RELAȚII SUPRAFAȚĂ SPECIFICĂ – UNIFORMITATE GRANULOMETRICĂ LA MATERIALELE PULVERULENTE DISPERSE
RELATIONSHIPS BETWEEN SPECIFIC SURFACE AREA AND PARTICLE SIZE UNIFORMITY FOR DISPERSE POWDERED MATERIALS

DOREL RADU, ZENO GHIZDĂVEȚ*
Universitatea POLITEHNICA Bucureşti, Str. G. Polizu nr. 1, sector 1, 011061, Bucureşti, România

A comprehensive characterization of the particle size of polygranular powders can be done by:
- selecting the parameters to be used in the design, optimization and process control of various technological processes;
- establishing correlations between the properties of the mixtures and their particle size features.
One of the parameters to characterize powder mixtures is the particle size uniformity degree. For its evaluation, this paper gives two new indicators calculated by some factors coming from information theory: Shannon entropy - H - and Onicescu's informational energy – E. Particle size uniformity calculated by these indicators (that are applicable to any granular materials) controls the specific surface area of the powder mixtures.
As applications, a series of quantitative relationships between the specific surface area of some Portland cements and their particle size uniformity were extracted. The results are characterized by a very good correlation for both several foreign cements as well as a set of local cements.

Caracterizarea granulometrică a amestecurilor poligranulare rezidă în:
- stabilirea unor mărimi cu care apoi să se opereze în proiectarea şi conducerea diverselor procese tehnologice;
- stabilirea unor corelații între proprietățile amestecurilor şi caracteristicile lor granulometrice.
Printre mărimile care caracterizează amestecurile pulverulente se numără şi gradul de uniformitate granulometrică. Pentru evaluarea acestuia, în lucrare se propun doi indicatori noi calculați pe baza unor mărimi provenind din domeniul statisticii informaționale: entropia Shannon – H – şi energia informațională Onicescu - E. Uniformitatea granulometrică calculată pe baza acestor indicatori (naturali şi general valabili) determină în mod important suprafața specifică a amestecurilor pulverulente.
Pentru exemplificare, în lucrare se prezintă o serie de dependențe cantitative între suprafața specifică a unor cimenturi Portland şi uniformitatea lor granulometrică. A rezultat o foarte bună corelație, atât pentru o serie de cimenturi străine, cât şi pentru un set de cimenturi autohtone.

Keywords: *informational energy, informational entropy, degree of uniformity, cement specific surface.*

1. Introduction

Nowadays almost all industries are processing powders or granular mixtures. Among them, an important place is taken by the cement industry, and this has at least two reasons:

- in the cement industry, the dry process (which is almost universal) involves processing of granular or powder mixtures practically on the whole production workflow, whether as raw materials, as semi-finished materials (clinker and various additives) or as the final product – cement;

- the processed disperse mixtures are really important, as quantities. The average, absolute output of an ordinary production line can be found, currently, in the range of 2000-5000t cement/24h. To attain these values, an amount of raw materials about 70% higher is necessary. This leads to processing - on a single technological line – of millions of tons of polygranular mixtures per year.

In addition, in order to obtain a cement clinker with given properties, among other technological requirements, the powder mixture of raw materials as well as the final product - cement - must provide a high degree of chemical homogeneity and an optimal particle size uniformity degree.

In order to characterize a polydispersed mixture, various particle-size distribution functions (semi-) empirical are used. Based on them, there were established several statistical indicators which are used on a case-by-case basis for assessing particle size uniformity degree of the powder (σ, λ *etc.*) corresponding to different types of distributions (normal, Laplace etc.).

This paper gives an attempt to use some indicators derived from information theory (informational entropy and energy) as parameters generally available to evaluate the particle size uniformity degree, regardless of the type of the associated particle size distribution.

There are also made applications on various foreign and local cements, with direct reference to correlation between the specific surface area and the degree of uniformity, accounted by the

* Autor corespondent/*Corresponding author,*
E-mail: zeno.ghizdavet@upb.ro

informational entropy and energy of the analyzed particle-size systems.

2. Theoretical basis

The particles that make up a polygranular mixture present, in most cases, irregular shapes with a lower degree of uniformity.

The size of the actual particles with irregular shapes is evaluated by a dimension defined in a conventional manner, most often depending on the determination method.

On the whole polygranular mixture, all particles that have diameters *x* between two imposed limits, make a particle size range *i*, whose gravimetric weight is given by the particle-size function *f(x)*. Taken as a whole and statistically processed, based on experimental data, this leads to the formulation of some particle-size distribution laws. These represent the density distribution; the corresponding Equations can be written in two cases:

- the discrete distribution of particle size:

$$\sum_{i=1}^{N} f_i = 1, 0 \leq f_i \leq 1, i = \overline{1..N} \quad (1)$$

- the continuous distribution of *f(x)*:

$$\int_{R^+} f(x)dx = 1,\ f(x) \geq 0 \quad (2)$$

Given the integral distribution law, *F(x)*, the differential, *f(x)*, $f(x) = \frac{dF(x)}{dx}$, is needed to compute statistical diameters with applications in technical calculations. It is the case of the average diameter $\bar{x}$, x_{50} – the sieve size corresponding to 50% passing. Parameters such as x', x_{80}, x_{20} can be calculated (x' represents the size at 36,8% of particles retained), being also useful in the cement industry (as well as other indicators) [1, 2] .

A general equation for calculating the average diameter for a discontinuous distribution may be written as:

$$\bar{x} = \left(\frac{\sum_{i=1}^{n} f_i \cdot x_i^p}{\sum_{i=1}^{n} f_i \cdot x_i^q}\right)^{\frac{1}{p-q}} \text{ [μm]},\ p,\ q \in N,\ p > q \quad (3)$$

where f_i is the relative frequency of different particle size classes with a diameter x_i, μm;

n – the number of particle size classes;

p, q – specific coefficients to the various types of distribution functions.

