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Trace elements in clinker
I. A graphical representation

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Abstract

The trace element content of clinkers (and possibly of cements) can be used for the qualitative identification (i.e. manufacturing works). Several hundred clinker sorts have been analysed (by replicated quarterly samples, collected from all Hungarian cement factories, as well as from factories in eight foreign countries) to determine their Mg, Sr, Ba, Mn, Ti, Zr, Zn and V content. The first six elements come from the main raw materials and are of dactylogrammatic value, while the last two elements mainly come from fuel (used tires and heavy fuel oil, respectively) and cannot be used for identification. In this paper, a graphical method is presented to facilitate the visualisation of the trace element content. © 2002 Published by Elsevier Science Ltd.

Keywords: Characterisation; Clinker; Trace elements

1. Introduction

The trace element content of clinkers is of high scientific interest and can be used to solve practical problems, too, for example, to determine the origin of the clinker (i.e. the manufacturing works). The first paper on a similar topic was published in 1993 by Goguel and StJohn [1,2], showing the Ba, Sr and Mn concentration of portland cements in New Zealand concretes. Advanced statistical methods, called "pattern recognition" or "fingerprinting" can help qualitative identification [3]. Data describing trace element content of clinkers and cements have been published, too [4–6]. A qualitative identification obviously requires a database in order to compare the trace element content of unknown clinkers/cements with characteristic known samples.

Not all trace elements can be used for fingerprinting; selection must follow certain principles. The most important item for selection is that the trace elements of "dactylogrammatic value" should come from the main raw materials (limestone, marl, clay) and not from fuel, furnace lining or grinding media wear; some other principles should be observed as well. More recently, six elements were used to characterize clinkers: Besides those used by Goguel and StJohn [1,2], Mg, Ti and Zr contents were measured, too [5,6]. Zn and V have no dactylogrammatic value (they come from fuel, if waste tyres or special sorts of heavy fuel oil are used, respectively), but their quantity can be interesting in cement performance.

The visualisation of trace element content of clinker/cement is not an easy task. At the 10th International Congress on the Chemistry of Cement, J.H. Potgieter [7] presented a method to construct "star plots", where the visual impact of chemical differences are more striking. However, he used not only trace elements but main ones, too, which are of less dactylogrammatic value (Mg, Ti, Mn, Fe, Al, Na, K and S). This "star plot" method has been further developed in this paper.

2. Experimental

2.1. Materials

For the qualitative "fingerprinting" of clinkers, obviously, a set of well-defined clinker samples is necessary: composite average samples of a longer period of kiln operation. Such samples were collected quarterly, over a

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longer period (2–3 years) in all Hungarian cement factories. A nationwide sample collection has a limited value only; to obtain a higher area, a Technical Committee "QIC" (Qualitative Identification of Clinkers and Cements) has been established in 1996, under the auspices of RILEM (Réunion Internationale des Laboratoires d'Essais et de Recherches sur les Matériaux et les Constructions) (TC 180-QIC). This enabled the authors to collect composite average samples from eight further countries (Austria, Portugal, South Africa, Slovakia, Slovenia, Spain, Switzerland and United Kingdom). Over 200 samples have arrived to date, which have already been analysed.[1]

2.2. Methods

The mass of clinker samples that arrived at this laboratory was approximately 2–3 kg, usually as noncrushed nodules. It was crushed, and a smaller average was taken according to sampling standards and was ground in a centrifugal mill. The final size reduction (to pass sieve 63 μm) was handmade in an agate mortar. (A previous experiment with pure quartz showed that the abrasion of grinding media or mill lining did not bring any considerable pollution into the sample of the elements analysed). Approximately 1 g of exactly weighed sample was dissolved in reagent grade hydrochloric acid, SiO_2 precipitated, filtered and washed, and the filtrate was analysed by inductively coupled plasma emission spectrography (ICP-ES). ICP-ES is advantageous when absolute parts per million values are needed, as standardization can be done by reagent grade chemicals of known concentration. Duplicate samples were prepared of all clinkers for analysis, and if the difference was > 10%, sample preparation and analysis were repeated.

