# CORRELATIONS RAW MIX COMPOSITION – PROCESSING – CEMENT PROPERTIES WITH PARTIAL SUBSTITUTION OF THE RAW MATERIALS WITH GLASS WASTES

# CORELAŢII COMPOZIŢIA AMESTECULUI DE MATERII PRIME – PROCESARE – PROPRIETĂŢILE CIMENTULUI LA SUBSTITUŢIA PARŢIALĂ A MATERIILOR PRIME CU DEŞEURI DE STICLĂ

**ZENO GHIZDĂVEŢ[1] * , OVIDIU DUMITRESCU[1], MIHAI EFTIMIE[1], ADRIANA MOANŢĂ[2], IONELA PETRE[2], NICOLETA CIRSTEA[2]**

*[1]University POLITEHNICA of Bucharest, 313 Spl. Independentei, Bucharest, Romania*
*CEPROCIM S.A., Blvd. Preciziei no. 6, Sector 6, Bucharest, Romania*

***Two classes of glass wastes, colored (C) and transparent (A), will be used for the partial substitution of the raw mixes, i.e. especially sand, in cement clinker production. Advanced statistical methods will help to identify and extract correlations composition – raw mix grinding – clinkering – cement grinding – properties. Investigations aim to clarify if and how the partial substitution of the raw materials with glass cullet could influence the most important cement properties, via clinker quality.***

***It is expected to find out, also, if the various mixes of raw materials and glass waste will show different raw mix grinding behavior; the same question will be answered for cement grinding. The major concern when sand is entirely substituted with glass is the higher alkali intake, that can influence both clinker phase composition and, therefore, quality and clinkering plant operation. Being one of the indices that define clinker quality, grindability directly affects operational costs, so it is an important feature that will also be evaluated and correlated; among other factors, grindability is related to the amount of alkali in clinker.***

***Două clase de deşeuri de sticlă, colorate (C) şi transparente (A), vor fi utilizate pentru substituţia parţială a amestecurilor brute, în special a nisipului, în obţinerea clincherului de ciment. Metode statistice avansate vor ajuta la identificarea şi extragerea corelaţiilor compoziţie–măcinare amestec brut–clincherizare–măcinare ciment–proprietăţi. Se urmăreste dacă şi cum înlocuirea parţială a materiilor prime cu sticlă ar putea influenţa unele proprietăţi ale cimentului. Se investighează dacă diversele amestecuri de materii prime şi deşeuri de sticlă vor prezenta un comportament diferit la măcinare. Substituţia totală a nisipului cu sticlă implică un aport mai mare de alcalii, care poate influenţa compoziţia şi calitatea clincherului dar şi funcţionarea instalaţiei de clincherizare. Aptitudinea la măcinare afectează direct costurile operaţionale, deci va fi şi ea evaluată şi corelată; printre alţi factori, aptitudinea la măcinare este legată de cantitatea de alcalii din clincher.***

***Keywords:*** *glass waste, clinker, partial substitution, correlations*

## 1.Introduction

Widespread efforts targeting the partial substitution of raw materials in clinker production or partial clinker substitution with other materials (hydraulically active or not) are made to conserve natural, raw materials and landscapes, to reduce pollution via $CO_2$ reduction and to decrease waste deposits. [1-7] If raw materials are partially substituted with industrial wastes, concerns arise about if and how the waste materials could influence: *i)* clinkering temperature [8,9], *ii)* clinker composition and quality (free CaO, phase composition, alkali, Sulphur and heavy metals content) [10,11] and *iii)* grinding effectiveness and energy requirement. To deal with all these concerns, proper experimental should be conducted in a heuristic approach, to balance raw materials, processing routes, microstructure and properties to identify the optimal substitution rate for each specific case. This research focuses on aiding the experimental with some statistical analysis techniques to uncover and quantify the chain of correlations that starts with raw materials/wastes composition and ends with product's (clinker) quality. Influences on processing (grinding and clinkering behavior) will also be addressed.

