements in mortars made with Drift sand and different cements

Ratios of elements						
Sample ID	Ba	Sr	Mn	Ti	K	Mg
LSA Duratech	1.56±0.01	0.16±0.01	0.81±0.01	1.38±0.02	1.63±0.24	0.84±0.01
LSA Powercrete	2.52±0.01	0.14±0.01	0.75±0.01	1.12±0.02	1.43±0.24	0.72±0.01
LSA Buildcrete	0.77±0.01	0.26±0.01	0.51±0.01	1.48±0.02	1.40±0.24	0.55±0.01
PPC OPC	0.18±0.01	0.23±0.01	0.70±0.01	0.60±0.02	0.09±0.24	0.61±0.01
PPC Surebuild	1.18±0.01	0.07±0.01	0.86±0.01	0.65±0.02	0.59±0.24	0.39±0.01
Holcim APC	0.13±0.01	0.22±0.01	0.55±0.01	0.93±0.02	0.60±0.24	0.45±0.01
IDM best build	1.70±0.01	0.58±0.01	1.04±0.01	1.29±0.02	1.36±0.24	1.37±0.01
Cemlock Cemsure	0.29±0.01	6.96±0.01	2.39±0.01	0.26±0.02	0.55±0.24	2.72±0.01
Castle cement	0.68±0.01	0.38±0.01	1.38±0.01	1.28±0.02	1.35±0.24	1.36±0.01

Table 7
The calculated ratios of trace elements in mortars made with Duarte sand and different cements

Ratios of elements						
Sample ID	Ba	Sr	Mn	Ti	K	Mg
LSA Duratech	0.53±0.01	0.60±0.00	0.44±0.01	0.52±0.02	0.00±0.24	0.00±0.00
LSA Powercrete	0.64±0.01	0.60±0.01	0.47±0.01	0.61±0.02	0.00±0.24	0.00±0.01
LSA Buildcrete	0.82±0.01	0.93±0.01	0.52±0.01	0.91±0.02	1.32±0.24	0.00±0.01
PPC OPC	1.83±0.01	1.06±0.01	2.26±0.01	1.88±0.02	1.18±0.24	3.09±0.01
PPC Surebuild	1.59±0.01	0.96±0.01	1.92±0.01	1.47±0.02	2.37±0.24	2.14±0.00
Holcim APC	0.85±0.01	1.06±0.01	0.52±0.01	1.02±0.02	0.80±0.24	0.00±0.01
IDM best build	0.89±0.01	1.48±0.01	0.86±0.01	0.84±0.02	0.70±0.24	1.12±0.01
Cemlock Cemsure	1.11±0.01	1.44±0.01	1.32±0.01	1.13±0.02	2.18±0.24	2.66±0.00
Castle cement	0.73±0.01	0.85±0.01	0.70±0.01	0.64±0.02	0.45±0.24	0.00±0.01

the same and different countries, with lesser contributions by the Mg and Sr concentrations in the clinkers of various producers. The fact that Ti can be used as a strong indication of cement fly ash blends is a new observation. It seems that in the case of cementitious mortars, regardless of whether they were produced by blended cements or OPC type cements, the combination of Ti and K can be used to fingerprint the origin of the cement. In the case of mortars made with OPC, Mn and Mg can further contribute to the distinction between the cement product used, while in the case of blended cements Sr and Mn to a lesser degree can be useful for discriminating purposes between the various cementitious products.

The largest draw back of this proposed method is that the visual impact of differences between sample sets is lost when more than 5 or 6 data sets are compared. This is illustrated when the star plots of all nine different cements investigated are compiled in a single graph (Fig. 11). A partial solution might be to plot up to six different data sets in a slightly different star plot configuration using *the different cements as coordinates* of the figure and plotting the six different element ratios as the various curves on the plot, as is shown in Fig. 12. This latter configuration illustrated that Lafarge cements differ most from those of PPC and Holcim in their Mg content, while PPC products differ distinctly from those of the other two cement manufacturers in their Mn content. Although only one Holcim product was investigated, it could be distinguished from cement products by PPC and Lafarge by its different Ti and Sr contents. This, bar the K, is the same combination of elements found above from the star plots in Figs. 1–10.