Details of ICP-ES analysis: In the beginning period, an ARL/3410, and later, a GBC-Integra-XM type ICP spectrometer, was used, with mini-plasma torch, using radiofrequency generators, 27 (40) MHz of 650 W (2 kW) power (data in parentheses refer to the new apparatus). Spectral range: 165–800 nm. Computation: Evolutionary Program for Instrument Control (EPIC) software, IBM PS/2 computer, with a PC DOS 3.0 system. The wavelengths used in this study (in nm): Mn = 257.610, Mg = 279.553, Sr = 407.771, Ba = 455.403, Ti = 336.121, Zr = 349.621, Zn = 213.856 and V = 310.230.

3. Construction of star plots

Star plots (for the visualisation of the chemical composition of natural waters) were first used by Maucha [8]. The "rays" or "twigs" of the star were proportional to the milligram equivalent of the considered ions, thus, the full area of these octagonal star plots is proportional to the gross concentration.

There are two exceptions: (1) in case of natural waters, the ion equivalent of the element can be used, but this would be meaningless in case of clinkers and (2) star plots of natural waters are always 'symmetric', as four cations and four anions are plotted on the right and left side of the plot, and the sum of equivalent weights of considered cations and anions is obviously identical, while this is not true in the case of clinkers. In that case, we have to use averages.

Averages can be calculated using data of the analysis of over 200 samples investigated so far for the eight considered elements. For practical reasons, these should be rounded values. Table 1 shows the maximum and minimum values (in mg/kg units), the standard deviation of data, as well as the real averages and the rounded ones used for plotting. (From this table, the variability of trace elements can be seen; by calculating relative deviations, Zr has the lowest variability, and Mg, followed by Mn, has the highest variability). A clinker of "standard trace element content" has 11.4 g/kg of considered impurities.

The concentration of each considered element is denoted by $c_i = 1, \ldots, 8$, and the sum of the concentration values is called T.

$$T = \sum_{i=1}^{8} c_i \tag{1}$$

The concentration values for the clinker of "standard trace element content" are denoted by c_i^s, thus $c_1^s = 0.2$, $c_2^s = 0.5$, $c_3^s = 0.5$, $c_4^s = 8.95$, $c_5^s = 1.0$, $c_6^s = 0.05$, $c_7^s = 0.1$ and $c_8^s = 0.1$, for Ba, Mn, Sr, Mg, Ti, Zr, Zn and V, respectively, and

$$T^s = \sum_{i=1}^{8} c_i^s = 11.4$$

The 'star plot' described in this paper is a 16-sided polygon; its area is proportional to the total trace element content,

$$A \approx T \rightarrow A = \lambda T \tag{2}$$

where λ represents a factor that enables the scaling of the star plot in a way to be described later.

Table 1
Maximum and minimum values, standard deviation, averages and rounded averages (used for star plots) of investigated clinkers (mg/kg)

Element	Maximum value	Minimum value	Standard deviation	Average	Rounded average
Ba	442	47	122.74	192.68	200
Mn	6538	15	995.06	507.02	500
Sr	2972	19	677.63	560.28	500
Ti	1691	175	289.78	1189.13	1000
Zr	149	4	17.33	47.32	50
Mg	24125	1751	6453.27	8976.93	8950
Zn	559	11	112.89	113.70	100
V	297	17	67.11	85.69	100

[1] Detailed analytical data can be obtained from the author. By the request of companies, factory and sampling data cannot be revealed, only the country and a code number.

The eight rays or twigs radiating from this polygon form quadrangles; their area is proportional to the percentage of the corresponding element

$$A_i \approx x_i = \frac{c_i}{c_i^s} 100\% \tag{3}$$

where A_i denotes the area of the $i = 1, \ldots, 8$ quadrangle, and x_i represents the percentage of the corresponding trace element.

As the sum of these areas has to be equal to the area of the polygon (Eq. (2)),

$$A = \sum_{i=1}^{8} A_i \tag{4}$$

a clinker of "standard trace element content" can be represented by a regular 16-sided polygon, with identical quadrangles (in that special case, these are isosceles triangles), where the area is computed as $A_i = 1/8A = 1/8\lambda T^s$.

For the construction of the star plot (16-sided polygon) of a given clinker, the following steps are necessary.

