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A Ten-Year Study on Alkali Content of Coal Fly Ash

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Abstract: After years of decline, coal consumption has risen significantly in the last year (2021), driven mainly by the ever-increasing demand in fast-growing Asian countries and fostered by rising gas prices in Europe and the United States. Coal is both the largest electricity production source and the largest source of carbon dioxide emission. Coal-fired plants produce electricity by generating steam by burning coal in a boiler, but also large amounts of coal fly ash. Coal fly ash contains essential constituents for cement production, such as Ca, Si, Al, and Fe. Application of coal-fired ash to produce clinker at high doses may reduce the limestone content in the raw mix. Furthermore, coal fly ash is one of the industrial source materials utilized in the development of low-carbon cements and concretes on account of its chemical characteristics. The monitoring methodology is based fundamentally on the analysis of a set of variables (Na_2O_e, Na_2O, K_2O, free CaO, and reactive silica content and fineness) over time. Weak relations between Na_2O and K_2O, and Na_2O_e, and reactive silica content were found. This applied research has been done to verify previously done research. The scope of this paper is to assess the alkaline content of coal fly ash over a period of 10 years. The Na_2O-equivalent of coal fly ash ranged from 0.35% to 2.53%, with an average value of 0.79%. These values should be taken into account producing concretes made with potentially reactive aggregates in order to mitigate the alkali–silica reaction (ASR).

Keywords: coal fly ash; alkalis; grate furnace combustion; cement constituent

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1. Introduction

Coal-fired electricity generation process has the disadvantage that generates large amounts of coal fly ash. Its properties strongly depend on the firing conditions and the original source of coal. It should be noted that the worldwide coal ash exploitation is poor causing a landfilling problem. World total production in 2020 was 7575 Mt (China: 3760 Mt; India: 760 Mt; Indonesia: 564 Mt; Australia: 493; USA: 485 Mt; Russia: 398 Mt; UE27: 301 Mt). China was the major producer, and the production grew up in Russia, Indonesia, India, and Turkey, while it declined in the United States and the European Union.

Following a record of over 10,000 TWh in 2018, in 2020 global coal-fired generation fell to 9440 TWh (35.2% world share in 2020) [1]. The use of renewables in many countries reduced the share of coal in the electricity mix prompted the 2020 drop in coal-fired generation. Nevertheless, coal-fired generation is showing strong recovery in 2021 by the rising gas prices. In addition, retrofitting coal-fired power plants with Carbon Capture, Use and Storage (CCUS) can help prevent the closure of coal-fired power plants in the context of the Net Zero Emissions by 2050.

Coal-fired power generation increased worldwide by almost 5% in 2021 and by a further 3% in 2022. The coal consumption in Spain for power generation increased a 9% in 2021. Spain consumes 10.4 million tons of coal (2020) leading to around 147,000 tons of coal bottom ash and 1.0 Mt of coal fly ash [2].

The European Circular Economy Action plan sets forth the principles, goals, and actions dealing with resource exploitation and waste [3]. In this respect, it is striking that the utilization of some industrial wastes, such as coal fly ash, as cementitious constituents in the production of Portland cements and concretes is a lever for achieving net-zero carbon dioxide emissions set in the cement industry roadmap to beyond net zero emissions [4]. In addition, the European construction sector is responsible of approximately 35% of the global waste generation. Accordingly, construction sector, in general, and cement sector, in particular, play a major role in circularity.

The main advantages of using coal fly ash in cements are the improvement of the concrete durability and the climate change mitigation by lowering the clinker factor. Furthermore, concrete carbonation is a physicochemical process that absorb carbon dioxide and, therefore, helps to tackle climate change and to enhance sustainable development. In addition, coal fly ash cement-based materials carbonate faster than common cement-based materials made without supplementary cementitious materials [5]. To summarize, coal fly ash utilized to produce Portland cements and concretes is a critical decarbonization lever.

The American Society for Testing and Materials (ASTM) classifies coal fly ashes as Class C and Class F based on the silica, alumina, iron oxide, and calcium oxide contents [2]. Class C originates from lignite and sub-bituminous coals, whereas Class F is produced from bituminous and anthracite coals. The amount of silica, alumina, and iron oxide is between 50% and 70% in Class C coal fly ash, while Class F contains more than 70%. In addition, Class C contains more than 20% calcium oxide, and, therefore, it presents pozzolanic activity itself, without the presence of any activator. By contrast, Class F has less than 10% CaO, and, then, it requires an activator for the pozzolanic reaction, such as Portland cement. According to the European standard EN 197-1:2011 [6], coal fly ash content in common Portland cement ranges from 6% to 20% (CEM II/A-V), from 21% to 35%, (CEM II/B-V), from 11% to 35% (CEM IV/A (V)) and from 36% to 55% (CEM IV/B (V)).

The advantages of coal fly ash as a cement component derive from its pozzolanic activity, i.e., it combines with calcium hydroxide generated by cement hydration reactions to form C-S-H gel, which is a calcium silicate hydrate that contributes to Portland cement strength [5]. Coal bottom ash also exhibits a good pozzolanic activity when it is grounded [7]. By contrast, one disadvantage of some coal fly ashes is a high level of alkalis, limiting its use in the Portland cement and concrete production.