However, a more elegant solution will be to resort to known chemometric techniques, such as for example Principal Component Analysis (PCA). PCA, referred to as an unsupervised technique, is a useful statistical technique that identifies natural groupings or clusters within a data set without prior information needed to perform the analysis. It has found many applications in the various scientific fields and is commonly used to find patterns in data of high dimension. Its application to cement

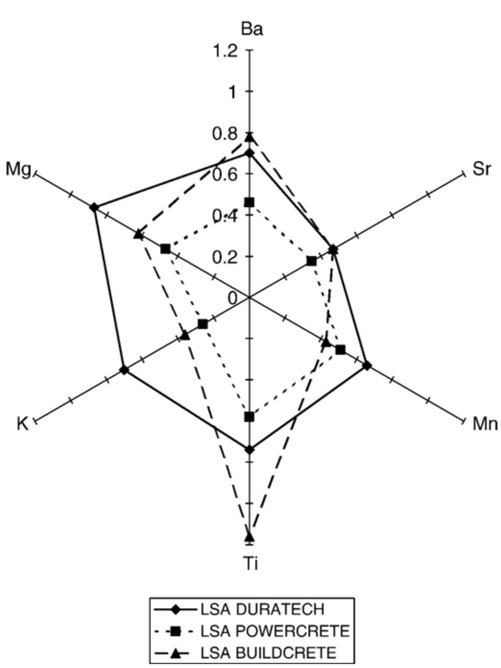

Fig. 1. Star plots of the ratioed values obtained for the six trace elements analysed originating from three different Lafarge cements.

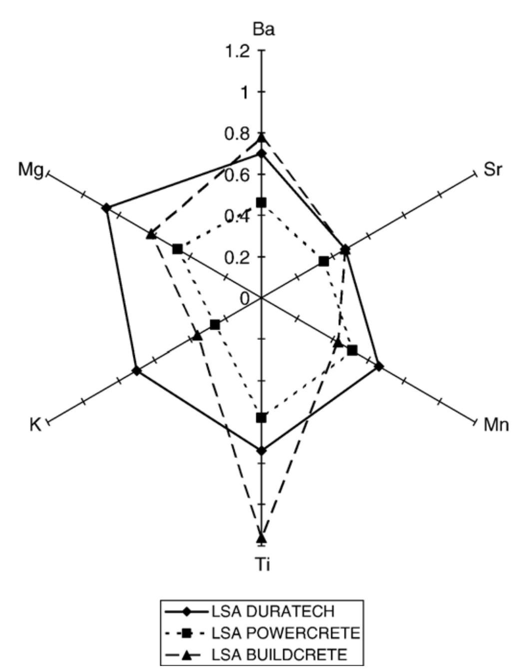

Fig. 2. Star plots of the ratioed values obtained for the six trace elements analysed originating from three different Lafarge cement mortars with Drift sand.

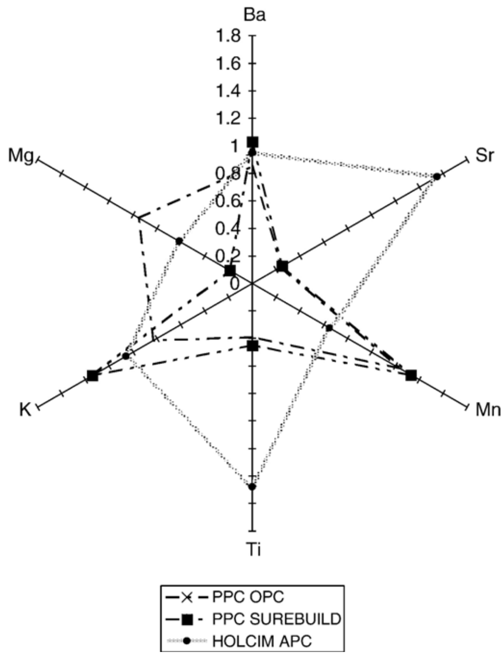

Fig. 3. Star plots of the ratioed values obtained for the six trace elements analysed originating from two different PPC and one Holcim cements.