3.1. Calculate the sum and the percentages of the trace elements

Calculate T, the sum of parts per million concentrations of the eight trace elements using Eq. (1), and the x_i percentages using Eq. (3).

3.2. Draw the skeleton of the polygon

Draw the coordinate system depicted in Fig. 1.

The solid lines are the even radii of a regular 16-sided polygon with a length r (solid lines). The remaining radii

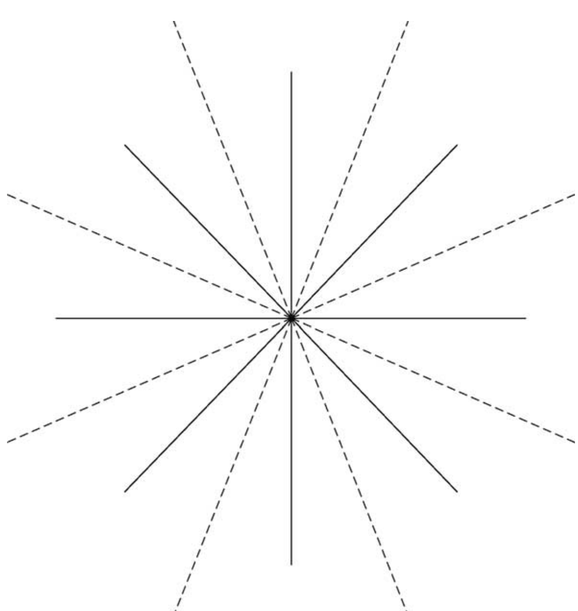

Fig. 1. Construction of star plots.

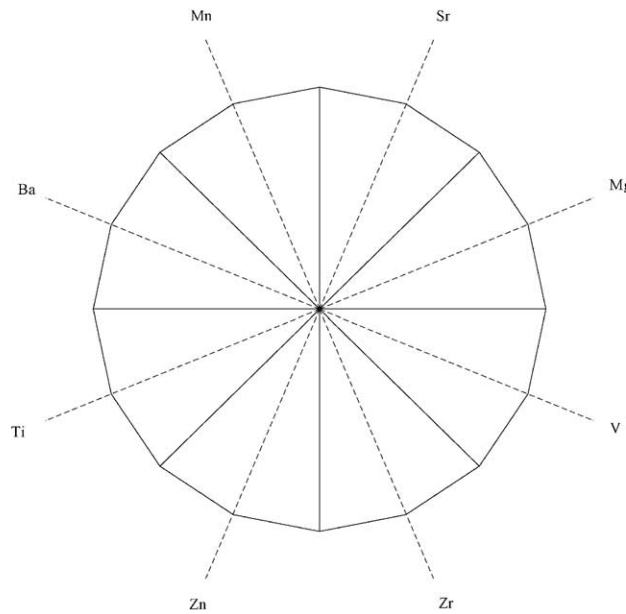

Fig. 2. Star plot of the standard trace element content.

will be referred to as the radii of the trace elements (dashed lines). These dashed lines will help to draw the quadrangles (twigs of the trace elements) with a given area, because the corner of the twig lies on the corresponding dashed line with a D_i distance from the center.

As r and D_i are unknown, only the lines originating from the center of the polygon are drawn as they are depicted in Fig. 1.

The percentages of bivalent elements (Ba, Mn, Sr, Mg) are plotted on the upper half of the horizontal diagonal, and the percentages of tetravalent elements (Ti, Zr) are plotted on the lower left quarter, in a way to be described later. The dactylogrammatically irrelevant oxides (Zn and V) are put to the lower right quarter of the star plot. (If, in the future, new, representative trace elements are found, they can be substituted for Zn and V.)

3.3. Calculate the radii and the distances

The D_i distance is chosen to be proportional to the percentage of the ith trace element.

$$D_i = x_i r \tag{5}$$

Hence, if the percentage of the trace element is bigger than 100%, the corresponding ray protrudes; otherwise, it intrudes (like a swallow's nest) from the circle.