The average diameter for a continuous particle size distribution is computed by the Equation:

$$\bar{x} = \int_{x_{min}}^{x_{max}} x \cdot f(x)\, dx\ [\mu m] \quad (4)$$

Where x_{min} and x_{max} represent the extreme values of the diameter *x*, μm.

Another parameter of interest for a polygranular mixture is the particle size uniformity degree. Its determination is useful to control a series of processes and to design equipment and devices where complex physico-chemical and/or thermal transfer processes occur. In terms of assessing the degree of uniformity, in size distribution laws one should obtain different, specific coefficients.

For various types of distribution functions, one could identify some drawbacks that may be associated with the quantification of the particle size uniformity degree. These are:

- the particle size uniformity assessment is done differently, depending on the type of distribution function;
- the coefficients by which the uniformity can be compared have different values in the case of statistical models for mixtures with multimodal distribution functions;
- the uniformity coefficients for different distribution functions cannot be compared;
- in essence, all these coefficients, determined by statistical modeling of some experimental results are empirical and have limited applicability, either in relation to specific materials or in relation to certain range of values for the particle diameters of the powder.

All these shortcomings, and also some others, can be removed by using a range of indicators derived from information theory: informational entropy, *H*, as defined by Shannon [3] and informational energy, *E*, as defined by Onicescu [4].

In this approach, a system consisting of a population having *N* features, each of these features existing at a certain weight (frequency of occurrence) has a specific structure. The characterization of this structure is made with the indicators *H* and *E* that define the degree of order/disorder, certainty/uncertainty, and uniformity/non-uniformity.

The equations for different forms of statistical indicators *H* and *E* are given in Table 1.

In particular, a polygranular material is a system composed of several entities. These are represented by the constituents' particle size classes. Size fractions, f_i, associated to the particle size classes are equivalent to the frequency (probability) of occurrence of the entity *i* from the classic definition of a system.

Considering a polygranular material composed of *n* size fractions, it can be inferred that its particle size uniformity degree, *U*, is equivalent to one of the parameters of statistical information, *H* or *E*, which, basically, gauges the order/disorder degree of a system.

Table 2 shows how to define and compute the degree of uniformity characteristic to a polygranular mixture, in relation to U_H and U_E indicators.

If the material is characterized by very different values of the particle size classes, it becomes more inhomogeneous though having a lower degree of uniformity (lower values for U_E). In this case, the informational entropy has higher values. Obviously, an Equation for the assessment of the particle size uniformity degree based on the informational entropy can be defined [5].

Both U_H and U_E are fundamental statistical

Table 1

Equations for computing some of information theory indicators
Definirea unor indicatori de statistică informațională

	Informational Entropy, Shannon, *H* [3] *Entropia informațională Shannon, H [3]*	Informational Energy, Onicescu, *E* [4] *Entropia informaționala Onicescu, E [4]*
1	For discrete random variables / *Forma pentru variabilele aleatoare discrete*	
	$H = -\sum_{i=1}^{n} p_i \cdot log p_i$	$E = \sum_{i=1}^{n} p_i^2$
	Conditions: $0 \le p_i \le 1, i = \overline{1,n}, \sum_{i=1}^{n} p_i = 1$, *n* – number of events (states) of the system, p_i – the probability that the system is in state / *Condiții:* $0 \le p_i \le 1, i = \overline{1,n}, \sum_{i=1}^{n} p_i = 1$, *n – numărul de evenimente (stări) ale sistemului,* p_i *- probabilitatea ca sistemul să fie în starea i.*	
2	For continuous random variables, *X / Forma pentru variabilele aleatoare continue, X*	
	$H(X) = \int_{R^+} p(X) \cdot log\, p(X) dX$	$E(X) = \int_{R^+} p^2(X) dX$
	Conditions: $p(X) \ge 0$ is a distribution density, so $\int_{R^+} p(X)dX = 1$ / *Condiții:* $p(X) \ge 0$ *este o densitate de repartiție, deci* $\int_{R^+} p(X)dX = 1$	

Table 2

Defining particle size uniformity, *U*, based on some information theory parameters
Definirea unor mărimi de evaluare a uniformității granulometrice, U, pe baza unor indicatori de statistică informațională

	U_H index from the informational entropy, *H* *Indicele* U_H *provenind din entropia informațională, H*	U_E index from the informational energy, *E* *Indicele* U_E *provenind din energia informațională, E*
I.	For discrete random variables / *Forme pentru variabilele aleatoare discrete*	
I.1	$U_H = -\sum_{i=1}^{n} f_i \cdot log f_i$	$U_E = \sum_{i=1}^{n} f_i^2$
I.2	Conditions: $0 \le f_i \le 1, i = \overline{1,n}, \sum_{i=1}^{n} f_i = 1$, *n* – the number of particle size fractions f_i / *numărul de fracții granulometrice* f_i	
I.3	Possible limiting cases / *Cazuri limită posibile*	
	I	II
	$f_1 = f_2 = \cdots = f_{n-1} = 0, f_n = 1 \rightarrow U_H = 0$, uniform, ideal material (monogranular); / *material ideal uniform (monogranular);*	$f_1 = f_2 = \cdots = f_{n-1} = 0, f_n = 1 \rightarrow U_E = 1$, uniform ideal material (monogranular); / *material ideal uniform (monogranular);*
	$f_1 = f_2 = \cdots = f_n \rightarrow U_H = \log n$ polygranular material distributed idealy, non-uniform (idealy disordered);/ *material poligranular distribuit ideal neuniform (ideal dezordonat);*	$f_1 = f_2 = \cdots = f_n \rightarrow U_E = \frac{1}{n}$ polygranular material distributed idealy non-uniform;/ *material poligranular distribuit ideal neuniform*
	in all other cases/ *în toate celelalte cazuri* $0 < U_H < \log n$ polygranular material non-uniform distributed / *material poligranular neuniform distribuit*	in all other cases / *în toate celelalte cazuri* $0 < U_E < \frac{1}{n}$ polygranular material non-uniform distributed / *material poligranular neuniform distribuit*
I.4	Normalized values of the particle size uniformity indicators *Valori normate ale indicatorilor de uniformitate granulometrică*	
	$U_{H_n} = \frac{U_H}{\log n}$ $U_{H_n} \in [0,1]$	$U_{E_n} = \frac{n \cdot U_E - 1}{n - 1}$ $U_{E_n} \in [0,1]$
	$U_{H_n} = 0 \rightarrow$ ideal uniform material (monogranular); *material ideal uniform (monogranular);*	$U_{E_n} = 0 \rightarrow$ ideal uniform material (monogranular); *material ideal uniform (monogranular);*
	$U_{H_n} = 1 \rightarrow$ polygranular material distributed idealy non-uniform / *material poligranular distribuit ideal neuniform*	$U_{E_n} = 1 \rightarrow$ polygranular material distributed idealy non-uniform *material poligranular ideal neuniform distribuit*
I.I	For continuous variables, *x / Forma pentru variabilele continue, x*	
	$\mathrm{U_H} = \int_{\mathrm{x_m}}^{\mathrm{x_M}} f(\mathrm{x}) \cdot \log f(\mathrm{x}) \mathrm{dx}$	$\mathrm{U_E} = \int_{\mathrm{x_m}}^{\mathrm{x_M}} f^2(\mathrm{x}) \mathrm{dx}$

