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RESEARCH CONCERNING THE UPCYCLING OF AIR-COOLED BLAST FURNACE SLAG FROM OLD *CĂLAN* DUMP AS ADMIXTURE IN CLINKER PRECURSOR

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Cement is produced at large scale worldwide i.e., more than 4 billion tonnes. Romania produced circa 10.2 tonnes in 2022. 1.5 tonne, mainly limestone (≈70%wt.) and clay (21%wt.), is consumed for 1 tonne of clinker while 0.9 tonne of CO_2 *is released in atmosphere. Also, energy consumption per tonne of clinker ranges from 3.68 to 6.87 gigajoules. Hence, there is a higher preoccupation to find out solutions for greening the cement industry. One of the best solutions is to replace the genuine raw materials with waste or by-product like ferrous slag. This paper shows that the substitution of a part of genuine clinker precursors with air-cooled blast furnace slag (ACBFS) has at least 3 advantages i.e., preserves genuine irreplaceable resources, diminish energy consumption and reduces the* CO_2 *footprint as ACBFS do not contain significant free CaO. The paper addresses the main technological characteristics of the clinker precursors i.e., grindability and clinker ability of four ACBFS admixed receipts. For a better valorization of the ACBFS deposited in Călan dump further research are envisaged to find out the optimum receipt of the ACBFS admixed clinker precursor.*

Keywords: air-cooled blast furnace slag, dump, upcycling, clinker, grinding ability, clinker ability

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1. Introduction

Cement is the main ingredient of concrete, and it is an essential material in civil, industrial and road construction. Hence, the cement industry has been developed at worldwide scale. The total volume of cement production worldwide is estimated at 4.1 billion tonnes in 2023 [1]. Romanian cement production in 2022 was estimated at 10.2 million tonnes while in 2023 it was estimated at 9.5 million tonnes [2].

Even though cement is essential for many constructions, its manufacturing process demands high energy, huge raw genuine materials and generates many pollutants among CO_2. It is estimated that the production of one tonne of clinker, needs about 1.5 tonne of precursors, mainly limestone and clay and releases 0.9 tonne of CO_2 into atmosphere [3-5]. Limestone is the main precursor of the clinker (≈77% of the precursors mass). It is admixed with clay/dolomite (≈21%wt) and some SiO_2 providers (≈2%), like pyrite ash, iron ore, tailings etc. [6, 7]. The ordinary Portland cement technology is schematically depicted in Fig. 1. i.e., raw materials (limestone, clay, iron ore etc.) are extracted from queries, grounded, mixed, heated (calcinated) to get clinker minerals (alite-$3CaO{\cdot}SiO_2$, belite-$2CaO{\cdot}SiO_2$, celite-$3CaO{\cdot}AlO_3$, felite-$4CaOAl_2O_3{\cdot}Fe_2O_3$). Obviously, the raw materials contain small amounts of different compounds as alkali (Na_2O, K_2O), magnesium (MgO), various traces of metals. The alkali and magnesium content must remain low, as these materials are detrimental for the cement. The raw mill is calcinated in huge rotative kiln systems using low quality fossil fuels or even wastes that provide heat through burning. These kiln systems evaporate the free water in the meal, calcine the carbonate constituents and form cement minerals [7, 8].