As the area of the ith wing (Eq. (6)) can be expressed as the area of two triangles,

$$A_i = 2 \frac{D_i r \sin(\pi/8)}{2} \tag{6}$$

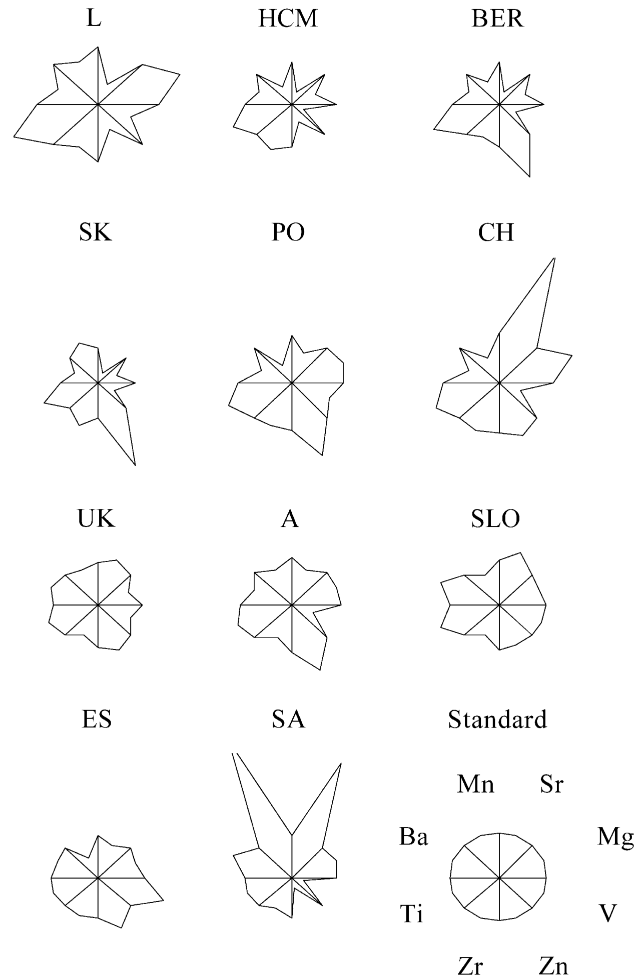

Fig. 3. Star plot of clinker averages from three Hungarian factories, marked by L, H and B, as well as averages of clinker samples coming from Slovakia (SK), Portugal (PO), Switzerland (CH), United Kingdom (UK), Austria (A), Slovenia (SLO), Spain (ES) and South Africa (SA).

by using Eq. (5), the area of the 16-sided polygon can be expressed as the sum of the area of the wings that should be equal to the sum of the trace element content (see Eq. (1)):

$$A = \sum_{i=1}^{8} \frac{2D_i r \sin(\pi/8)}{2} = r\sin(\pi/8) \sum_{i=1}^{8} D_i$$
$$= r^2 \sin(\pi/8) \sum_{i=1}^{8} x_i = \lambda \sum_{i=1}^{8} c_i \tag{7}$$

From Eq. (7), the radius can be expressed as

$$r = \sqrt{\frac{\lambda \sum_{i=1}^{8} c_i}{\sin(\pi/8) \sum_{i=1}^{8} x_i}} \tag{8}$$

3.4. Draw the wings of the star plot

The D_i distances expressed by Eqs. (5) and (8) are measured to the radii of the trace elements. From this point, two straight lines are drawn to the crossing of the radius of the trace element and the neighbouring two radii of the circle. Thus, quadrangles are obtained. For a clinker of "standard trace element content", this method results in a regular 16-sided polygon as shown in Fig. 2.

As the size of the plot is an important characteristic, it is safe to draw a star plot of "standard trace element content" within the figure, as figures are often magnified or scaled down during printing. As a clinker of standard trace element content forms a regular 16-sided polygon, of $r = 0.5715\sqrt{11.4\lambda}$ mm radius, based on its desired radius, the λ scaling factor (Eq. (9)) can be chosen as

$$\lambda = \left(\frac{r}{0.5715}\right)^2 / 11.4 \tag{9}$$

Two figures are shown for visualisation. In Fig. 3, star plots representing the trace element content of three Hungarian factories, marked by L, H and B, as well as averages of samples coming from Slovakia (SK), Portugal (PO), Switzerland (CH), United Kingdom (UK), Austria (A), Slovenia (SLO), Spain (ES) and South Africa (SA) are shown, together with three reference plots (Fig. 4) of a Hungarian clinker (code number 5L5), a Spanish one (code number 89ES1) and a South African one (code number

