

CHEMOMETRIC STUDY OF THE SINTER MIXTURES USED IN SINTER PLANTS IN POLAND

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Preliminary Note – Prethodno priopćenje

The main goal of the study was the analysis of chemical parameters of sinter mixtures used in sinter plants in Poland. For this purpose the chemometric method was used, in this case hierarchical clustering analysis. This method allowed to examine the similarities and differences between the studied sinter mixtures.

Key words: iron ore sintering process, chemical composition, hierarchical clustering analysis, Poland

INTRODUCTION

Preparation of the sinter mixture is the first stage of the iron ore sintering process [1]. In this paper chemometric method was used to examine the similarities and differences between the studied sinter mixtures. Hierarchical clustering analysis (HCA) was used to investigate 30 chemical parameters in the sinter mixtures. HCA can be applied to multidimensional data sets, in order to study similarities, dissimilarities of objects in the variables space, or variables in the objects space. Detailed description of the HCA and their applications were presented by Vogt et al. [2], Kaufman and Rousseeuw [3], Romesburg [4], Ward [5] and Massart and Kaufman [6].

Any agglomerative hierarchical clustering method is characterized by:

- the similarity measure used, and
- the way the resulting sub-clusters are merged (linked).

For continuous variables, popular similarity measures are Euclidean or Manhattan distance. Among the linkage methods, the most popular ones are single linkage, often called the nearest neighbor, complete linkage, average linkage, centroid linkage and Ward linkage. A choice of a clustering method depends on the data studied and the particular purpose for application. Final results of HCA are presented in form of a dendrogram. On axis x of the dendrogram the indices of clustered objects (or variables) are displayed, whereas axis y represents the corresponding linkage distances (or an adequate measure of similarity) between the two objects or clusters, which are merged. The HCA can not be used in tracing the similarities between objects and measured parameters simultaneously. This problem may be, how-

ever; overcome by complementing the cluster analysis with a visual display of studied data sets (sorted in the objects and parameters direction from the dendrograms), which enables direct interpretation of clustering in terms of original variables [7].

MATERIALS AND METHODS

The raw materials used in this study were obtained from integrated steelworks in Poland, 30 chemical parameters of the raw materials were analysed in the accredited Laboratory of Solid Waste Analysis of the Central Mining Institute. The composition of the sinter mixtures (S1 - S7) used in the study was presented in Table 1.

The studied data was organized in the matrix $\mathbf{X}(7 \times 30)$, which rows represent 7 different sinter mixtures (S1-S7), whereas the columns represent measured parameters (Table 2).

Table 1 **Composition of the studied sinter mixtures / wt. %**

Raw materials	S1	S2	S3	S4	S5	S6	S7
Hematite	31,12	15,74	0,00	0,00	30,91	15,63	0,00
Magnetite 1	24,78	33,44	42,32	39,35	24,62	33,20	41,99
Magnetite 2	24,86	33,54	42,47	39,49	24,69	33,31	42,14
Mill scale	0,00	0,00	0,00	7,66	0,00	0,00	0,00
Burnt lime	2,96	3,00	3,04	3,11	2,95	2,98	3,01
Dolomite	1,22	1,24	1,25	1,27	1,21	1,23	1,24
Lime stone	10,69	8,69	6,63	4,85	10,90	8,90	6,85
Coke breeze	4,37	4,35	4,29	4,27	4,25	3,80	3,34
Anthracite	0,00	0,00	0,00	0,00	0,47	0,95	1,43

The studied data set is standardized according to the formula:

$$x_{ij} = \frac{(x_{ij} - \bar{x}_j)}{s_j}$$

where \bar{x}_j , s_j denote the mean of the j-th column and its standard deviation, respectively:

$$\bar{x}_j = \frac{1}{m} \sum_{i=1}^m x_{ij}$$

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Table 2 Chemical parameters measured in the studied sinter mixtures

No	Parameter	Unit
1	C	kg/Mg
2	S	kg/Mg
3	Cl	kg/Mg
4	Al	kg/Mg
5	Fe	kg/Mg
6	Ca	kg/Mg
7	Mg	kg/Mg
8	Na	kg/Mg
9	K	kg/Mg
10	Ti	kg/Mg
11	P	kg/Mg
12	Ag	mg/Mg
13	As	mg/Mg
14	Ba	mg/Mg
15	Br	mg/Mg
16	Cd	mg/Mg
17	Co	mg/Mg
18	Cr	mg/Mg
19	Cu	mg/Mg
20	Hg	mg/Mg
21	Mn	mg/Mg
22	Mo	mg/Mg
23	Ni	mg/Mg
24	Pb	mg/Mg
25	Rb	mg/Mg
26	Sb	mg/Mg
27	Sn	mg/Mg
28	Sr	mg/Mg
29	V	mg/Mg
30	Zn	mg/Mg

$$s_{ij} = \sqrt{\frac{1}{m} \sum_{i=1}^m (x_{ij} - x_{ij})^2}$$

where m denotes number of objects (examined sinter mixtures). The chemometric analyses were carried out using Matlab software version 6,0 [8] and authors' written routines.