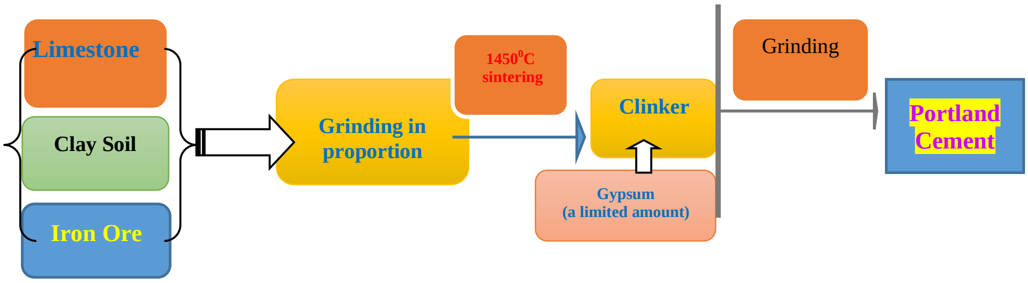


Fig.1. Schematic drawing of the ordinary Portland cement technology

Cement industry consumes huge quantities of genuine minerals, mainly limestone of good quality (>75% wt. $CaCO_3$), clay, marl etc. Hence, in the frame of enhancing the circularity of the EU economy, important effort has been devoted to find some technological solutions regarding the possibility of CO_2 emission reduction, diminish the energy consumption per tonne of cement and substitution, as much as possible, the genuine cement precursors with alternative materials resulting as by-products/waste from other industries such as the energy and metallurgic industries [9, 10]. In this regard, the issue of using ferrous slag and iron ore tailings as admixture in clinker manufacturing was considered a solution for resource saving in Romania, as well as for diminish the landfilled slag [11-17]. The ferrous slag is the main by-product of the steel industry, and the current policy of the metallurgical industry is to recycle all their by-products, to close the sustainable production loop [17, 18]. Slags are generated during hot metal production in ironmaking and steelmaking plants. Hence, the ferrous slag is considered as a part of the whole steel production process [18, 19]. The granulated blast furnace slag (GBFS) was considered the best fitted for recycling in the cement industry considering that fine grained GBFS show pozzolanic properties and can be used as admixture in cement, replacing partially gypsum and/or limestone [19, 21].

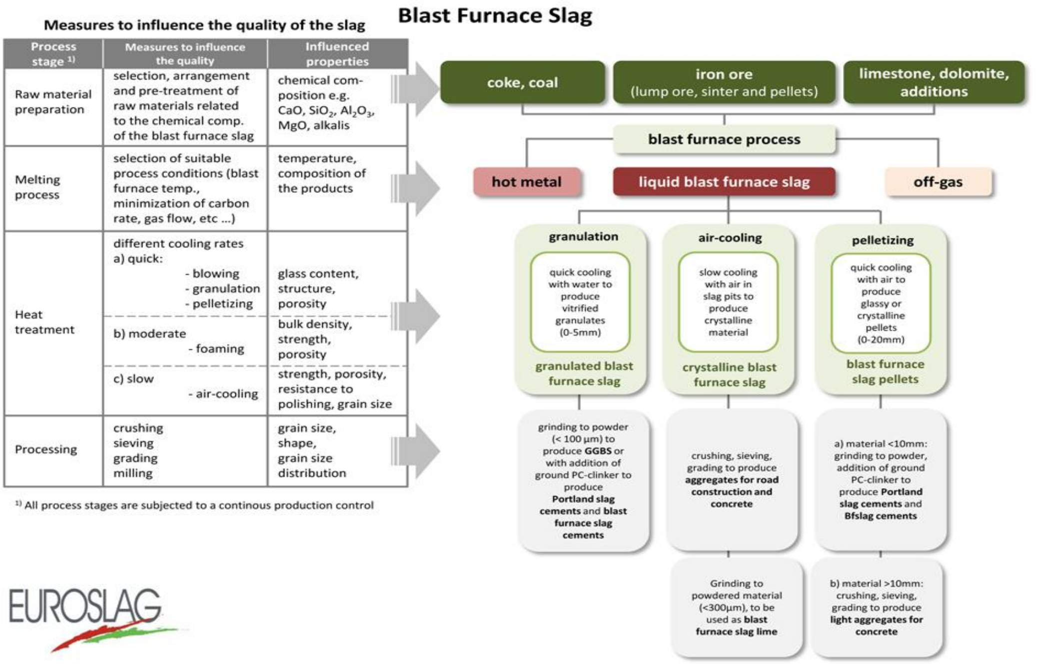
The production of GBFS implies specific installations and additional costs, therefore, in the past, the ferrous slags were landfilled in excavated pits or natural large cavities resulting in huge metallurgical waste piles, usually called slag dumps as Buituri (Hunedoara), Galați (Călan) slag dump etc. [20-22]. The recovery of the metal and mineral contents deposited in such dumps have been done by some private companies using classical technology i.e., digging for iron logs, crushing, deferizing and sieving non-ferrous fraction. The driving force of this recycling activity seems to be for the profit and lesser the environmental benefit [22]. Therefore, the elimination of the ferrous slag from old dumps is done at slow speed and still there are huge quantities that can be valorized in different application like road construction, aggregates in civil building construction, aggregates in pavement, but in more valuable way as precursor for clinker manufacturing [14,16, 22].