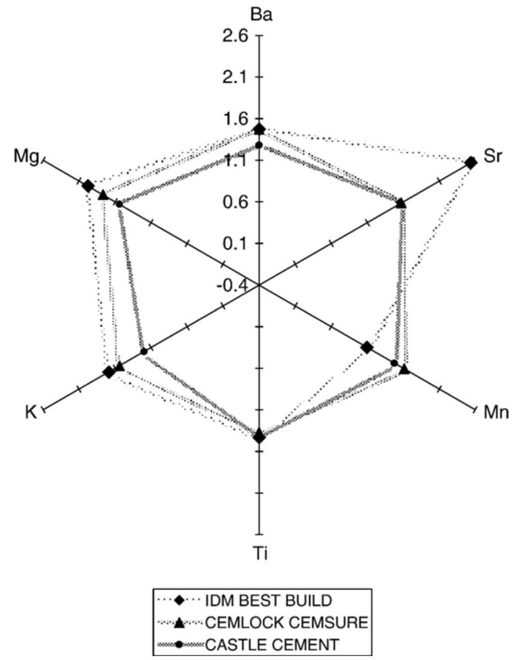

Fig. 5. Star plots of the ratioed values obtained for the six trace elements analysed originating from three different third party blenders cement products.

clinker fingerprinting has previously been described [4,10] and a recent publication by Rampazzi and co-workers [14] used PCA to characterise and cluster the binders in historical mortars, based on the chemical analysis of the specimens. The purpose of the PCA method is to represent the variations present in the data in such a way that dimensionality is reduced, without losing significant information and relies on the fact that most of the parameters are intercorrelated. From a set of correlated parameters a new set of uncorrelated parameters are designed, called the Principal Components (PC), which contain all the information as a linear combination of the original variables. The principal components obtained in this way represent the linearly independent variance present in the data of original variables.

By definition the first principal component accounts for the maximum variation in the original data set and the second PC (orthogonal to the first) for the most of the remaining variance.

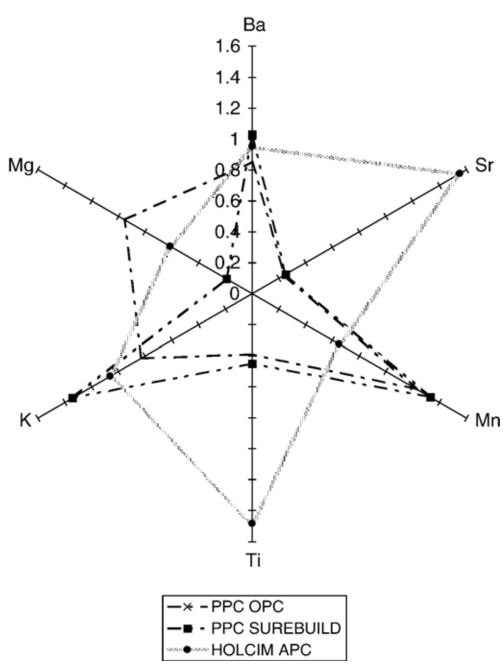

Fig. 4. Star plots of the ratioed values obtained for the six trace elements analysed originating from two different PPC and one Holcim cement mortars with Drift sand.