indicators, quantifiable for any polygranular system (in particular) and for any system characterized by several states (in general). This may be proved for a range of common distribution functions when a correlation between specific parameters that measure the dispersion or the distribution uniformity (*σ, n, a* etc.) and U_H and U_E parameters can be found (Table 3). The uniformity parameters were calculated in this paper by employing equations given in Table 1, case 2 (continuous random variables).

Analyzing the results shown in Table 3, it can be observed:

- *H* entropy and the disorder degree of a system increase as the dispersion parameters (*σ, λ, n, a*) increase; in particular, this reveals a less uniform particle-size distribution;

- the degree of uniformity has a negative correlation with dispersion parameters of some distributions (normal, Laplace, exponential); in other cases, for example Rosin - Rammler - Sperling, Dinger-Funk distributions, interdependencies can be explained

Table 3

Relationships between specific parameters assessing the uniformity distribution and the parameters U_H and U_E calculated for different usual distribution functions [5] / *Corelații dintre parametri specifici care măsoară dispunerea sau uniformitatea distribuției şi mărimile U_H şi U_E calculate pentru diferite funcții uzuale de repartiție [5]*

Item	Distribution type *Tipul de repartiție*	The differential form of the distribution function, *f(x)* *Forma diferențială a funcției de distribuție, f(x)*	U_H	U_E	Comments
1	Normal distribution *Repartiția normală*	$\frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}}$ $x \in R^+$ $\sigma > 0$	$\log(\sigma \cdot \sqrt{2\pi})$	$\frac{1}{2\sigma\sqrt{\pi}}$	$U_H + logU_E = -log\sqrt{2}$
2	Laplace Distribution *Repartiția Laplace*	$\frac{1}{2\lambda} e^{-\frac{\lvert x-\mu \rvert}{\lambda}}$ $x \in R^+, \mu \in R^+$ $\lambda > 0$	$\log(2e\lambda)$	$\frac{1}{2\lambda}$	$U_H + logU_E = loge$
3	Exponential distribution *Distribuția exponențială*	$\frac{1}{\lambda} e^{\frac{x}{\lambda}}$ $x \in R^+$ $\lambda > 0$	$\log(e\lambda)$	$\frac{1}{\lambda}$	$U_H + logU_E = loge$
4	Rosin – Rammler – Sperling Distribution *Distribuția Rosin – Rammler – Sperling*	$\frac{n}{(x')^n} x^{n-1} e^{-\left(\frac{x}{x'}\right)^n}$	$\int_{x_{min}}^{x_{max}} f(x) \cdot \log f(x) dx$ See Table 4	$\frac{n \cdot 2^{\frac{1}{n}}}{4x'} \Gamma\left(2 - \frac{1}{n}\right)$ $\Gamma(b) = \int_0^\infty x^{b-1} \cdot e^{-x} dx$ See Table 4	$U_H = 2.01 - 17.13 \cdot U_E$ R^2=0.916 See Fig. 1

Table 4

Relationships between particle size uniformity, *U*, and RRS distribution parameters *x'* and *n*. The particle size range for cement is $x \in$ (1, 200)μm / *Relații de dependență uniformitate granulometrică, U, vs. parametrii distribuției RRS, x' şi n. Granulometria considerată a cimentului $x \in$ (1, 200)μm.*

x'	$U_H = a_0 + a_1 \cdot n + a_2 \cdot n^2$				$U_E = b_0 + b_1 \cdot n$		
μm	a_0	a_1	a_2	R^2	b_0	b_1	R^2
10	1.348	0.036	-0.047	0.99	0.012	0.027	0.97
40	1.053	1.814	-0.707	0.96	0.009	0.020	0.87

by more complicated relations.

Such direct correlations between classical statistical dispersion parameters and those derived from information theory (that assess the degree of uniformity of the polygranular material) can be highlighted also for other distribution laws. It is revealed that, in addition to the fundamental task of defining the degree of uniformity, it has also the benefit of providing normalized values (between 0 and 1).

3. Linking the particle size uniformity and the specific surface area

In cement industry, the specific surface area is a geometrical parameter important in characterizing raw materials mixtures. This parameter affects the efficiency of grinding operations, classification and homogenization of the raw materials [6-12]. It also significantly controls the intensity of the heat transfer from hot gases to material on the system preheater (cyclones tower) - calciner - rotary kiln, including solid-phase chemical reactions. [13, 14]

Finally, the specific surface area of the cement is, along with its chemical composition, a key factor in shaping up cement properties [13, 15-19].