The recycling of the old slag dump as filler and aggregate can be considered as downcycling when compared to the recycling route as admixture in cement or as additive precursor in clinker manufacturing, which may be called upcycling [16, 20]. Where or not a ferrous slag can be upcycled depends on its chemical and mineralogical composition and on its cooling treatment [21]. Thus, the decision on the best way to valorize a slag must be based on slag characteristics appraisal. In this regard, the paper addresses the air-cooled blast furnace slag (ACBS).

The objectives of this study are: 1) to find out a new way to minimize the disposal of industrial waste from Călan ACBFS dump and 2) to examine if it is possible to lower energy and raw materials (limestone, clay, iron ore etc.) consumption in the cement manufacturing process.

Experiments were conducted to estimate the grinding ability aka grindability and clinker ability of a conventional clinker precursor admixed with different amounts of ACBFS sampled from Călan dump. Four raw mixtures were prepared with lower limestone and clay amounts than reference one. The specimens under study were characterized by X-ray fluorescence spectrometry (XRFS), Lossof-Ignition (LOI) and sieving methods. Obviously, all these methods imply weighing with adequate exactness.

The grindability study shows that the energy consumption during grinding the admixed precursors is comparable with that of reference sample. The clinker ability is a compound parameter consisting of the temperature value and calcination duration which led to decreasing the free CaO concentration less than 2% wt. The calcination duration was 30 min for all samples.



Measures to influence the quality of the slag

Process stage [1]	Measures to influence the quality	Influenced properties
Raw material preparation	selection, arrangement and pre-treatment of raw materials related to the chemical comp. of the blast furnace slag	chemical composition e.g. CaO, SiO_2, Al_2O_3, MgO, alkalis
Melting process	selection of suitable process conditions (blast furnace temp., minimization of carbon rate, gas flow, etc ...)	temperature, composition of the products
Heat treatment	different cooling rates a) quick: - blowing - granulation - pelletizing	glass content, structure, porosity
	b) moderate - foaming	bulk density, strength, porosity
	c) slow - air-cooling	strength, porosity, resistance to polishing, grain size
Processing	crushing sieving grading milling	grain size, shape, grain size distribution

[1] All process stages are subjected to a continous production control

Fig. 2. Ferrous slags and their characteristics according to Euroslag [23]

The reference specimen attains free CaO <2% after 30 min exposure at 1540°C. The clinker abilities of the four ACBFS admixture specimens were better than that of reference specimen i.e., the free CaO in all admixture samples were less than 2% wt. after 30 min calcination at 1400 °C.

2. Materials, methods and experimental procedures

For a systematic presentation, this section is divided in the following subsections i.e., raw materials, measurement methods, mixtures, grinding ability and clinker ability.

Raw materials

The rationale for using the dumped slag as a corrective admixture to the conventional clinker precursor start from the fact that the main materials currently used in the manufacture of cement clinker are limestone, clay/marl and pyrite ash (corrective addition of Fe_2O_3) [6]. The limestone and clay were sourced from Medgidia area which is a traditional supplier of precursors for Portland clinker.

The ACBFS slag was taken from Călan dump which was build up by the former SIDERMET SA Călan plant (45°44'55"N 22°59'53"E). The comminution of the old ACBFS at Călan dump is done through DESTRO technology. The entire comminution process is described in a previously published paper [16]. The sieving process was adjusted to produce 5 dimensional sorts i.e., *Sort 1: 32-63 mm; Sort 2: 16-32 mm; Sort 3: 8-16 mm; Sort 4: 4-8 mm and Sort 5: 0-4 mm*; For this study we choose Sort 3 and Sort 4 as they fulfill one of the requirements of clinker manufacturing i.e., apparent diameter less than 25 mm. The sampling and specimen preparation for XRFS measurements are also fully described in [16].

Measurement methods

The granulometric measurement of the slag sorts and of the fine-grained clinkers were performed through sieving methods with adequate column of sieves using sieve shakers machine and calibrated Mettler Toledo balances. The raw materials were analyzed through X-ray fluorescence spectrometry (XRFS) to determine the chemical composition of the materials of the clinker precursor recipes. An energy dispersive XEPOS spectrometer with 3D X-ray irradiation geometry, Spectro-AMETEK, was used to measure the elemental composition of the specimens. The software of the XEPOS can provide the results as elemental mass concentrations or as oxide (%wt.). XRFS technique is largely accepted as standard technique for waste characterization as oxide contents [24].

