УДК 550.428:553.93

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# DEFINITE OECULIARITIES OF TOXIC AND POTENTIALLY TOXIC ELEMENTS DISTRIBUTION IN COAL SEAMS OF PAVLOGRAD-PETROPAVLOVKA REGION

Викладені методики та результати визначення складу геохімічних та парагенетичних асоціацій токсичних елементів в основних робочих пластах Павлоград-Петропавлівського району Західного Донбасу, факторного та кластерного аналізу їх вмістів.

Изложены методики и результаты определения состава геохимических и парагенетических ассоциаций токсичных элементов в основных рабочих угольных пластах Павлоград-Петропавловского района Западного Донбасса, факторного и кластерного анализа их содержаний.

Procedures and results to determine composition of toxic element geochemical and paragenetic assemblages within mother working coal seams of Pavlograd-Petropavlovka district in Western Donbass as well as their factor and cluster analysis are represented.

Strengthening of requirements for environmental protection gives rise to innovative new scientifically grounded forecasting techniques concerning toxic elements in rock mass and waste rock and coal.

To assess effect of coal-mining industry and energy enterprises on ecological situation while planning measures aimed at its improvement, it is required to have information on distribution nature and level of toxic element concentration in coal and enclosing rocks extracted. To obtain such information, SHEI "National Mining University" performed detailed study involving the most promising region in Western Donbass – Pavlograd-Petropavlovka geological and industrial region. Classification of coal seams according to toxic elements content; connection between them and "small" elements; indication of the elements connection with organic and mineral part of coal; composition of their geochemical and paragenetic assemblages were basic problems while studying geochemistry toxic elements in mother working coal seams.

To solve the problems, there were used results of spectrum analysis of 76 coal combined samples from drill-hole and mine workings of current mines. Comparison of toxic elements content with clark values and MAC was performed with the help of $C_к$ and $C_т$ coefficients calculated by:

$$C_к = TEC / CTE,$$

where $C_к$ is aspect ratio to clark content, TEC is toxic element content, and CTE is clark content of toxic element;

$$C_т = CTE / MAC,$$

where $C_т$ is aspect ratio to MAC (maximum admissible concentration of the element in coal).

While assessing connection of toxic elements with organic or mineral part of coal, coefficient of consanguinity with organic matter $F_o$ was used; it demonstrates ratio of element content in coal having small density (< 1.6) and big density (> 1.7); coefficients of reduced concentration $F_{пк}$ demonstrating ratio of element content in $i(C_i)$ fracture to their content in initial coal; correlation coefficients of considered elements and coal ash-content; and coefficients of reduced element extraction in different density fraction. Analysis of the results makes it possible to determine following series of considered elements consanguinity with organic part of coal:

Be, Co, Cr, Pb, F, As, V, Ni, Hg, Mn

Classification of geochemical assemblages for toxic and potentially toxic elements was performed on the basis of calculations and analysis of linear- and gamma-correlation coefficients, and Spearman-Kendal correlation. The assemblage covered elements between which more than 50 % of correlation coefficients were no less than 0.5. Such an approach considers geochemical assemblage as a set of elements united either by general or competitive process or concentration types.

As assemblage involves Cr and V with positive correlation, and Be with negative one. “Small” elements are represented by Mo, Cu, Ag and Ti with positive correlation, and Bi and Ce with negative one.

Be has negative correlation with As, Cr and Hg; as for the “small” elements, Bi and Ce have positive correlation, and Cu and Mo have negative one.

**Hg assemblage is Be with negative correlation, and “small” Sr and La elements with positive correlation, and Ce with negative one.**

As and Mn are assemblage with F; they are characterized with it by positive correlation; as for the “small” elements, there is Nb with positive correlation as well as Sn and Sr with negative one.

Co, Ni and F with positive correlation are in Mn assemblage. Such “small” elements as Sc, Y, Mo and Yb having positive correlation are in the assemblage.

Co Pb can not associate any toxic elements; only Nb of “small” ones has positive correlation.

**Ni assemblage consists only of positive correlation with potentially toxic Co and Mn, and of such “small” elements as Sc, Ti and Yb.**

As and Cr have positive correlation with V as well as such “small” elements as Mo, Ti, Cu, Y, Ag, and Zn; Bi has negative correlation.

Cr assemblage consists of As and V with positive correlation, and Be with negative one. “Small” elements are represented by Cu and Mo with positive correlation and Bi with negative one.