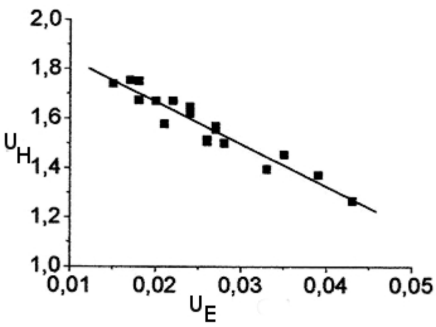

Fig. 1- Correlation between U_H and U_E for cement (application on data in [5]) / *Corelarea indicatorilor U_H şi U_E pentru ciment (aplicație pe datele din lucrarea [5]).*

3.1. Equations for the evaluation of the specific surface area

For a series of polygranular materials (cement, limestone, clay, raw mix) [15] their specific surface area is computed by the Equation:

$$S = \frac{6}{\rho} \cdot \sum_i \frac{W_i}{x_i} \; [cm^2/g] \qquad (6)$$

Where W_i is the percentage of material with the diameter x_i, cm; ρ - density of the material, g/cm^3.

For size fractions smaller than 14μm, equation (6) is written as:

$$S = \frac{6}{\rho} \cdot \sum_i \frac{W_i}{x_i} + \frac{500}{\rho} \cdot \sum_i \frac{W_i}{\sqrt{x_{50}}} [cm^2/g] \qquad (7)$$

Where x_{50} is the diameter which corresponds to a passing of 50%, μm.

In [16] there are given statistical equations for S calculation in two hypotheses:

- if the parameter x' is known,

$$S = 41048 \cdot (x')^{-0.394} \cdot n^{-0.195} \cdot \rho^{-1.078}\ [cm^2/g] \quad (8)$$

- if the diameter x_{80} is known.

$$S = 57477 \cdot x_{80}^{-0.416} \cdot n^{-0.470} \cdot \rho^{-1.151}\ [cm^2/g] \quad (9)$$

where n – the uniformity index, x_{80} – the diameter that corresponds to 80% passing, μm.

Similarly, the following equation is reported in [8]:

$$S = 5024.8(x' \cdot n)^{-0.4902}/\rho\ [cm^2/g] \quad (10)$$

These equations should be considered as succeeding the classical relation of Anselm on cement.

$$S = \frac{36.8 \cdot 10^4}{x' \cdot n \cdot \rho} \cdot f\ [cm^2/g] \quad (11)$$

where f is a shape factor of materials.

From the fundamental equation for calculating the specific surface area (9) for a polygranular mixture it follows that this size is defined in relation to:

- a dimensional feature of the particles, representing an associated diameter (x);

- a function $f(x)$ representing a distribution density that best approximates the particle-size distribution of the system;

- a material's property, density ρ.

As specific surface area is closely related to any type of particle size distribution, it, thus, becomes appealing to find a potential correlation with particle size uniformity. This goal constitutes the main part of the paper.

3.2. Correlation specific surface area and particle size uniformity. Results and discussion

To verify such a hypothesis, there were used primary information regarding a range of foreign cements from literature, and experimental data concerning local cements. The degree of uniformity U was assessed by U_E and U_H parameters. The associated size parameter for the grains in the mixture was either $\bar{x}$ or x_{50}. Finally, density, ρ, was considered as a property of the material.

3.2.1. Analysis of foreign cements

In paper [17] for a number of 16 cements there are given values for the dependent variable, the specific surface area S, in m^2/kg, and the independent variables of the RRS type, n and x' in μm and also the density, ρ in g/cm^3. (Table 5)

These values allowed the calculation of $\bar{x}$ and x_{50} and of the particle size uniformity degree, given by U_H and U_E.

Based on data in Table 5, the correlations between S and U_E, respectively between S and U_H for the analyzed cements, are represented in Figures 2 and 3.

Note that in all analyzed cases there were obtained mathematical equations characterized by high correlation coefficients. This indicates a close interdependence between the specific surface area and the particle size uniformity degree. No net distinctions can be considered between U_H and U_E. This result is somehow expected because between U_H and U_E there is an independence as is revealed in Figure 4 (see Tables 2 and 3).

Table 5

Primary data for cements given in paper [17] / *Date primare pentru cimenturile prezentate în lucrarea [17]*

Item	*S, m^2/kg*	*x', mm*	*$\bar{x}$, mm*	*x_{50}, mm*	*ρ, g/cm^3*	*n*
1	525	9.50	9.166	6.808	2.94	1.10
2	482	12.60	12.963	8.460	2.93	0.92
3	392	17.54	12.930	13.113	2.92	1.26
4	672	8.09	9.031	5.146	2.91	0.81
5	354	30.85	21.357	18.275	3.15	0.70
6	699	10.45	12.538	5.841	3.15	0.63
7	398	20.36	19.402	13.229	2.91	0.85
8	488	14.58	15.011	9.613	2.92	0.88
9	574	10.89	11.684	7.076	2.91	0.85
10	409	16.85	17.029	10.585	3.13	0.79
11	574	10.50	11.107	6.923	3.13	0.88
12	345	18.32	16.884	13.849	3.18	1.31
13	400	19.08	17.843	14.094	2.72	1.21
14	426	19.08	17.843	14.094	2.72	1.21
15	384	15.46	14.659	11.272	3.22	1.16
16	333	30.85	22.313	18.924	3.15	0.75

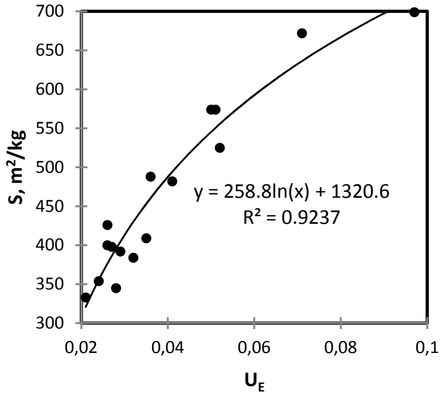

Fig 2 - The correlation $S - U_E$ for cements from Table 5.
Corelația $S - U_E$ pentru cimenturile din tabelul 5.