Loss-on-ignition (LOI) as a method for estimating carbonate content is largely used in geoscience [25]. LOI method we have used is described in detail in a previous paper [26]. Herein, we present the specific application of LOI in this study. Thus, the LOI measurement have been carried with a Caloris muffle furnace. The fine-grained specimens of about 25 g were previously dried at 105 °C for 6 h in a thermostatic electric oven. Also, the crucible used in LOI tests were calcinated at 1000 °C for 3 h. An electronic balance, KERN ABJ 220-4M type, with a 2*10-4 g accuracy was used for specimens weighing before and after heating.

The LOI at 1000 °C is calculated as:

$$LOI = \frac{m_{105} - m_{1000}}{m_{105}} * 100\% \quad (1)$$

where m_{105} is the specimen mass after drying at 105°C and m_{1000} is the specimen mass after calcination at 1000°C.

Three reproducible LOI measurements were performed to ensure data reliability.

The grindability of the raw material mixtures was estimated based on the energy consumption during sequential grinding of the raw materials up to a final fineness of approximately 10% residue on the 90 μm sieve as is described in [27, 28]. The amount of the residue on the 90 μm sieve in percent is denoted R009. Subsequently, the grinded raw mixture outcoming from grindability experiments were calcinated (clinkered) in a laboratory kiln heated with methane gas to ensure similar conditions like industrial ones. During heating up, specimens of circa 25 g were sampled at temperatures 1300, 1350, 1380, 1400 and 1450 ^{o}C. The clinkering temperatures were set up at 1450 ^{o}C and then at 1400 ^{o}C. The clinkering duration was 30 minutes. The clinker ability was estimated according to SR EN 196-5:2011 standard [29].

Raw mixtures preparation

When designing the precursor mixture of a clinker, one must consider the clinker manufacturing constrains expressed as clinker moduli as follows [6, 30]:

- Lime saturation ratio aka KH modulus range 0.96-:-1.06:

$$KH = \frac{CaO - 1.65Al_2O_3 - 0.35Fe_2O_3}{2.8SiO_2} \tag{2}$$

where CaO, Fe_2O_3, Al_2O_3 and SiO_2 denote the mass concentrations of these oxides.

Silica modulus, SM, range 2.2-:-2.4:

$$SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \tag{3}$$

Alumina modulus (IM), range 1.45-:-1.75:

$$IM = \frac{Al_2O_3}{Fe_2O_3} \tag{4}$$

The raw mixtures were calculated based on the chemical compositions of the materials composing the precursor recipes (Table 1) on condition of the moduli constrains.

The receipts of the clinker precursors were designed based on the compositions of the primary raw materials given in Table 1, as to fulfil the moduli requirements.

Table 1

The oxide compositions (wt.%) and LOI of the materials under study

Oxide (% wt.)	Limestone	Clay	Sand	ACBFS		Pyrite ash
				Sort 3	Sort 4	
CaO	54.98	6.07	0.83	34.46	33.83	
SiO_2	0.40	53.00	96.92	33.46	34.94	
Al_2O_3	0.31	18.30	0.50	10.85	10.52	

Fe_2O_3 total	0.10	7.07	0.39	11.03	9.51	75.00
MgO	0.2	1.98	0.40	3.13	3.03	
SO_3	0	0.32	0.35	1.27	2.06	
Na_2O	0.37	0.78	0	0.34	0.28	
K_2O	0.02	2.39	0.10	0.34	0.5	
LOI	43.60	9.36	0.5	4.77	3.72	-

The receipts of the reference sample and of the 4 ACBFS admixed clinker precursors are shown in Table 2. The rationale behind the chosen receipts was to admix ACBFS as much as possible on condition of ensuring proper moduli, as is shown in Table 2.

Table 2

The contents of the tested clinker precursors and their moduli values

Raw materials		Clinker precursor compositions (%wt.)				
		Reference	ACBFS Sort 3 11.6%	ACBFS Sort 3 14.5%	ACBFS Sort 4 15.4%	ACBFS Sort 4 19.5%
Limestonnee		76.5	71.6	71.2	70.1	69.4
Clay		18.2	14.2	10.5	12.3	8.0
Sand		3.9	2.7	3.7	2.3	3.1
Cynder ash		1.4	0	0	0	0
ACBFS	Sort 3	11.6	11.6	14.5	0	0
	Sort 4	0	0	-	15.4	19.5
Moduli						
S_k		0.99			0.98	
M_{Si}		2.18			2.21	
M_{Al}		1.57			1.70	

Data processing method

Experimental data interpretation in case where it is based on comparison between reference characteristics and those obtained in trials must be based on reliable outcomes. Noteworthy, the comparison between two numerical values is meaningless in case their uncertainties are unknown. [31]. Thus, we conducted a synthetical data comparison of the grindability using the slopes and intercepts of the regression lines calculated for each raw meal based on experimental results. This approach is new when compared to other studies on the same characteristics [14, 32].