Ni and Mn are positively connected with Co; “small” elements are represented by Ba and Ti.

The authors suppose that determination of toxic element paragenetic assemblages is another important problem. Factorial analysis was applied; its approach and results are described below. It should be noted that factorial analysis results used to determine composition of chemical element paragenetic assemblage means a set of elements having either common or competitive aggregation reason.

First, factorial analysis makes it possible to obtain minimum of new variables being linear aggregate of initial ones; moreover, the variables will cover prescribed amount of information from initial variables. Second, analysis of interrelations between new variables and initial ones enables to identify consanguinities interpreting them in geological view.

The paper applies one of the types of factorial analysis – R-variant of method of principal components in determinant alternative when object selection is studied and no conclusions are drawn concerning general totality objects.

In this case, according to [1], following solution algorithm is assigned.

Matrix of initial variables $X^{N*p}$ (where N is the number of rows (coal seams are objects); p is the number of columns of initial variables being toxic and potentially toxic elements) was carried out to $Y^{N*p}$ matrix data in the form of variations. Previously, matrix $X^{N*p}$ columns were standardized to reduce initial variables to [0 – 1] interval and transition to nondimensional values. The procedure is essential as variables describing objects can be measured variously; in this case factorial analysis is incorrect.

Covariance matrix $S^{p*p}$ was determined as dispersions of variables are within its diagonal.

There were calculated proper numbers $\lambda_i$ of $S^{p*p}$ matrix as well as proper vectors $U_i$ corresponding to proper numbers.

There was also determined k number of principal components (required number of components specifying basic share of initial variables dispersion). To do that value P of the following expression was used:

$$P = (\sum_{i=1}^{k} \lambda i / trS) * 100\% ,$$

where $trS$ is a track of $S^{p*p}$ matrix (total of elements within principal diagonal).

Point out that it is convenient to calculate per vent of contribution to P dispersion for successive values k=1, 2, 3… ceasing the process for such a k when the per cent meet the researcher demands (e.g., if P is more than 75, 90 or 95%).

k of minimal proper numbers $\lambda_i$ were shown in the form of $\lambda_i^{k*k}$ matrix which diagonal elements were proper numbers of covariance matrix $S^{p*p}$. Proper vectors, corresponding to k of minimal proper numbers were represented in the form of $U_k$ matrix (in our situation, it is load matrix $A=U_k$).

$F^{n*k}$ matrix of basic component values was determined (Table 1):

$$F=Y*A.$$

Table 1

Values of basic components interpreting no less than 95% of dispersion of toxic and potentially toxic elements within basic working seams of Western Donbass

| Seams | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $c_{11}$ | -0.266 | 0.264 | 0.483 | 0.018 | -0.016 |
| $c_{10}^{B}$ | -0.428 | 0.105 | 0.114 | 0.024 | -0.435 |
| $c_9$ | 0.768 | -0.19 | -0.45 | 0.247 | -0.203 |
| $c_8^{B}$ | 0.506 | 0.281 | -0.031 | -0.482 | -0.295 |
| $c_8^{H}$ | -0.489 | -0.207 | -0.123 | 0.082 | 0.215 |
| $c_7^{B}$ | 0.695 | -1.301 | 0.485 | 0.006 | 0.049 |
| $c_7^{H}$ | -0.646 | -0.166 | -0.054 | 0.256 | 0.282 |
| $c_6^{1}$ | 0.897 | 0.487 | 0.408 | 0.439 | 0.188 |
| $c_6$ | 0.472 | 0.794 | 0.582 | -0.272 | 0.26 |
| $c_5$ | -0.689 | 0.016 | 0.098 | 0.257 | -0.173 |
| $c_4$ | -0.364 | -0.254 | -0.55 | -0.807 | 0.158 |
| $c_1$ | -0.454 | 0.171 | -0.144 | 0.202 | 0.03 |

$C^{p*k}$ matrix of correlation coefficients between initial variables and basic components was determined (Table 2). The matrix helps to draw conclusions on degree of connection between new variables with initial ones, i.e. basic components were interpreted.

Alternately: $F \cong X * U_k * \lambda_k^{-1/2}$.