## 2. Materials and methods

Limestone, clay or marl, pyrite cinder and sand or glass culets (to substitute, mainly, sand) were used to obtain 6 clinkers. 3 of them were made with clay (*Ea – reference, SCa – with colored glass cullet, SAa – with transparent glass cullet*) and the other 3 with marl (*Em - reference, SCm – with colored glass cullet, SAm – with transparent glass cullet*). Moduli composition were set to be $S_k$ = 0.98; $M_{Si}$ = 2.5; $M_{Al}$ = 1.6.

* Autor corespondent/*Corresponding author*,
E-mail: zghizdavet@gmail.com

Fig. 1 - From the left to the right, green mix, shaped green specimen and clinker
*De la stânga la dreapta - amestec brut, specimen crud și clincher*

Grinding has been made in a laboratory mill in two steps: primary grinding with steel balls grinding media up to a fineness of 40-45% residue on sieve with sieve mesh of 90μm; finishing grinding up to about 12% residue on sieve with sieve mesh of 90μm [12]. Mixes of raw materials/waste were homogenized with water and manually shaped in parallelepipeds which were dried at 100°C. Raw mixes were subjected to burning in a chamber kiln with gas at the maximum temperature of 1450°C, maintaining a 30 minutes plateau, followed by fast cooling in air.

Resulting clinkers were characterized for: free CaO content in clinker ($f_{CaO}$), initial (*iSt*) and final (*fSt*) setting time, flexural strength at 2, 7, 28 days ($B_2$, $B_7$, $B_{28}$), compressive strength at 2, 7, 28 days ($S_2$, $S_7$, $S_{28}$). Required times (in seconds) for grinding the cement to a residue of 27% and of 0.94% on sieve with sieve mesh of 90μm, respectively, were recorded and used as grindability indices (see Table 3). A statistical analysis consisting in basic exploratory techniques (means, standard deviation, correlation coefficients) and more advanced techniques such as PCA and dendrogram has been performed on all data, both inputs and results.

Variables can be different through their nature, measurement units and order of amplitude; however, they can influence other variables in a simple or complex, i.e. mutual and difficult to describe mathematically. *Principal Component Analysis* (PCA, see Fig. 1) can be an useful instrument to address complex interrelations between variables or cases, uncover the relationships between observations and among variables. [13]

The concept of the PCA method is to reduce the number of variables of a dataset as much as possible while still maintaining the most of their information (variance). This can be done by maximizing the variance of the datapoints' projection on the constructed coordinate and minimizing residual variance in the least square sense. [13, 14]

The first principal component accounts for the largest possible variance in the dataset, the second principal component for the largest possible part of the remaining, with the condition that it is uncorrelated with (i.e., perpendicular to) the first principal component and so on. [14]

The efficiency of the PCA results is related to reducing the number of the principal components (if possible, to up to only two) while covering almost the entire variance. *n* – dimensional space observations are thus plotted (projected) on only pairs of coordinates (2 – dimensional space), providing the opportunity to extract positive/negative relationships. Closed variables on the projection space tend to have a similar behavior being positively corelated; when two or more variables are situated opposite along a coordinate, they are negatively corelated. Variables situated far away from the origin (which is the average point) will exert a stronger influence than the ones near origin.

## 3. Results and discussions

Recipes of raw materials and materials used to obtain the six clinkers are given in Table 1.

**Table 1**
Raw materials and materials used to obtain the six clinkers
*Materii prime și materiale folosite pentru a obține cele șase clinchere*

| | Limestone, % | Clay/marl, % | Pyrite cinder, % | Sand/glass (S/G), % |
|---|---|---|---|---|
| Ea | 81.23 | 13.03 | 0.94 | 4.80 |
| SCa | 79.90 | 13.52 | 0.99 | 5.59 |
| SAa | 79.85 | 13.45 | 1.00 | 5.50 |
| Em | 75.95 | 18.69 | 0.74 | 4.61 |
| SCm | 74.49 | 19.37 | 0.78 | 5.36 |
| SAm | 74.52 | 19.40 | 0.79 | 5.28 |

Raw mix grinding showed no significant differences, that is, all mixes needed a time of 37±1 min. to reach a residue $R_{009}$ = 12%. Green, shaped specimens were thermally processed at various temperatures and time intervals given in Table 2.