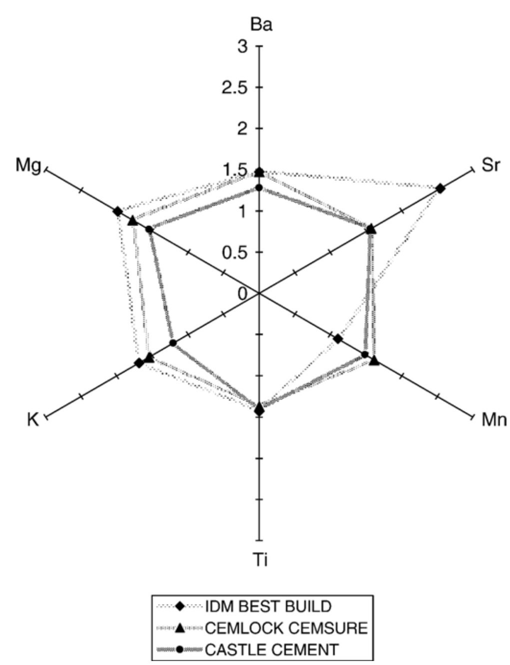

Fig. 6. Star plots of the ratioed values obtained for the six trace elements analysed originating from three different third party blenders cement mortars with Drift sand.

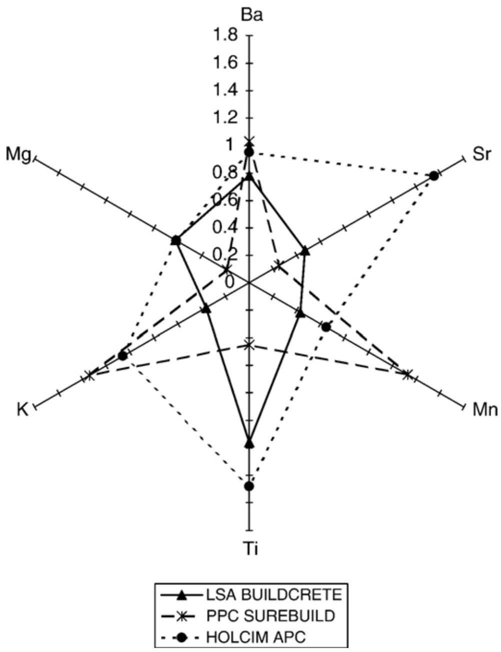

Fig. 7. Star plots of the ratioed values obtained for the six trace elements analysed originating from three different cement–fly ash blends from the recognised cement producers.

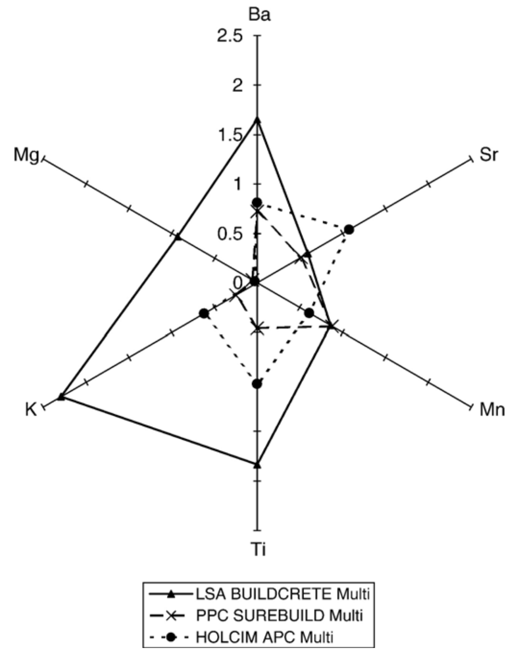

Fig. 9. Star plots of the ratioed values obtained for the six trace elements analysed originating from mortars of the three different cement–fly ash blends from the recognised cement producers with Multi sand.

Maximum retention of variation is achieved, by retaining only the first components, whereby significant information can be separated from irrelevant noise and a reduction of the data set is achieved. By studying the first two or three principal components, the most important sources of the variance are examined. More complete mathematical descriptions can be found in the general literature [15–21].