Data inTable 1 explain that distribution of toxic and potentially toxic elements within coal seams can be very accurately described with the help of 5 new variables characterizing different reasons of their concentration (no less than 95% of initial data dispersion. Analysis of Pavlograd-Petropavlovka mining and industrial district geology and history as well as correlation with estimated values of basic components makes it possible to formulate following conclusions:

1. Values of each basic component are characterized by repeatability in a structure section; the repeatability reflects general periodicity of coal-bearing rock mass formation conditions.
2. Maximums of component 1 correspond to central part of coal formation area; their minimums correspond to beginning.
3. Maximums of component 2 correspond to maximum dispersion of coal accumulation mode as well as maximum of coal sulfur-content.
4. Maximums of component 3 register periods of basal complex maximum tectonism and fracture formation.
5. Maximums of component 4 reflect maximum stability of coal accumulation and stability of coal seam formation.
6. Maximums of component 5 correspond to the most favourable regional coal accumulation environment.

Table 2

Correlation values between toxic elements content and basic components

| Elements | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| As | 0.88 | -0.02 | -0.09 | 0.06 | -0.12 |
| Hg | 0.27 | 0.34 | 0.71 | -0.34 | -0.03 |
| Be | -0.71 | -0.31 | -0.26 | 0.03 | -0.34 |
| F | 0.54 | -0.53 | -0.21 | -0.49 | -0.24 |
| Mn | 0.34 | -0.64 | 0.51 | 0.0004 | -0.11 |
| Pb | -0.18 | -0.68 | -0.08 | -0.4 | 0.39 |
| Ni | -0.31 | -0.68 | 0.33 | 0.37 | -0.02 |
| V | 0.71 | 0.36 | -0.15 | 0.32 | 0.2 |
| Cr | 0.75 | 0.19 | -0.14 | 0.35 | -0.03 |
| Co | -0.05 | -0.67 | 0.41 | 0.35 | -0.14 |

Data in Table 2 explain polygenic and dispersive nature of toxic and potentially toxic elements accumulation in mother working coal seams of Pavlograd-Petropavlovka district. Analysis of the results helps forming following conclusions:

1. Period and stability of coal accumulation processes reflecting in seam thickness and continuity play important role for F concentrations.

2. Variability of coal accumulation mode and plant remains carbonification results in Pb-Ni-Co-Mn-F paragenetic assemblage formation. Maximums of the elements are typical for coal seams with low ash-content and sulfur content.

3. Tectonic activation of basal complex as well as fracture formation in coal-bearing rock mass results in Hg-Mn geochemical assemblage formation.

4. Coal formation zone shaping is followed by initiation As-Be-Cr-V-F paragenetic assemblage; moreover, accumulation of Be mainly takes place at the initial stage of the area formation, and As, Cr, V and F – at the principal stage.

5. Regional conditions of coal accumulation poorly influence on variability of assemblage composition and content of toxic and potentially toxic elements in coal of Pavlograd-Petropavlovka district. Their maximum influence falls to Be and Pb concentrations.

To classify mother working coal seams of Pavlograd-Petropavlovka district as for toxic and potentially toxic element content, we performed cluster analysis within basic components. Iterated division method of k-mean was applied. Seams were considered as five-dimension points of Euclidean space (depending upon the number of basic components). Following clusterization algorithm was adopted:

1. Authors specify the number of clusters determining their gravity centers;
2. Points are shifted into the nearest cluster;
3. Gravity centers of new clusters are determined;
4. Points 2 and 3 are repeated until stable cluster configuration is identified;
5. New cluster number is preset, and points 2-4 are repeated.

Thus, the procedure was applied for 2, 3, 4, 5, 6, 7, 8, 9, and 10 cluster numbers. Fig. 1 demonstrates the clusterization result in the form of classification dendritogram.

While dividing into two clusters, one of them includes seams with negative values of component 1 and the other includes those with positive ones. Dividing into three clusters cannot vary composition of the first one leading to cluster of $C_7^в$ seam separating into independent. It is unique as for toxic and potentially toxic element content as maximum average F, Mn, Ni, V, Co content is typical for it as well as almost maximum concentrations of Hg, Pb, and Cr. Four-cluster division results in independent $C_4$ seam separation from cluster 1. Its distinctive feature is maximum average concentration of Pb, almost maximum content of Be and F, and negative values of four basic components; moreover value of the fourth one is minimum to compare with the whole group of considered seams.

Scientific importance of the determined consanguinity set of toxic and potentially toxic elements with coal organic substance, and their geochemical and paragenetic assemblages is the possibility to make their quantitative estimation from the viewpoint of genetics. Practical importance is in the representation of methodology to forecast toxic and potentially toxic elements in coal seams, rock mass, products and coal processing waste on the basis of component and cluster analysis.