The experimental data were fit based on ordinary least-square regression (OLSR) approach to assess the correlations among the grindability of the studied mixture. OLSR is the standard method applied in linear regression practice designed to give the best straight line [33]. OLSR is applied to homoscedastic entry data i.e., in case where the uncertainty of the entry measurand X is neglected and there is no correlation between X measured values [33-35]. Also, the OLSR was used to estimate the uncertainties assigned to the slopes and intercepts to facilitate their comparison. The OLSR approach for uncertainty assessment is described in detail in our previous paper [35]. Herein, we present the main core of the data processing approach to facilitate the understanding and even the appliance of such a method by the readership.

In case where the values (y) of the variable Y depends on the value of X variable (x) in a linear manner:

$$y = a * x + b \tag{5}$$

where *a* is the slope and b is the intercept of the regression line

According to OLSR, the mathematical expression of a and b are:

$$a = \frac{\sum_{i=1}^{n}(x_i-\bar{x})*(y_i-\bar{y})}{\sum_{i=1}^{n}(x_i-\bar{x})^2} = \frac{\overline{xy}-\bar{x}*\bar{y}}{\overline{x^2}-\bar{x}^2} = f(x_i; y_i; i = 1 \ldots n) \tag{6}$$

$$b = \bar{y} - a \cdot \bar{x} = g(\bar{y}, a; \bar{x}) \tag{7}$$

where *n* is the number of the regression points (x_i, y_i), i=1...n, used in OLSR procedure; $\bar{x}$ and $\bar{y}$ are the arithmetic means of the X and Y values, respectively; $\overline{x^2}$ is the mean of squared xi i.e.,

$$\overline{x^2} = \frac{\sum_{i=1}^{n} x_i^2}{n} \tag{8}$$

and $\overline{xy}$ is calculates as:

$$\overline{xy} = \frac{\sum_{i=1}^{n} x_i * y_i}{n}$$

The regression parameters **a** and **b** are function of X entry values and of dependent Y values, denoted f and g, respectively. According to the classical approach, the uncertainty assigned to *a* is calculated as:

$$u(a)^2 = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial y_i}\right)^2 * u(y_i)^2 = u_o^2 * \frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n^2 \cdot \left(\overline{x^2}-\bar{x}^2\right)^2} = \frac{u_o^2}{n*\left(\overline{x^2}-\bar{x}^2\right)} \tag{9}$$

where u_o is the uncertainty assigned to Y variable which is calculated as:

$$u_o = \sqrt{\frac{\sum_{i=1}^{n}(y_i-\tilde{y}_i)^2}{n-2}} \tag{10}$$

where $\tilde{y}_i$=a*x_i+b and n-2 are the number of degrees of freedom.

The uncertainty assigned to b is calculated as:

$$u(b)^2 = \left(\frac{\partial g}{\partial \bar{y}}\right)^2 * u(\bar{y})^2 + \frac{\partial g}{\partial a})^2 * u(a)^2 = \frac{u_o^2}{n} + \bar{x}^2 \cdot u(a)^2 = u(a)^2 * \overline{x^2} \tag{11}$$

Eq.(11) shows that u(b) is directly proportional to u(a), multiplied by $\sqrt{\overline{x^2}}$.

3. Results and discussion

The grindability experiments show that the energy consumption increases exponentially as the residue amount retained by the 90 µm sieve, denoted R009, decreases as is shown in Figs. 3 and 4.