In order to investigate the fingerprints in the composition of the cements, the ratios calculated from the ICP-OES analyses were used as the input for the study of the principal component analysis (PCA). The data matrix containing the abundance (ratio) concentration values of the six different elements as variables and the nine cementitious samples as objects, were subjected to PCA, without z-transformation prior to the analysis.

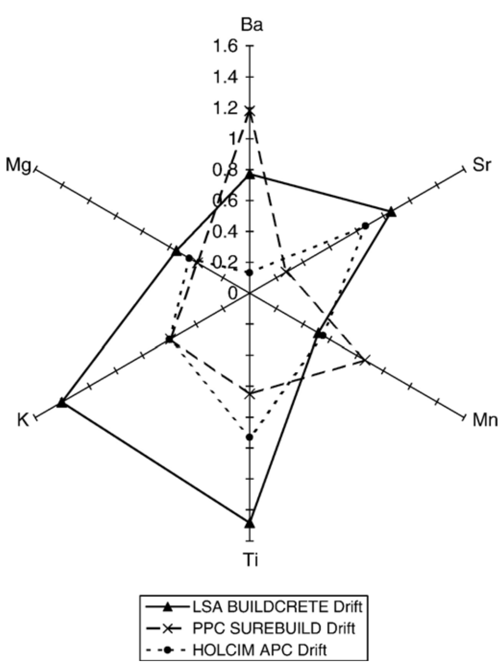

Fig. 8. Star plots of the ratioed values obtained for the six trace elements analysed originating from mortars of the three different cement–fly ash blends from the recognised cement producers with Drift sand.

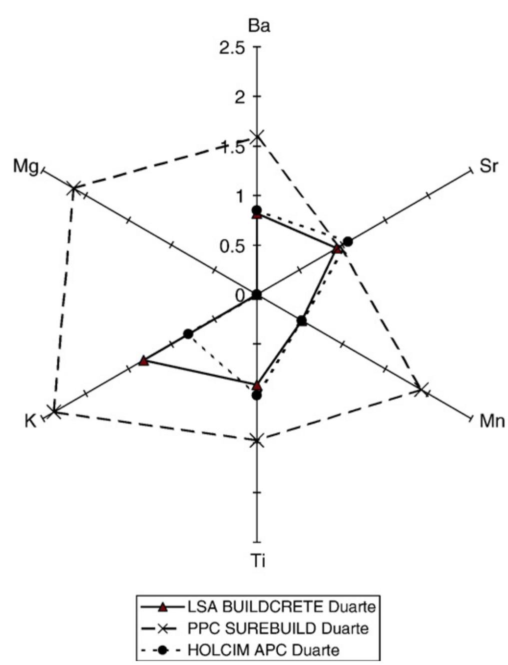

Fig. 10. Star plots of the ratioed values obtained for the six trace elements analysed originating from mortars of the three different cement–fly ash blends from the recognised cement producers with Duarte sand.

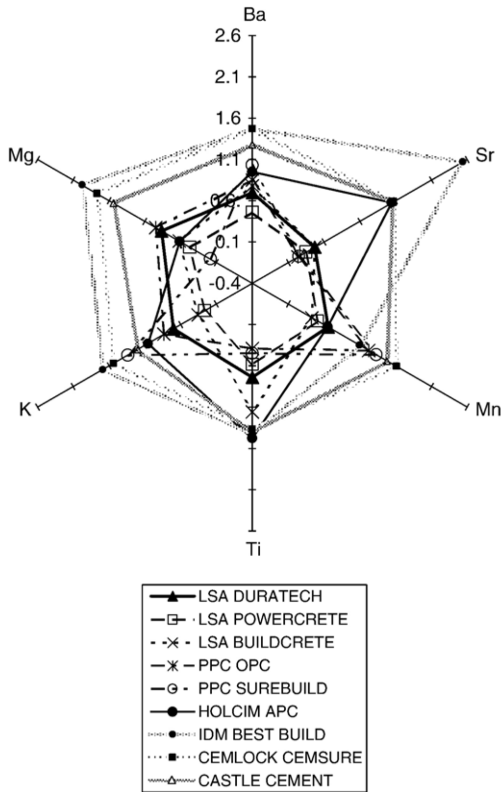

Fig. 11. Star plots of the ratioed values obtained for the six trace elements analysed originating from all the different cements investigated.