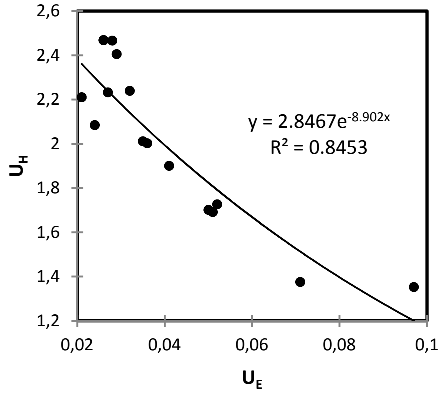

Fig 4 - Correlation between U_H and U_E for cements from Table 5 / *Corelația $U_H - U_E$ pentru cimenturile din tabelul 5.*

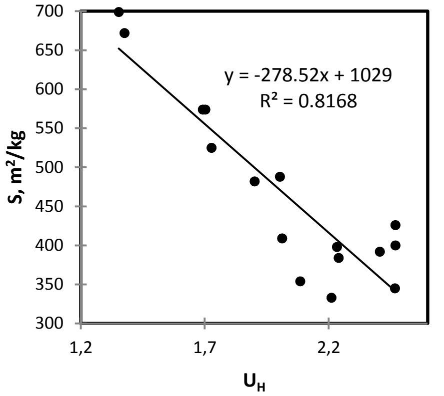

Fig 3 - The correlation $S - U_H$ for cements from Table 5
Corelația $S - U_H$ pentru cimenturile din tabelul 5

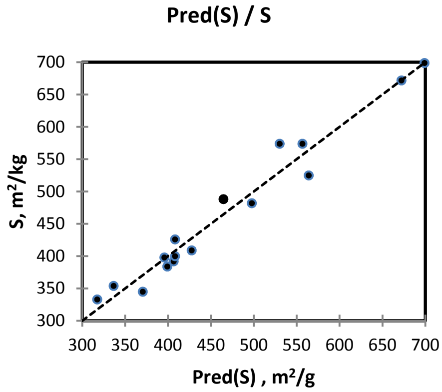

Fig.5- Correlation between measured S vs. predicted S for cements in Table 5. The case $S = f(U_E, x_{50},\rho)$/ *Corelația S măsurat vs. S predicționat pentru cimenturile din tabelul 5. Cazul $S = f(U_E, x_{50},\rho)$.*

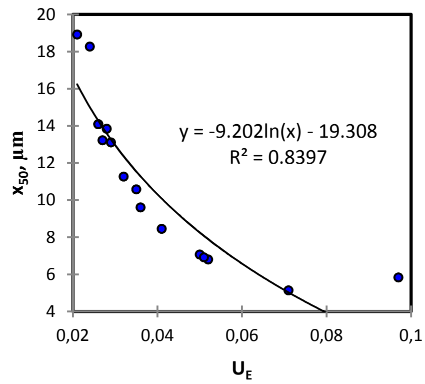

Fig. 6 - Correlation between x_{50} and U_H for cements in Table 5.
Corelația $x_{50} - U_E$ pentru cimenturile din tabelul 5.

This simple explanation of the relationship between specific surface area with uniformity, only, can be clarified by the fact that even geometrical features of the particles (of various diameters) correlate with the uniformity of the mix.

Statistical analysis of the data in Table 5 led to a series of equations that correlate independent variable S with the dependent variables (U_E, U_H, $\bar{x}$, x_{50}, ρ). A summary of the results is presented in Table 6.

The highlighted correspondence between measured and calculated values of the specific surface area is exemplified in Figure 5. A good agreement between the two sets of values is revealed, also demonstrated by the good value of the correlation coefficients R^2 (Table 6).

Table 6

Regression equations for calculating the specific surface area of the cements from Table 5.
Ecuații de regresie pentru calcularea suprafeței specifice a cimenturilor din tabelul 5

Regression parameters	*Regression Equation*	R^2	*RMSE*
$S = f(U_E, x_{50},\rho)$	$S = 5980.69 \cdot U_E^{0.39} \cdot x_{50}^{-0.15} \cdot \rho^{-0.82}$	0.965	23.994
$S = f(U_E, x',\rho)$	$S = 7240.87 \cdot U_E^{0.48} \cdot x'^{-5.35E-02} \cdot \rho^{-0.92}$	0.960	25.567
$S = f(U_H, \bar{x},\rho)$	$S = 3306.15 \cdot U_H^{-1.03} \cdot \bar{x}^{-9.12E-02} \cdot \rho^{-0.94}$	0.931	33.390
$S = f(U_E, \bar{x},\rho)$	$S = 7845.32 \cdot U_E^{0.52} \cdot \bar{x}^{-2.25E-02} \cdot \rho^{-0.98}$	0.959	25.912
$S = f(U_H, x',\rho)$	$S = 2850.92 \cdot U_H^{-0.85} \cdot x'^{-0.17} \cdot \rho^{-0.71}$	0.948	29.110
$S = f(U_H, x_{50},\rho)$	$S = 2786.82 \cdot U_H^{-0.65} \cdot x_{50}^{-0.26} \cdot \rho^{-0.69}$	0.954	27.466

* RMSE - root-mean-square error (standard deviation between values predicted by a model estimator and the values actually observed)

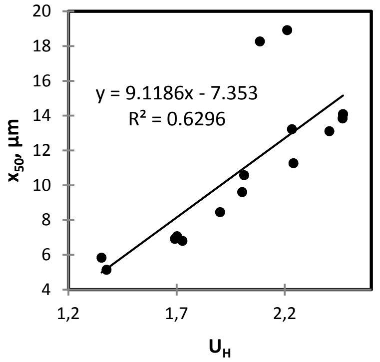

Fig. 7 - Correlation between x_{50} and U_H for cements in Table 5
Corelația x_{50} – U_E pentru cimenturile din tabelul 5.