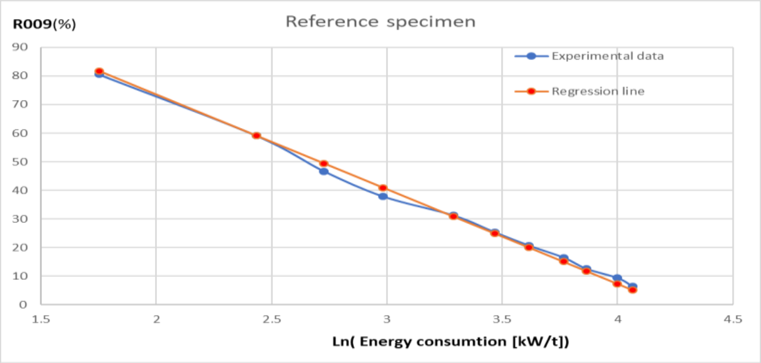


Fig. 3. Graph of the R009 quantity on the natural logarithm of energy consumption and its associated regression line for reference sample

Fig. 3 depicts the grindability of the reference sample. The dependence of R009 characteristic of the milled precursor on the natural logarithm (Ln) of the energy consumption (kW/t) is quite linear as OLSR shows up (Fig. 4)

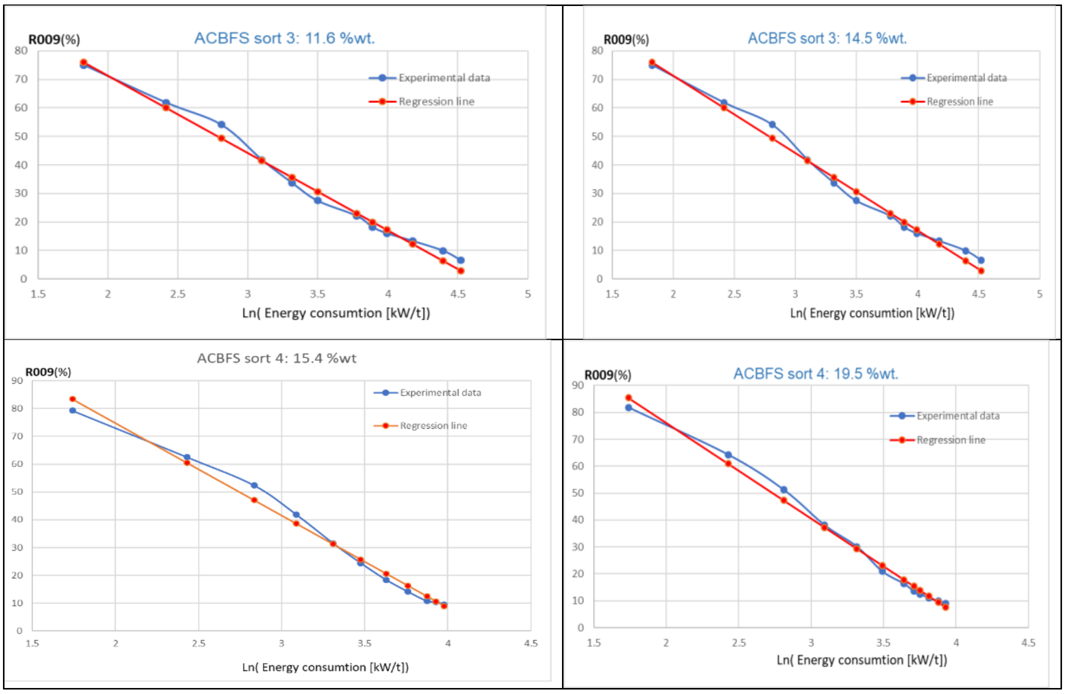


Fig. 4. Graphs of the R009 dependence on the natural logarithm of energy consumption and their associated regression lines for clinker precursor admixed with different amounts of ACBFS. The graph captions specify the type of specimens.

The values of the slope (a), intercept (b) and their associated expanded uncertainties Ua(95%), Ub(95%) for each specimen were calculated as was posted above. Also, the correlation coefficients (correl.) were calculated (Table 3). The indicator of the quality of data fitting through OLS regression is the correlation coefficient of the entry and dependent data**.** As could be seen in Table 4 and in Fig. 5 the correlation coefficient values are negative and their absolute values a higher than 0.99 except that of sample Sort 4 19.5% which is close to -0.99 i.e., -0.95. Thus, the regression lines associated to the experimental data are reliable.