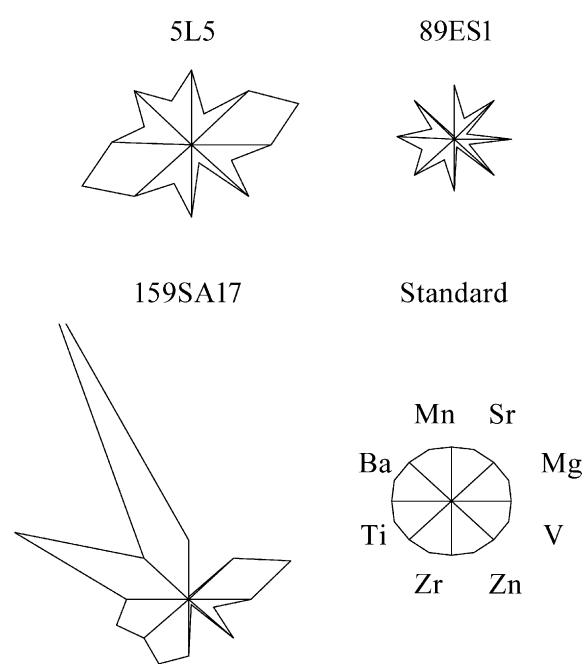

Fig. 4. Star plot of a Hungarian clinker (code number 5L5), a Spanish one (code number 89ES1) and a South African one (code number 159SA17).

Table 2
Trace element content of selected clinkers (averages of X samples), used for the construction of Figs. 3 and 4 (mg/kg)

Symbol	Ba	Mn	Sr	Ti	Zr	Mg	Zn	V	T	X
L	139	404	191	1485	39	12682	56	48	15045	7
H	145	222	149	1324	57	4964	31	46	6929	10
B	145	278	152	1574	43	5893	35	182	8313	11
SK	136	611	157	1517	64	4703	46	288	7483	7
PO	124	203	340	1292	49	9871	83	163	12124	24
CH	120	260	1364	1250	51	13172	45	115	16375	7
UK	222	462	575	1164	40	6774	78	117	9431	8
A	153	408	410	1104	36	8724	46	147	11027	10
SLO	264	380	645	1329	36	8408	97	101	11258	6
ES	192	254	410	1067	50	7981	155	135	10243	53
SA	266	1761	1456	1041	40	9657	29	26	14278	23
5L5	124	318	215	1476	30	12721	55	27	14966	1
89ES1	84	26	206	621	23	2278	28	17	3283	1
159SA17	604	2933	19	1242	63	15838	13	44	20756	1

159SA17) (of medium, low and high trace element content). Analysis data are given in Table 2.

A computer program has been written for the construction of the star plots (in MATLAB). It can be downloaded from www.fmt.vein.hu/softcomp.

4. Conclusions

The trace element content of clinkers (and possibly of cements) can be used for the qualitative identification (i.e. manufacturing works). For this purpose, several hundred clinker sorts of all Hungarian factories, as well as samples coming from eight foreign countries have been analysed to determine their Ba, Mn, Sr, Mg, Ti, Zr, Zn and V content. The first six elements come from the main raw materials and are of dactylogrammatic value, while the last two elements mainly come from fuel (used tires, heavy fuel oil, etc.) and cannot be used for identification. Based on the analyses, the averages and standard deviations of these trace elements were calculated: Zr is present in the lowest concentrations, and Mg in the highest concentrations; while Zr has the lowest variability, and Mg, followed by Mn, has the highest variability. Using rounded averages, the "standard trace element content" of clinkers was determined.

To facilitate the visualisation of the trace element content, a graphical method (star plotting) is presented where every clinker is compared to the proposed standard. In this "star plot", the area of the star is proportional to the gross amount of the considered trace element, and the eight "rays" of the star to the eight elements themselves. A detailed description helps the construction of star plots; still easier, a program has been constructed, which can be downloaded from the Internet.

Acknowledgments

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