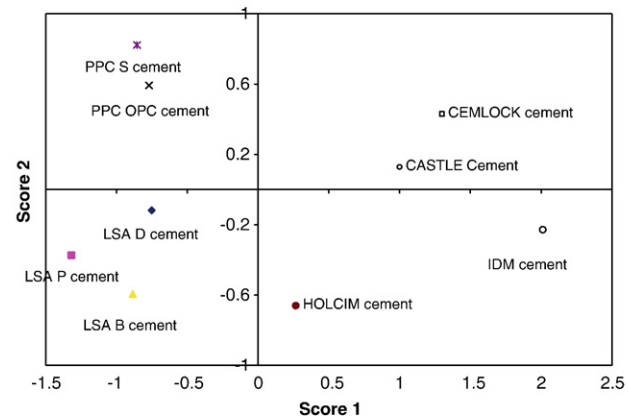

Fig. 13. PCA plot of the ratioed values obtained for the six trace elements analysed originating from all the different cements investigated.

The first two components were sufficient to describe about 90% of the variance of the data set. The interpretation of the results was performed by evaluating the score plot, giving information about the samples and the loading plot, giving information about the variables. A score and loading plot of these components are represented in Figs. 13 and 14, respectively.

By investigating these plots, it is possible to deduce similarities between the cements according to their respective chemical composition. The score plot in this case indicates the clusters of cement types based on their respective elemental concentrations. From the score plot presented in Fig. 13, it could be concluded that the cement types under the investigations form four, clearly separated groups. Since the criterion of the separation is the chemical similarity of the samples inside a particular cluster, the observed groups therefore suggest a definitive chemical correlation between the samples. One could therefore conclude that the cements inside a particular group are of similar origin or the final mixture is of a particular type. The

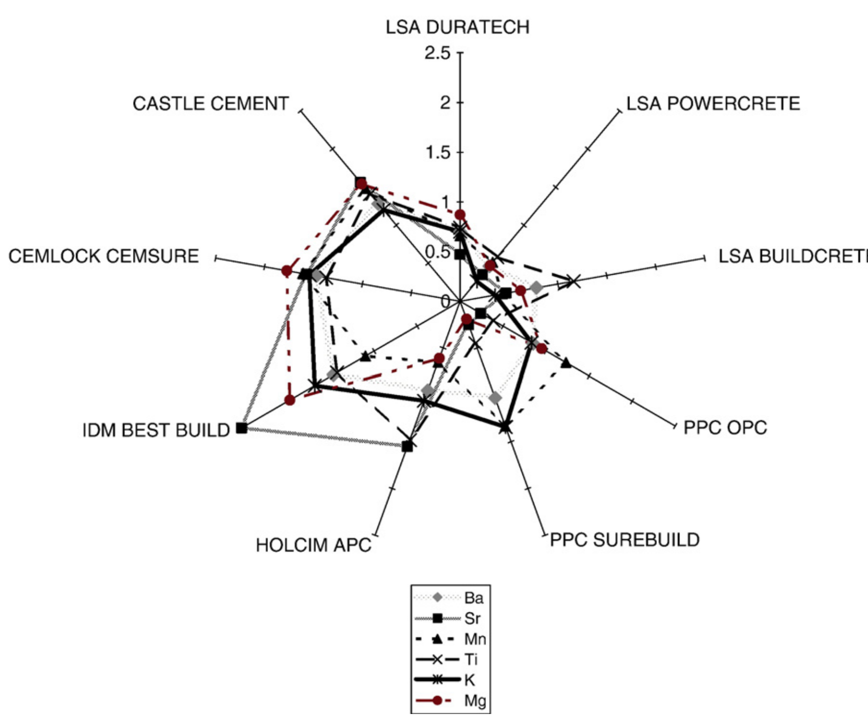

Fig. 12. Star plots of all the different cements investigated originating from the ratioed values obtained for the six trace elements analysed when plotted in an alternative configuration.