**Table 2**
Free CaO content (%) in clinkers with glass waste intake in various conditions (temperature and plateau time)
*Conținutul de CaO liber (%) în clinchere cu deșeuri de sticlă în diferite condiții de procesare (temperatură și timp de palier)*

| Heating conditions | Clinker | | | |
|---|---|---|---|---|
| | SCa | SAa | SCm | SCa |
| 1400°C + 20 min | 3.77 | 3.72 | 3.79 | 2.98 |
| 1430°C + 20 min | 2.58 | 2.55 | 2.61 | 2.25 |
| 1430°C + 30 min | 1.72 | 1.38 | 1.50 | 1.44 |

**Table 3**

Grinding times, properties and oxide composition of the 6 clinkers, used in PCA
*Timpii de măcinare, proprietățile si compoziția oxidică a celor 6 clinchere, utilizate în PCA*

| | $t_{R009 = 27\%}$, s | $t_{R009 = 0.94\%}$, s | iSt, min | fSt, min | $B_2$, MPa | $B_7$, MPa | $B_{28}$, MPa | $S_2$, MPa | $S_7$, MPa | $S_{28}$, MPa | $f_{CaO}$, % | $Na_2O_e$ % | S/G, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ea | 600 | 1305 | 190 | 240 | 4.3 | 6.4 | 8.1 | 24.2 | 36.2 | 46.1 | 1.06 | 0.31 | 4.80 |
| SAa | 840 | 1910 | 190 | 240 | 3.7 | 6.1 | 7.2 | 22.6 | 36.2 | 44.7 | 1.63 | 1.50 | 5.50 |
| SCa | 855 | 1900 | 200 | 250 | 3.8 | 6.2 | 7.1 | 23.8 | 35.5 | 43.1 | 1.91 | 1.56 | 5.59 |
| Em | 600 | 1780 | 220 | 300 | 3.8 | 6.3 | 7.5 | 22.5 | 36.2 | 45.2 | 1.10 | 0.38 | 4.61 |
| SCm | 720 | 1740 | 210 | 270 | 3.7 | 6.2 | 7.1 | 21.6 | 33.5 | 42.8 | 1.80 | 1.55 | 5.36 |
| SAm | 660 | 1660 | 200 | 240 | 4.2 | 6.5 | 7.8 | 23.1 | 35.7 | 44.2 | 1.68 | 1.62 | 5.28 |

Remarks: S/G means sand (S) or glass (G); $Na_2O_e$ is the alkali amount in the raw mix expressed as the equivalent in $Na_2O$

**Table 4**

Computed correlation coefficients on all considered data / *Coeficienții de corelație obținuți pentru toate combinațiile de variabile*

Correlations (Book1)
Marked correlations are significant at p < .05000
N=6 (Casewise deletion of missing data) tR009 = 27%