RESULTS AND DISCUSSION

The HCA was used to explore the studied data set X (7 x 30) and to examine the similarities between the studied sinter mixes. HCA helped to reveal the internal data structure and thereof its clustering tendency.

The HCA results presented in Figure 1 were based on the Euclidean distance and the Ward linkage algorithm.

The dendrogram presented in Figure 1a allows revealing two clusters: cluster A grouping sinter mixtures S1, S2, S5 and S6 (objects nos 1, 2, 5 and 6), cluster B, composed of sinter mixtures S3 and S7 (objects nos 3 and 7); and one non-clustered sinter mixture S4 (object no. 4). In the cluster A additional sub-clusters can be distinguished. Sub-cluster A1 groups sinter mixtures S1 and S5 (objects nos 1 and 5) whereas sub-cluster A2 is composed of sinter mixtures S2 and S6 (objects nos 2 and 6, respectively).

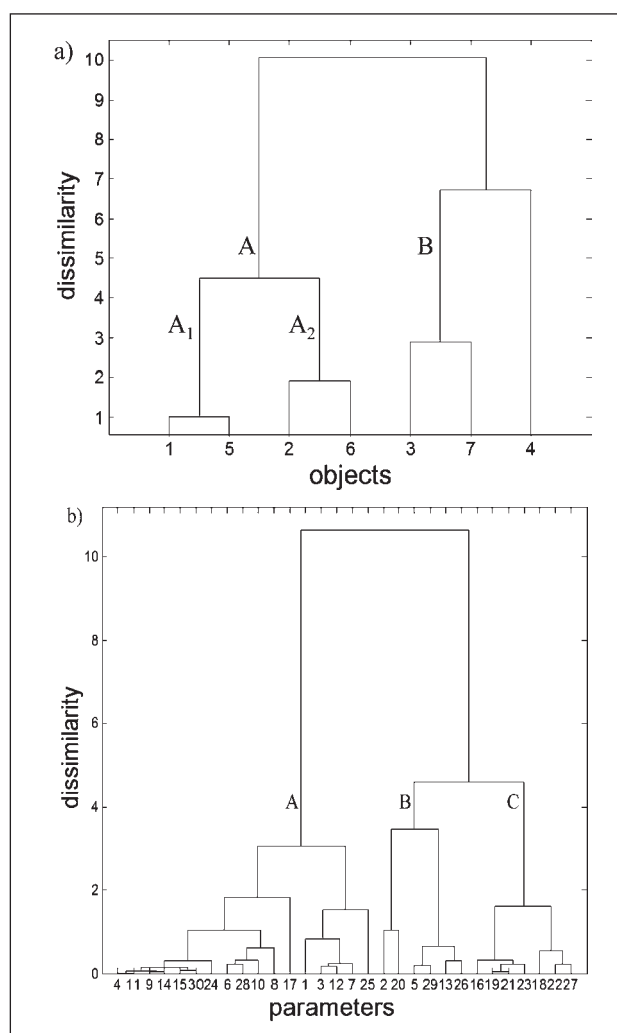


Figure 1 The dendrograms of (a) studied sinter mixtures (objects) in the space of the 30 studied parameters (listed in Table 2) and (b) the studied parameters in the space of 7 objects by the Ward linkage method using Euclidean distance as the similarity measure.

The analysis of the dendrogram of 7 sinter mixtures in the space of the 30 chemical parameters sorted according to the Ward linkage method with the data color map allowed more in-depth investigation of the resulting clustering tree (Figure 2).

The dendrogram constructed for the studied chemical parameters in the space of 7 objects (see Figure 1b) revealed three main groups:

- group A, including parameters nos 1, 3, 4, 6-12, 14, 15, 17, 24, 25, 30 (C, Cl, Al, Ca, Mg, Na, K, Ti, P, Ag, Ba, Br, Co, Pb, Rb and Zn, respectively),
- group B, composed of parameters nos 2, 5, 13, 20, 26 and 29 (S, Fe, As, Hg, Sb and V, respectively), and
- group C, collecting parameters nos 16, 18, 19, 21-23 and 27 (Cd, Cr, Cu, Mn, Mo, Ni and Sn, respectively).

The dendrogram showed in Figure 1a presents the data structure, but does not allow investigating the observed patterns in terms of the chemical parameters. To solve this problem HCA could be complemented with a color map of experimental data sorted according to the