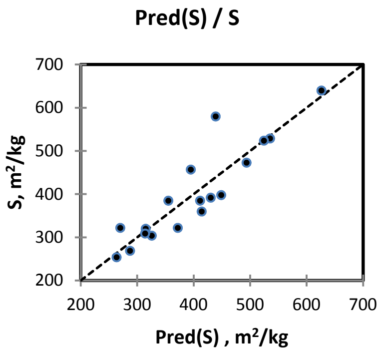

Fig. 8 - Correlation of the experimental and the calculated specific surface area / *Corelarea suprafeței specifice experimentale cu cea calculată.*

Note that in the derived statistical equations for computing S, particle size uniformity degree U_E or U_H significantly influences the value of S. The values for R^2 can be considered good, given that, as shown in Fig. 6 and 7, two or three of these records may be removed because they are outliers.

Moreover, functions such as $S = f(U, \rho)$ or $S = f(U)$ can be counted on a first analysis because also the variation of x_{50} or $\bar{x}$ is closely linked with the U_E or U_H parameters (see Figures 6 and 7, for example).

Somehow surprisingly, the derived complex regression functions showed modest R^2 values. For example, for the relationship $S = f(U_E, x_{50}, \rho)$ it was obtained $R^2 = 0.811$. Also in this case it was

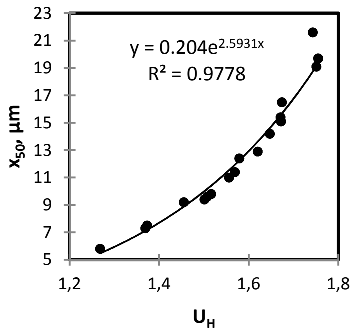

Fig. 9 - Correlation. x_{50} vs U_H for cements given in Table 7. *Corelația x_{50} vs. U_H pentru cimenturile prezentate în tabelul 7.*

Table 7

Primary data for grain size distributions of cements given in [16]
Date primare pentru distribuțiile granulometrice ale cimenturilor prezentate în [16]

Cement code	S, m^2/kg	ρ, g/cm^3	x', μm	n, -	$\bar{x}$, μm	x_{50}, μm	U_H	σ
C_{11}	385	3.15	31.3	0.99	25.8	21.6	1.743	22.25
C_{12}	304	3.10	24.8	0.90	22.1	16.5	1.674	20.88
C_{13}	254	3.03	19.6	0.80	18.7	12.4	1.579	19.62
C_{21}	473	3.18	21.0	1.11	19.8	15.1	1.672	16.90
C_{22}	392	3.10	16.0	0.99	15.8	11.0	1.556	15.00
C_{23}	320	3.13	11.3	0.84	12.1	7.3	1.369	13.41
C_{31}	640	3.15	13.0	1.14	12.4	9.2	1.455	10.55
C_{32}	529	3.10	10.8	1.02	10.6	7.5	1.373	10.00
C_{33}	457	3.05	8.6	0.92	8.9	5.8	1.268	9.21
C_{41}	385	3.12	27.6	1.09	24.6	19.7	1.755	20.49
C_{42}	322	3.05	22.7	0.94	21.1	15.4	1.671	19.74
C_{43}	269	3.00	15.3	0.83	15.8	9.8	1.516	16.90
C_{51}	580	3.04	26.5	1.12	24.0	19.1	1.751	19.77
C_{52}	360	2.98	18.8	0.98	18.2	12.9	1.620	17.18
C_{53}	309	2.92	14.5	0.85	15.0	9.4	1.501	16.01
C_{61}	524	3.04	19.7	1.12	18.6	14.2	1.647	16.56
C_{62}	398	3.01	16.5	0.99	16.2	11.4	1.569	15.96
C_{63}	322	2.96	15	0.82	15.6	9.6	1.507	15.49

confirmed the rule regarding the correlation between U_H and U_E parameters. For this dataset, the relationship with the highest statistical significance (R^2 = 0.811 and RMSE = 52.85) was:

$$S = 18408.10 \cdot U_E^{2.88} \cdot x_{50}^{2.20} \cdot \rho^{1.23} \text{ [m}^2\text{/kg]} \quad (12)$$

Such dependences were found for other sets of cements. Thus, on the basis of the primary data provided in [16] the parameters of interest given in Table 7 were calculated.

Correlation between experimental S vs. calculated S is shown in Fig. 8. Strong correlations (R^2>0.9) between specific parameters can be found in Figures 9-11.

As a conclusion, the analysis for these cements certified, also, the existence of a strong correlation between U_E and U_H.

3.3. Analysis of Romanian cements

A series of slag cements from a cement plant in Romania were also analyzed. These cements containing different proportions of slag (40%, 50%, 60%) and a cement without slag (the reference) were characterized by specific surface areas - Blaine method - and the particle size distributions using a CILAS 920 laser particle size analyzer. The particle size features are summarized in Table 8. Based on these values, particle size uniformity degrees U_E, U_H and parameters $\bar{x}$, x_{50}, n were obtained. For C1-C3 cements, the slag was separately grinded and then homogenized with cement while the C4-C6 cements were ground together with slag. C0 is the reference cement.