Table 3

The values of a, b and their associated expanded uncertainties U_a(95%) U_b(95%)

Specimen	Reference	Sort 3 11.6%	Sort 3 14.5%	Sort 4 15.5%	Sort 4 19.5%
Slope (a)	-33.6	-28.7	-26.7	-33.3	-33.5
U_a(95%)	0.3	0.1	1.6	0.2	0.1
Intercept (b)	139.7	129.2	124.3	141.4	147.2
U_b(95%)	0.9	1.5	5.7	2.4	1.2
Correl.	-0.9986	-0.9934	-0.9956	-0.9934	-0.9536

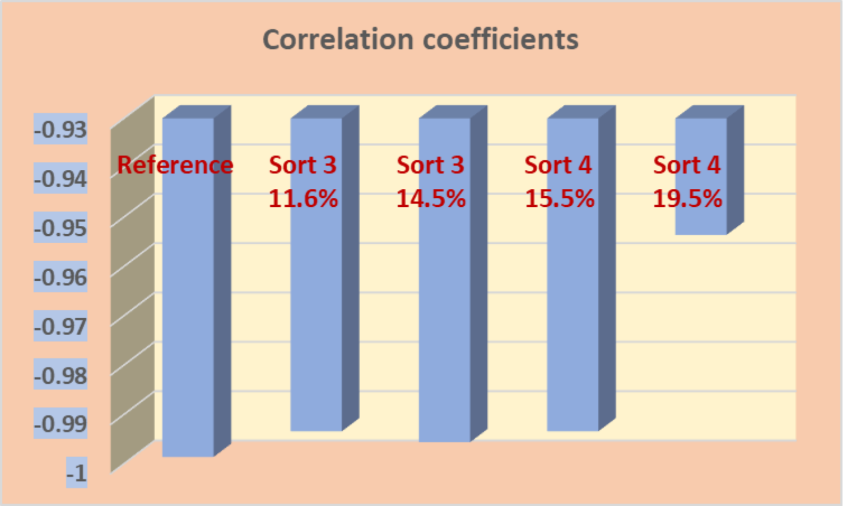


Fig. 5. Histogram of the correlation coefficient values

The slope indicates the grindability gradient i.e., the increasing rate of energy consumption as fines increases i.e., as the absolute value of the slope increases as the energy consumption increases. The relative expanded uncertainties assigned to the slopes are of the order of 1%, except Sort 3 14.5% sample, whose assigned relative expanded uncertainties is about 6%. Hence, the slopes of the studied precursors can be reliable compared as is shown in Fig. 6.

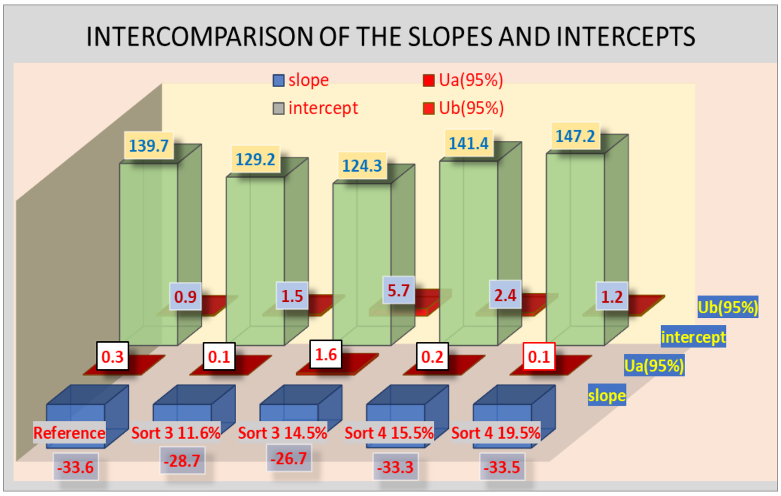


Fig. 6. Histograms of the slope, intercept and their associated values for studied samples

Thus, the sample Reference and Sort 4 have close grindability values while Sort 3 specimens have better grindability. The better grindability of the Sort 3 can be explained by the higher granularity of the ACBFS lumps whose crushing into smaller lumps help as grinder particles acting as crusher for softer lumps of limestonnee and clay. The intercept can be interpreted as initial energy necessary to crush huge lumps. The Ub(95%) of the intercepts are higher than those of the slopes, but their U(95%) values do not affect their intercomparing. Thus, Sort 4 samples show smaller intercepts values compared to Reference and Sort 3 samples.

The clinkering ability of the raw mixture was evaluated by measuring the free CaO contents of the samples extracted at different temperatures. Clinkering process is considered as complete when the free CaO concentration value is below 2% wt. The free CaO values, denoted as CaO_f, corresponding to the temperatures at which the samples were extracted are posted in Table 4.