| Variable | Means | Std.Dev. | tR009 = 27% | tR009 = 0.94% | iSt | fSt | B2 | B7 | B28 | S2 | S7 | S28 | fCaO | Na2O e | S/G |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **tR009 = 27%** | 712.500 | 113.7431 | 1.000000 | 0.734816 | -0.349701 | -0.370237 | -0.604559 | -0.743615 | -0.772515 | -0.058689 | -0.157245 | -0.601353 | 0.788114 | 0.735349 | 0.899246 |
| tR009 = 0.94% | 1715.833 | 222.8097 | 0.734816 | 1.000000 | 0.283457 | 0.237799 | -0.848787 | -0.682487 | -0.879625 | -0.470649 | -0.142350 | -0.611296 | 0.627289 | 0.604321 | 0.581090 |
| iSt | 201.667 | 11.6905 | -0.349701 | 0.283457 | 1.000000 | 0.941763 | -0.399702 | 0.019371 | -0.276079 | -0.574042 | -0.334544 | -0.265486 | -0.103941 | -0.178071 | -0.393761 |
| fSt | 256.667 | 24.2212 | -0.370237 | 0.237799 | 0.941763 | 1.000000 | -0.458831 | -0.130893 | -0.253176 | -0.530795 | -0.181160 | -0.052569 | -0.316967 | -0.400353 | -0.536735 |
| B2 | 3.917 | 0.2639 | -0.604559 | -0.848787 | -0.399702 | -0.458831 | 1.000000 | 0.883705 | 0.941548 | 0.677110 | 0.379470 | 0.563817 | -0.443628 | -0.373425 | -0.396717 |
| B7 | 6.283 | 0.1472 | -0.743615 | -0.682487 | 0.019371 | -0.130893 | 0.883705 | 1.000000 | 0.844168 | 0.398321 | 0.226816 | 0.383859 | -0.382736 | -0.304498 | -0.481121 |
| B28 | 7.467 | 0.4131 | -0.772515 | -0.879625 | -0.276079 | -0.253176 | 0.941548 | 0.844168 | 1.000000 | 0.565985 | 0.498747 | 0.778244 | -0.704582 | -0.610344 | -0.646520 |
| S2 | 22.967 | 0.9438 | -0.058689 | -0.470649 | -0.574042 | -0.530795 | 0.677110 | 0.398321 | 0.565985 | 1.000000 | 0.614536 | 0.453663 | -0.262190 | -0.319841 | -0.113096 |
| S7 | 35.550 | 1.0483 | -0.157245 | -0.142350 | -0.334544 | -0.181160 | 0.379470 | 0.226816 | 0.498747 | 0.614536 | 1.000000 | 0.779616 | -0.563742 | -0.482963 | -0.378303 |
| S28 | 44.350 | 1.2566 | -0.601353 | -0.611296 | -0.265486 | -0.052569 | 0.563817 | 0.383859 | 0.778244 | 0.453663 | 0.779616 | 1.000000 | -0.909421 | -0.812692 | -0.742322 |
| fCaO | 1.530 | 0.3621 | 0.788114 | 0.627289 | -0.103941 | -0.316967 | -0.443628 | -0.382736 | -0.704582 | -0.262190 | -0.563742 | -0.909421 | 1.000000 | 0.963714 | 0.943097 |
| Na2O e | 1.153 | 0.6277 | 0.735349 | 0.604321 | -0.178071 | -0.400353 | -0.373425 | -0.304498 | -0.610344 | -0.319841 | -0.482963 | -0.812692 | 0.963714 | 1.000000 | 0.932428 |
| S/G | 5.190 | 0.3954 | 0.899246 | 0.581090 | -0.393761 | -0.536735 | -0.396717 | -0.481121 | -0.646520 | -0.113096 | -0.378303 | -0.742322 | 0.943097 | 0.932428 | 1.000000 |