Available data has been analyzed and a series of functional relationships between the specific surface area S and various statistical parameters associated to the analyzed particle size distributions were extracted. The results are shown in Table 9. A brief analysis of the results reveals that:

- between specific surface area S and the statistical parameters considered there is, in most of the cases, a very good correlation; however, the values for R^2 are somewhat smaller than those given in Figure 8. An explanation may be given by the smaller number of experimental points considered in Table 8;

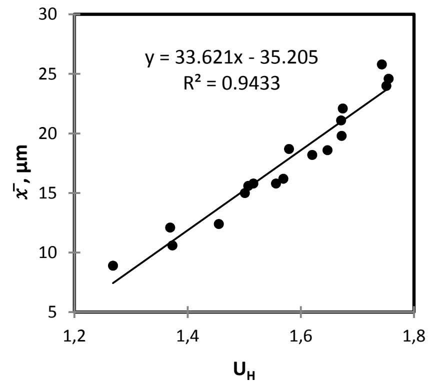

Fig. 10 - Correlation. $\bar{x}$ vs U_H for cements given in Table 7 / *Corelația $\bar{x}$ vs. U_H pentru cimenturile prezentate în tabelul 7.*

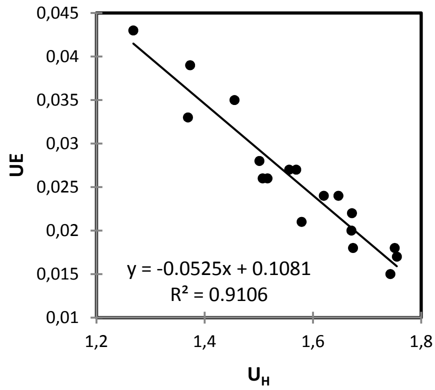

Fig. 11- Correlation. U_E vs U_H for cements given in Table 7 / *Corelația U_E vs. U_H pentru cimenturile prezentate în tabelul 7*

- neither in case of this experiment, a clear choice cannot be made between U_E and U_H as concerning the degree of correlation with S; an advantage of using U_E as the particle size uniformity degree is that it is easier to compute;
- both the results presented for a range of foreign cements and indigenous cements showed that among all analyzed cases, the higher correlation degrees were found for functional dependencies on the type $S = f(U_E, x_{50}, \rho)$.

Table 8

Primary data for a series of Portland cements containing different proportions of slag
Date primare determinate experimental pentru o serie de cimenturi portland cu zgură

Code	S, m^2/kg	x', μm	$\bar{x}$, μm	ρ, g/cm^3	n
C0	304	25.8	22.2	3.07	0.85
C1	301	30.0	21.9	3.00	0.74
C2	340	30.4	21.6	2.77	0.72
C3	356	31.0	20.7	3.00	0.67
C4	270	48.1	22.8	3.00	0.71
C5	321	31.3	21.4	3.00	0.70
C6	286	35.0	22.9	3.00	0.75

Table 9

Statistical equations between specific surface area *S* and a series of grain size parameters for cements in Table 8
Relații statistice între suprafața specifică S și o serie de parametri granulometrici pentru cimenturile din tabelul 8

Regression parameters	Regression Equation	R^2	RMSE
$S = f(U_E, x_{50}, \rho)$	$S = 3144.05 \cdot U_E^{0.52} \cdot x_{50}^{6.14E-02} \cdot \rho^{-0.45}$	0.939	10.485
$S = f(U_E, x', \rho)$	$S = 1402.78 \cdot U_E^{0.43} \cdot x'^{5.37} \cdot \rho^{-2.09}$	0.894	16.691
$S = f(U_E, \bar{x}, \rho)$	$S = 693.21 \cdot U_E^{0.62} \cdot \bar{x}^{0.72} \cdot \rho^{-0.57}$	0.862	15.853
$S = f(U_H, x', \rho)$	$S = 8649.79 \cdot U_H^{-1.37} \cdot x'^{-0.456} \cdot \rho^{-0.629}$	0.939	10.489
$S = f(U_H, x_{50}, \rho)$	$S = 11218.71 \cdot U_H^{-1.72} \cdot x_{50}^{-0.29} \cdot \rho^{-1.23}$	0.662	24.738

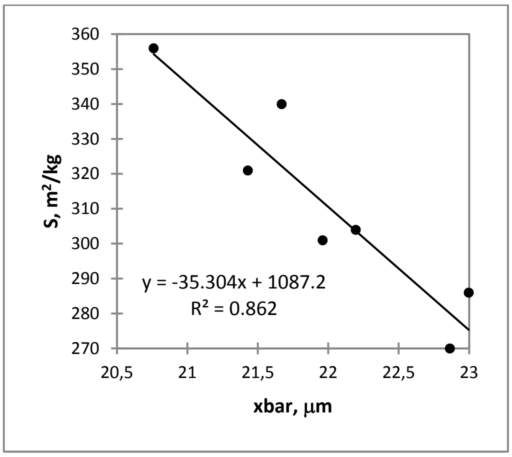

Fig. 12- Dependence *S* - $\bar{x}$ for local slag portland cements.
Dependența S-$\bar{x}$ pentru cimenturile portland cu zgură autohtone.

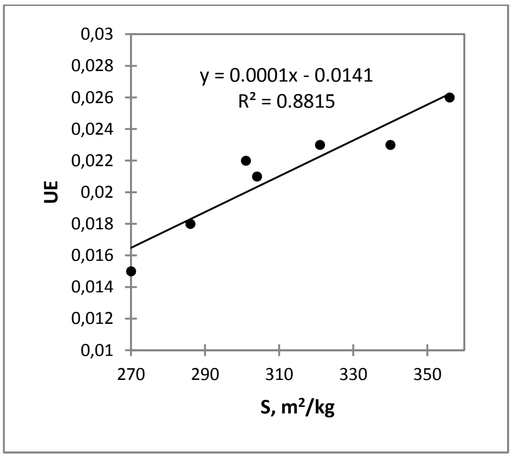

Fig. 13 - Dependence *S* – U_E for local slag Portland cements / *Dependența S-U_E pentru cimenturile portland cu zgură autohtone.*

It should be noted that a series of functional dependencies between *S* and various parameters associated with the particle size distribution for local cements were highlighted. Thus, in Figure 11 the dependency between *S* and $\bar{x}$ for local cements is plotted. In Figure 12 it is shown the relationship between *S* and U_E – this relationship can be quantified by using the equation:

$$S = 10^4 U_E + 141, \; R^2 = 0.882 \qquad (13)$$

Although in the examples shown in Figures 11-13 the regression equations have R^2 values of only 0.86-0.88 (smaller than those given in Table 6), it should be noted that in all cases the degree of uniformity was found to be a major influence factor that correlates with both specific surface area, and statistically determined diameters, for different types of cement.