Table 4

CaO_f values (%wt.) for temperatures at which the samples were extracted

Temperature (^{0}C)	Reference	Sort 3 11.6%	Sort 3 14.5%	Sort 4 15.5%	Sort 4 19.5%
1350	4.22	7.09	5.14	7.61	5.05
1380	2.84	4.57	2.07	5.68	2.28
1400	2.33	211	0.62	2.83	0.18
1450*	1.12	0.39	0.14	0.28	0.09
1450**	0.92	0.02	0.01	0.01	0.00

* at the start of calcination stage at 1450 ºC; **at the end of calcination stage at 1450 ºC for 30 min

The clinker abilities of the admixed clinker precursors are better than of the reference sample. This can be explained by the diminish of the $CaCO_3$ which was replaced by ACBFS which contains much lesser calcite than limestonnee. The clinker ability behavior of the tested samples in the experiment conducted up to 1450ºC is clearly depicted in Fig. 7.a. which shows that CaO_f values of the ACBFS admixture specimens are always smaller than those of reference sample at each temperature. Fig. 7.b. depicts the same behavior of the ACBFS admixed precursors calcinated up to 1400 °C.

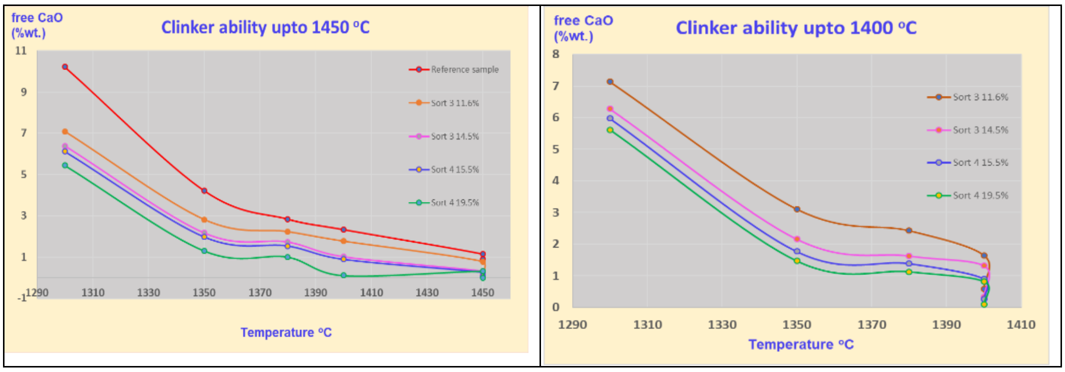


Fig. 7. Clinker ability graphs: a) calcination up to 1450 °C; b) calcination up to 1400 °C

The concentration values of CaO_f at 1400 °C (Table 4) let us suppose that ACBFS admixture may be calcinated at 1400 °C.

Table 5

CaO_f values (%wt.) during calcination up to 1400 °C

Temperature (^{0}C)	Sort3 11.6%	Sort 3 14.5%	Sort 4 15.5%	Sort 4 19.5%
1300	7.14	6.28	5.98	5.62
1350	3.11	2.16	1.77	1.47
1380	2.43	1.63	1.39	1.13
1400*	1.65	1.32	0.91	0.82
1400**	0.58	0.33	0.26	0.09

* at the start of calcination stage at 1400 °C **at the end of calcination stage at 1400 °C for 30 min

Table 5 presents the data obtained in calcination trial up to 1400°C with 30 min exposure at 1400°C. The 50 °C reduction can be explained by the ACBFS mineralogy developed during slowly cooled given rise to crystalline phased mainly silicates and aluminosilicates. Also, it leads to a significant energy saving and CO_2 footprint reduction in clinker manufacturing.

4. Conclusions

The way of grindability assessing based on OLSR is a novelty posted in the paper. This assessing approach attests that the grindability of the clinker precursors admixed with ACBFS are close to that of conventional precursor in cases of the Sort 3 and even better in case of Sort 4 specimens. This finding could lead to energy saving during grinding stage in clinker manufacturing. Another significant finding is the possibility of decreasing the calcination temperature with 50 °C which implies decreasing the energy consumption and pollution caused by gases and energy releasing in atmosphere by the clinkering kilns. This study opens a way of valorization of approximately 2 million tonnes of ACBFS landfilled at Călan. The outcomes of this study ground further research toward assessing the whole set of technological characteristics like clinker mineralogy, reactivity, heat of hydration etc., to establish the optimum amount of ACBFS in clinker precursor.

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