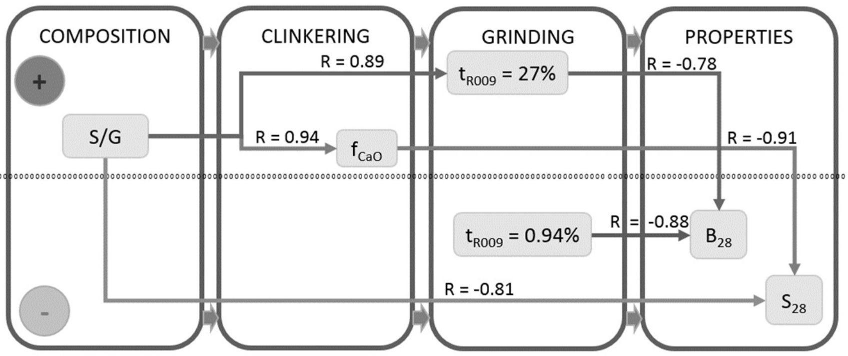


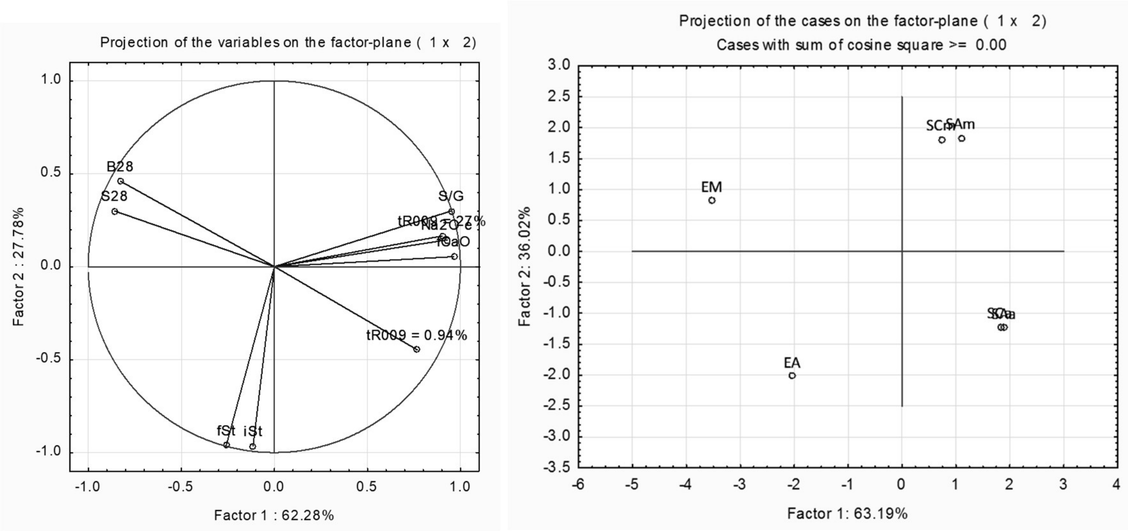

Fig. 2 - Identified positive/negative correlations composition - processing – properties / *Corelații pozitive/negative compoziție – procesare – proprietăți*

The results show that the optimal processing conditions are temperature of 1430°C and a 30 minutes plateau, to attain a free CaO content lower than 2%. It can be observed that clinkering temperature lowers from 1450°C to 1430°C; various benefits could be inferred due to lowering the clinkering temperature, mainly by reducing the amount of fuel intake and reducing waste deposits.

For each clinker produced, all inputs/outputs – excluding composition, which is self-correlated – can be found in Table 3. Statistical analysis was performed on these records. For start, basic statistical exploratory techniques show that the coefficient of correlation, *R*, may be an important index; positive or negative correlations with $R > 0.8$, significant at $p < 0.05$ were identified (see Table 4).

Based on these results, two strong chains of correlations were identified between composition (*S/G* – sand/glass content in raw materials) – clinkering ($f_{CaO}$ percentage in clinker), clinker grindability ($t_{R009}$) and flexural and compressive strengths. In Fig. 2 it can be seen that, due to the increase in alkali content of the raw mixes, glass intake increases the $f_{CaO}$ content ($R = 0.94$), most probably due to the decomposition of $C_3S$ by the alkali with free CaO formation; the consequence of the lowering $C_3S$ content in clinker is that $S_{28}$ decreases ($R = -0.91$). The second consequence of the increase in alkali content is the lowering of the clinkering temperature, so the amount of liquid phase (after cooling becomes vitreous phase) increases; the result is that grindability is negatively affected, as the vitreous phase has a lower grindability, so the time ($t_{R009=27\%}$) and energy required to attain a given cement fineness will increase, as well ($R = 0.89$). Lower grindability affects mechanical properties, especially $B_{28}$. The third identified correlation relates directly $S_{28}$ to *S/G* content, augmenting the prior observations that the increase of glass intake will decrease the compressive strength ($R = -0.81$).

PCA helps to identify, visually, the behavior of the variables (compositions, properties, grinding times) and of the cases (clinkers Ea, SAa, …, SAm). The basic is, the closer the variables/cases are in the plot, the more likely their behavior is [13, 14]. If two or more variables/cases are opposite on an




a) b)

Fig. 3 - Projection of the variables, a), and cases, b), on the factor-plane / *Proiecția variabilelor, a), și a cazurilor, b), pe planul factorilor*