4. Conclusions

In this paper, two parameters coming from information theory are used to assess the degree of uniformity of polygranular mixtures. These parameters - informational energy, *E*, and informational entropy *H*, are defined in an unique and natural way for the numerical evaluation of particle size uniformity for any granular/powder mixture, characterized by either discontinuous or continuous distribution functions, U_E and U_H.

Both for several cements found in literature, and for some local cements there were obtained a series of statistical relationships that correlate cement's specific surface area with the uniformity (U_E or U_H), density and some statistically defined diameters. In all cases there were recorded high correlation coefficients R^2, which certifies the validity of the tested hypothesis.

Further applications of the results of this paper should not be restricted to cement or powdery/granular materials. Currently (see [20-26], for example), the assessment of the particles size in powders or in various sintered ceramic bodies – ranging from nano to macroscopic scales and obtained by various synthesizing methods – provide an average particle size or a range of values. If properties are to be finely tuned to microstructure or if it is intended to compare microstructures obtained by different routes – these assessment options in use are not sufficient. In such cases, one should consider a more refined size distribution instrument, that could be, in our belief, either U_E or U_H (or, at least, they can bring additional, useful information).

Nonlinear regression equations were obtained using the software XLSTAT 2014 Addinsoft; the calculation of the parameters which characterize the particle size uniformity was made in MathCAD environment.

REFERENCES

1. T. Allen, Particle size measurement, Powder Technology Series, 4th edition, Chapman and Hall, 1991.
2. H. Masuda et al, Powder technology, Fundamentals of Particles, Powder beds and Particle Generation, 2007
3. C. E. Shannon, A mathematical theory of communication part I and II, Bell Syst. Tech. Journal, 1948, **27**, p 379-423, 623-656.
4. O. Onicescu, Energie informationelle, Comptes Rendues l'Academie des Sciences, Paris, Seria A, 263, 1966.
5. D. Radu, and C. Ibriş, Gradul de uniformitate – indicator statistic generalizat de apreciere a dispersiei unor amestecuri poligranulare, Revista Romana de Materiale, 2004, **34**(4), 313.
6. P. Gonzalez-Tello et all, A modified Nukiyama-Anasawa distribution function ans a Rosin-Rammler model for the particle size distribuion analysis, Powder Technology, 2008, **186**(3), 278.
7. C. Dimofte, L. Mihuț, and I. Baltog, Rosin – Rammler – Sperling window for ground powder analysis, J. Phys, France, 1994, **4,** 2617.
8. K. Kaczmarski and J. Ch. Bellot, Effect of particle-size distribution and particle porosity changes of mass- transfer kinetics, Acta Cristalografica, 2003 (13).
9. M. Meyer et all, Generally aplicable breakage functions derived from single particle cominution data, Powder Technology, 2009, 194 (1-2), 33.
10. G. Unland, Y. and Al-Khasawneh, The influence of particle shape on parameters of impact crushing. Minerals Engineering, 2009, 22, (3), 220.
11. N.S. Lameck, K.K. Kiangi, and M.H. Moys, Effects of grinding media shapes on load behaviour and mill power in a dry ball mill, Minerals Engineering, 2006, **19**, (13), 1357.
12. H. Otwinowski, Energy an population balances in cominution process modeling based on the informational entropy, Powder Technology, 2006, **167**(6), 33.
13. D. Radu, A. Volceanov, and A. Toader, Gradul de uniformitate al amestecurilor granulare si pulverulente, Materiale de constructii, 1996, **26**(1), 59.
14. J. Zheng, PF Johnson, and JS Red, Improved Equation of the continuous particle size distribution for dense packing, J. Am. Ceram Soc, 1990, **73**(5), 1392.
15. M. E Asim, Particle size distribution of cement, Zement-Kalk-Gips, 1986, **39**(6), 321.
16. S. Tsivilis, and S. Tsima, Estimation of the specific surface of the cement industry material according to their particle distribution, Zement Kalk Gips, 1992, **3** (45), 131.
17. X. Zhongming, Z. Datong, New interpretation on the physical meaning of characteristic diameter and uniformity coefficient in RRB relationship, 4th International Congress on the Chemistry of Cement, Bijing, China, 1998, **1**, oct 27-30.
18. K. Kuhlmann, H.G. Ellerbrock, and S. Sprung, Kornogrößenverteilung und Eigenschaften von Zement, Teil I: Festigkeit von Portlandzement, Zement – Kalk – Gips 1985, **38**(4), 169.
19. B.I. Celick, The effects of particle size distribution and surface area upon cement strenght development, Powder Technology, 2009, **188**(3), 272.
20. E. Dinu, C. Ghițulică, G. Voicu, M. Bîrsan, E. Andronescu, The influence of the pyrosol sinthesis temperature on the HAp powders' characteristics, Romanian Journal of Materials, 2013, **43** (1), 64.
21. S. Stoleriu, E. Volceanov, A. Volceanov, Ceramic composite based on silicon carbide and vitreous silicon dioxide obtained under unconventional sintering treatment, Romanian Journal of Materials, 2013, **43** (2), 175.
22. A. Melinescu et al, Removal of Pb2+ toxic ions from aqueous solutions on porous Hap granules, 2013, **43** (2), 224.
23. M. Eftimie, A. Popescu, V. Dima, Experiments to obtain composites based on glass matrix reinforced with SiC powder, Romanian Journal of Materials, 2013, **43** (2), 191.
24. C. Matei et al, Synthesis of Ceria nanoparticles with controlled morphology, Romanian Journal of Materials, 2014, 44 (1), 76.
25. R.C Voinițchi et al, The assessment of efficiency of thermo-mechancial treatment applied on recycled concrete aggregate, Romanian Journal of Materials, 2014, **44** (3), 207.
26. E. Olinic et al, Optimal material for embankments: mixture of clayey soils with granular material and insutrial waste, Romanian Journal of Materials, 2014, **44** (4), 391.

****