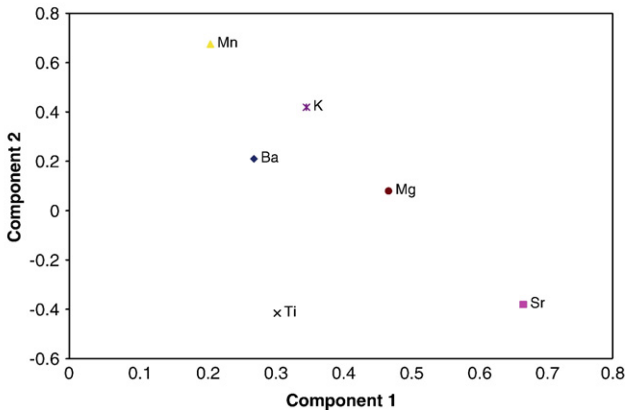

Fig. 14. PCA plot indicating the most discriminating ratioed values obtained for the six trace elements analysed originating from all the different cements investigated.

chemical correlation indicates that the elemental concentration of the cements from the four different groups differ significantly from each other to identify the source of each cement.

The loading plot indicates which element(s) contributed most to the PC's. From the loadings plot, represented in Fig. 14, it is noticed that the elements: Mn, K, Mg and Sr are lying on the same vector. This correlates with the star plots shown earlier that also identified these four elements as the ones with the largest discriminating potentials in most of the cases investigated and being the primary distinctive elements for fingerprinting purposes.

Comparing the position of the samples on the score plot with those of the elements on the loadings graph it can be seen that the chemical character of PPC cement types, situated in the area of the negative values of the first component, is strongly determined by the ratios of Mn followed by K. On the other hand the IDM and Holcim type of cements, representing the positive values of the first, but negative values of the second component, is characterised by the high contribution of Sr. However the position of the Holcim cement sample also suggested an influence of Ti, while in the case of IDM cement type the influence of Mg should be considered. The position of the LSA cement types suggests the highest contribution by Ti. The group of Cemlock and Castle cement is positioned in the area of the positive values of both the components.

The main advantage of both methods is that it utilises a suite of elements that can uniquely identify the material in question. The star plot method is furthermore visually striking and easy to use when the star plots represent all the producers with reference to the six trace elements analysed and vice versa, as illustrated in this work. It is evident that selected elements can be found in any combination of cements, blended cements and mortars made from any combination of them to uniquely fingerprint and identify one particular cementitious product and pinpoint its origin.

4. Conclusions

It has been proven previously that star plots are a useful tool to discriminate various cement clinkers from each other, based on their respective elemental concentrations [10] and based on the results obtained in this investigation, it can be discerned that the star plot approach offers a unique and exciting way to characterise and fingerprint different materials involved in cement and mortar production. It seems to indicate a very worthwhile route for future investigations into more materials utilised by the building and construction industries in the compilation of cement blends and concretes. The method of presentation makes discrimination between the various samples easy to visualise, explain and understand. This latter fact should make it ideally suitable as a marketing tool, especially to non-technical audiences. The successful application of PCA to the elemental concentrations of the various cement types investigated, to distinguish them from each other, suggests that it will be worthwhile to explore other materials and mixtures thereof. Furthermore, this work illustrates that it should be possible to extend this approach to concretes as well and that one should be able to finally pinpoint the source of any particular concrete made from the raw materials available in the region. Further work is planned to investigate this, as well as the applicability of PCA to a more exhaustive data set of cements, cement blends and mortars.

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