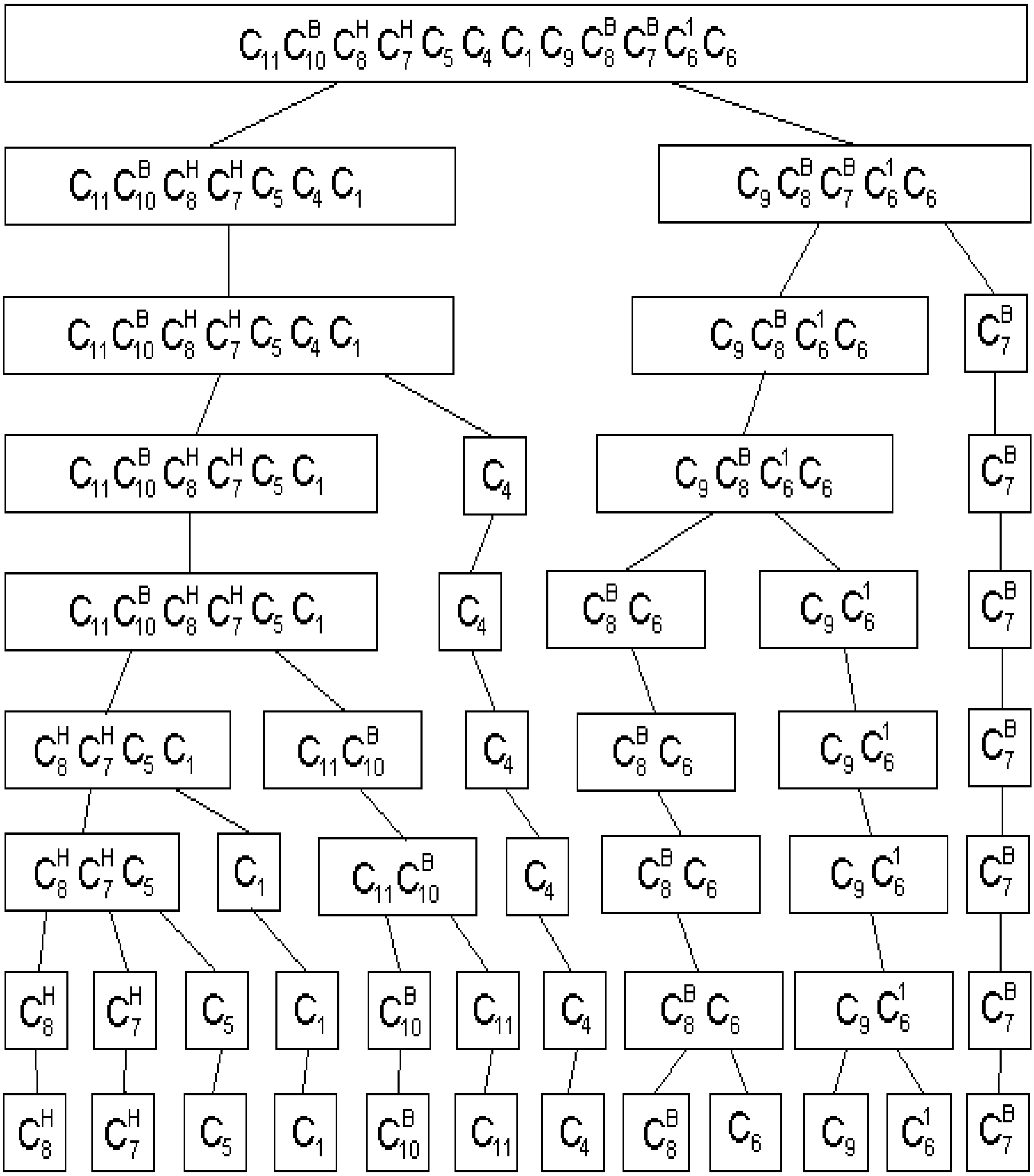


Fig. 1. Classification dendritogram of mother working coal seams of Pavlograd-Petropavlovka district

References


1. Йереског К.Г., Клован Д.И., Реймет Р.А. Геологический факторный анализ: Пер. с англ. – Л.: Недра, 1980. – 223 с.



*Рекомендовано до публікації д.г-м.н. Нагорним Ю.М.*

*Надійшла до редакції 19.11.13*