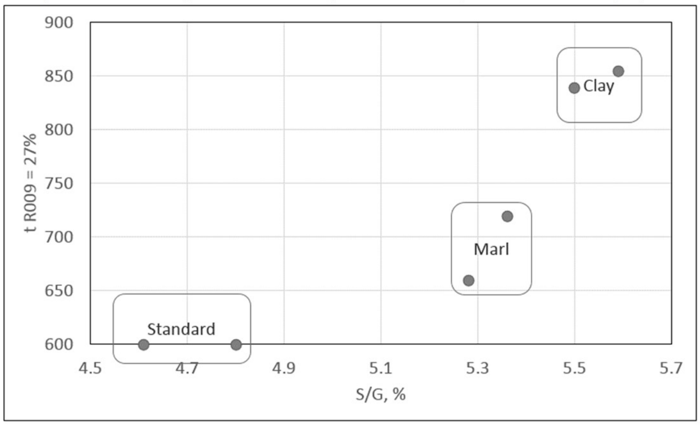



Fig. 4 - Required clinker grinding time (in seconds) for a residue of 27% on sieve with sieve mesh of 90 microns / *Timpul (în secunde) necesar pentru măcinarea clincherului la un reziduu de 27% pe sita cu diametrul ochiului de 90 microni*

axis, their behaviors are opposite (if one increases, the other decreases). Higher values of their projection on a factor means the particular variable/case explains more of the variance of the data so they are more influential.

By analyzing Fig. 3 a), a cluster of variables can be easily identified and found at values close to 1 on the factor 1, which means that these variables are very important (influential) and, also, have a similar behavior (they are positively correlated); this cluster is made of *S/G*, $Na_2O_e$, $f_{CaO}$, $t_{R009=27\%}$. Opposite to these variables one can found the mechanical properties, close to -1 when projected on the factor 1. The implication is that their behavior is inversely to the one of the cluster on the positive side of the factor 1. On factor 2 it can be found the setting time which is not related to any other variable. Factor 1 explains more than 62% of the data variance and, in conjunction to Factor 2 they explain around 90%, thus making the analysis a reliable one.

Setting times were extracted and the analysis was reiterated, aiming to identify the behaviors of the cases, this time. Fig. 3, b) show that the color of the glass makes no difference; the influential role is played by the clay or marl added in the raw mix. Specifically, clinkers are grouped in two distinct pairs (made with glass), the first being SAa + SCa and the second SAm + SCm, and the two references, Ea and Em (made with sand). It results that clinkers obtained from mixes containing marl are separated from the other ones containing clay on the factor 2 axis while clinker obtained from glass or sand containing mixes are separated along the factor 1 axis.

Figure 4 shows that the S/G content strongly influences grinding time; moreover, there is a strong influence of the raw mix composition. The highest grindability has the two standard mixes, without glass (Ea and Em, referred as “Standard” group in the plot). When glass is used instead, the lowest grindability was obtained for the clay-containing raw mix (referred as “Clay” group in the plot), where the glass intake had to be the highest in order to obtain the moduli imposed to the raw mix.

Dendrogram in Figure 5 depicts in an intuitive approach how variables are linked together. A first cluster links $f_{CaO}$, *S/G*, $Na_2O_e$ and $B_{28}$, showing that these variables are closely

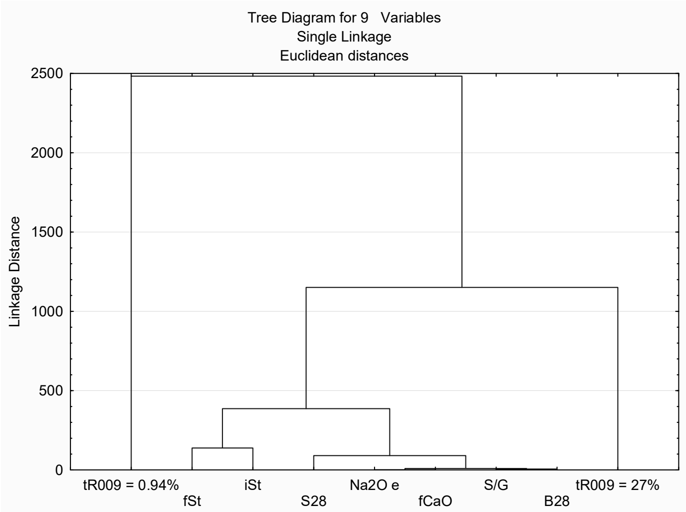



Fig. 5 - Dendrogram showing the hierarchical connections of the variables / *Dendrogramă care evidențiază ierarhizarea variabilelor*