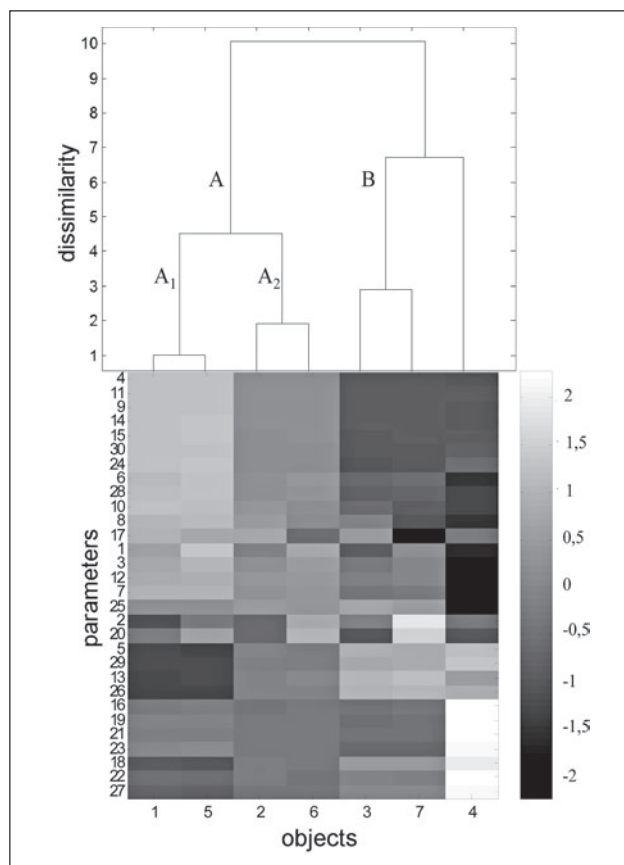


Figure 2 The dendrogram of 7 studied sinter mixture (objects) in the space of the 30 parameters with a color map of the studied data sorted according to the Ward linkage method

specific order of objects (studied sinter mixtures) and parameters adopted from the above described dendrograms.

The compounds of cluster A (objects nos 6, 15, 16, 19, 20 and 29) were characterized by higher C, Cl, Al, Ca, Mg, Na, K, Ti, P, Ag, Ba, Br, Pb and Zn contents (parameters nos 1, 3, 4, 6-12, 14, 15, 24 and 30) and relatively low Fe, As, Cr, Mo, Rb and Sb contents (parameters nos 5, 13, 18, 22, 25 and 26) in comparison with the respective values for the remaining sinter mixtures.

Furthermore, the sinter mixtures S1 and S5 (objects nos 1 and 5) collected in sub-cluster A1 were characterized by the highest C, Cl, Al, Ca, Mg, Na, K, Ti, P, Ag, Ba, Br, Pb and Zn contents (parameters nos 1, 3, 4, 6-12, 14, 15, 24 and 30) and the lowest Fe, As, Cr, Mo, Rb and Sb contents (parameters nos 5, 13, 18, 22, 25 and 26) among all tested sinter mixtures.

Moreover the sinter mixtures S1 and S5 were uniqueness due to the lowest S content (parameter no. 2) and the highest C content (parameter no. 1) among all tested sinter mixtures. The sinter mixture S6 (object no.6) in sub-cluster A2 was uniqueness due to the highest S and Hg contents (parameters nos 2 and 20) among all the tested compounds in cluster A.

Cluster B contains sinter mixtures S3 and S7 characterized by a low values of parameters nos 4, 6, 9, 10, 11, 14-16, 19, 21, 23, 24, 28 and 30 (corresponding to content of Al, Ca, K, Ti, P, Ba, Br, Cd, Cu, Mn, Ni, Pb, Sr

and Zn), high Fe, Cr, Mo, Sn, and V contents (parameters nos 5, 18, 22, 27 and 29) and the highest As and Sb contents (parameters nos 13 and 26) in the studied sinter mixtures. Additionally the sinter mixture S7 was uniqueness due to the lowest Co content (parameter no. 17) and the highest S and Hg contents (parameters nos 2 and 20) among all tested sinter mixtures.

The uniqueness of sinter mixture S4 was observed due to the lowest C, Cl, Ca, Mg, Na, Ti, Ag, Rb, and Sr (parameters nos 1, 3, 6, 7, 8, 10, 12, 25 and 28) and the highest Fe, Cd, Cr, Cu, Mn, Mo, Ni, Sn and V contents (parameters nos 5, 16, 18, 19, 21, 22, 23, 27 and 29), among all tested sinter mixtures.

CONCLUSIONS

The sinter mixture S1, S2, S5 and S6 were characterized by higher C, Cl, Al, Ca, Mg, Na, K, Ti, P, Ag, Ba, Br, Pb and Zn contents and relatively low Fe, As, Cr, Mo, Rb and Sb contents then the remaining sinter mixtures.

The sinter mixtures S1 and S5 were characterized by the highest C, Cl, Al, Ca, Mg, Na, K, Ti, P, Ag, Ba, Br, Pb and Zn contents and the lowest Fe, As, Cr, Mo, Rb and Sb contents among all tested sinter mixtures.

The sinter mixtures S1 and S5 had the lowest S content and the highest C content. The sinter mixtures S3 and S7 characterized by a low values of Al, Ca, K, Ti, P, Ba, Br, Cd, Cu, Mn, Ni, Pb, Sr and Zn), high Fe, Cr, Mo, Sn, and V contents and the highest As and Sb contents in the studied sinter mixtures.

The sinter mixture S7 had the lowest Co content and the highest S and Hg contents. The sinter mixture S4 had the lowest C, Cl, Ca, Mg, Na, Ti, Ag, Rb, and Sr and the highest Fe, Cd, Cr, Cu, Mn, Mo, Ni, Sn and V contents.

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Note: I. Golczyk is Responsible for English language, Katowice, Poland