interconnected. This cluster forms another one with $S_{28}$ variable being at a very small linkage distance. This observation could be interpreted as variables are being connected, thus having an interdependency or being similar/dissimilar in their behavior. A distinct cluster is made of *fSt* and *iSt*; this cluster is situated at a more consistent linkage distance from the previously clustered five variables ($f_{CaO}$, *S/G*, $Na_2O_e$, $B_{28}$ and $S_{28}$). That shows that the distinct cluster is poorly connected with the 5-variables cluster an no specific influences can be observed. Further, the cluster made of the two mentioned clusters links in two distinct steps with the grinding times. This observation means that we can interpret it as being the hierarchical arrangement of the relationships within variables.

## 4. Conclusions

A miscellaneous of variables describing raw mix compositions, clinker quality, clinker grinding time, clinker quality and cement stone mechanical properties were statistically analyzed. Strong chains of correlations explain how substitution of the raw materials with glass waste influence, in cascade, through a series of relationships, up to cement stone mechanical properties.

These investigations will help further assessing the optimal substitution rate of the raw materials with glass waste, subjected to *conflicting constraints* such as: clinker quality, energy consumption, costs related to raw materials extraction and preparation, $CO_2$ emissions etc.

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**REFERENCES**

[1] R. Gowtham, S. Manikanda Prabhu, M. Gowtham, R. Ramasubramani, A review on utilization of waste glass in construction field, IOP Conf. Series: Materials Science and Engineering, 2020

[2] G. Chen, H. Lee, K. L. Young, P.L.Yue, A. Wong, T. Tao, K. K. Choi, Glass recycling in cement production—an innovative approach, Waste Management, 2002, **22**, 747

[3] A. Bouregba, A. Diouri, F. Amor, H. Ez-zaki and O. Sassi, V. Mohammed, Valorization of glass and shell powders in the synthesis of Belitic clinker, MATEC Web of Conferences, 2018, **149**, 01021.

[4] O. A. Miryuk, The effect of waste on the formation of cement clinker, IOP Conf. Series: Materials Science and Engineering, 2019**, 510**, 012012

[5] J Halbiniak, M Major, The Use of Waste Glass for Cement Production, IOP Conf. Series: Materials Science and Engineering, 2019, **585**, 012008

[6] O, Savin, M. Baran, S. Demir, Mechanical and physical properties of cementitious composites containing fly ash o slag classified with help of particle size distribution, Romanian Journal of Materials, 2021, **51** (1), 67

[7] I. Diaz-Loya, M. Juenger, S. Seraj, R. Minkara, Extending supplementary cementitious material resources: Reclaimed and remediated fly ash and natural pozzolans, Cement and concrete composites, 2019, **101**, 44

[8] M. Schneider, Process technology for efficient and sustainable cement production, Cement and Concrete Research, 2015**, 78**, Part A, 14

[9] M. M. R. A. Lima, L.F.C. Braz, R. C. C. Monteiro, J.P. Veiga, Effect of Phosphogypsum on the Clinkerization Temperature of Portland Cement Clincker, Materials Science Forum, 2013**, 730-732**, 94

[10] L. Luo, Y. Zhang, S. Bao, T. Chen, Utilization of Iron Ore Tailings as Raw Material for Portland Cement Clinker Production, Advances in Materials Science and Engineering, 2016, 1

[11] A.Moanță, I. Mohanu, J. Paceagiu, D.C. Năstac, I. Petre, R.M. Fechet, Valorization of mill scales in materials with added value, Romanian Journal of Materials 2017, **47** (2), 276

[12] INC CEPROCIM, Guidebook of the cement industry engineer, Technical Publishing House, Bucharest, 1994

[13] Ghizdăveț, Z., Năstac, D., Eftimie, M., Stanciu, I., Volceanov, A., Correlations composition-processing-microstructure on some clinkers. Implications, Romanian Journal of Materials 2016, **46** (4), 453-464

[14] Jolliffe IT, Cadima J, Principal component analysis: a review and recent developments. *Phil. Trans. R. Soc. A* 374: 20150202, 2016

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