The primary compounds for all types of coal fly ashes are silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), and calcium oxide (CaO). Bituminous coal fly ash has higher contents of SiO_2, Fe_2O_3 and ignition loss, by contrast it has lower amounts of CaO and MgO than the rest of ashes. Table 1 shows the average coal fly ash alkali content in Europe, USA, China, India, and Australia and in function of the coal type [8,9]. The values range from 0.1% to 4.7%. Accordingly, low-alkali content coal fly ash would be recommendable to produce concrete made with potential reactive aggregates, such as slates, quartzite, hornfels, granites, gneiss, and serpentine, to minimize alkali-aggregate reactivity (AAR). As was well known, the alkali ions content in the concrete pore solution affects negatively concrete durability with regard to the alkali–silica reaction (ASR), when potentially reactive aggregates are used. ASR generates swelling gel products from the reactive aggregates leading to a significant expansive pressure in the concrete promoting the appearance of cracks. Furthermore, alkalis enhance coal fly ash reactivity [10], but also, promote the generation of a passive layer on the steel reinforcement preventing the steel corrosion. Then, it should be taken into account that coal fly ash alkali content also influences the final amount of the alkalis in the concrete pore solution.

Table 1. Coal fly ash alkalis by region and coal type [8,9].

Alkali	Europe	USA	China	India	Australia	Bituminous	Sub-Bituminous	Lignite
Na_2O	0.1–1.9	0.3–1.8	0.6–1.3	0.5–1.2	0.2–1.3	0–4	0–2	0–6
K_2O	0.4–4	0.9–2.6	0.8–0.9	0.8–4.7	1.1–2.9	0–3	0–4	0–4

Finally, a critical review on the application of coal fly ash is provided in reference [2].

It is now widely acknowledged that the level of risk of degradation and loss of serviceability induced by the alkali–silica reaction (ASR) is mainly related to the alkali-reactivity degree of the aggregates, the total alkali content of the concrete and the environment severity. Furthermore, it is also a well-known fact that, when using potential reactive aggregates, the most important criteria to consider while defining a mix design to minimize or to prevent the deleterious alkali-silica reaction (ASR) expansion in concrete are [11]:

- Restricting the concrete pore solution alkalinity by utilizing blended cements containing active mineral additions such as coal fly ash. They must meet a well-defined limit of alkali content;
- Constraining the ASR gel expansion by modifying the gel nature by using lithium-containing products;
- The use of low-alkali cements, i.e., $Na_2O_e = Na_2O + 0.658\ K_2O < 0.6\%$.

In this work, fly ashes from the combustion of a South African coal were investigated for use in concrete and Portland cement. Assessment of the aggregates with potential alkali–silica reactivity is currently a widespread practice owing to the limited availability of natural aggregates free of potentially alkali-reactive constituents. Therefore, the main objective of this project is to gain more in-depth knowledge of the alkali content variability in the coal fly ash that occur along the time in the combustion process for a correct selection of the coal fly ashes as one of the most appropriate alkali–silica reaction (ASR) preventive measure. In addition, the authors will seek to achieve various relations between some data (Na_2O_e, Na_2O, K_2O, free CaO and reactive silica content and fineness).

2. Materials and Methods

2.1. Coal Fly Ash Sampling

In total, 765 spot coal fly ash samples were collected at the point of release for 10 years. The aim of this research was to characterize the alkali content of samples generated from South African coal at Carboneras power plant. Almería, Spain (Table 2). Samples were gathered with the coal-fired power plant running at full load (Table 3). Henceforth, alkali content of these samples is truly representative of coal-fired power plants under similar combustion conditions and by using a similar equipment.

Table 2. South African coal analysis.

Ultimate Analyses	Analyses Method	Not Dried	Dried with Air	Dry Basis
Moisture (%)	ASTM D 5142:2004	4.97	2.15	-
Carbon (%)	ASTM D 5373:2008	67.21	69.20	70.72
Hydrogen (excluido el H de la humedad) (%)	ASTM D 5373:2008	3.62	3.73	3.81
Nitrogen (%)	ASTM D 5373:2008	1.54	1.59	1.62
Total sulphur (%)	ASTM D 4239:B:2005	0.35	0.36	0.37
Ash content (%)	ISO 1171:1997	14.97	15.41	15.75
Volatile matter (%)	ISO 562:1998	23.38	24.07	24.06
The percentage of oxygen is found by difference (excluding moisture oxygen from the analysis) (%)		7.34	7.56	7.73
Gross calorific value (kcal/kg)	ISO 1928:2009:E	6265	6451	6593
Hard grove grindability index (HGI) with a moisture content of (%)	ISO 5074:1994	54 1.41	-	-
CO_2 emission factor (Directive 2003/87/EC) (tCO_2/TJ)		97.0		

Table 3. Data with regard to the power station.

Equipment/General	Part	Group 1	Group 2
General	Power	576.9	582
	Year	1985	1997
Boiler	Type	Combustion in tangential swirl burners	Combustion in tangential swirl burners
	Producer	Combustion Engineering	ABB
	Coal burners	24	24
	Main steam flow-rate	1679 t/h	1679 t/h
	Superheated steam flow-rate	1525 t/h	1525 t/h
	Initial steam pressure	176 bar	176 bar
	Superheated steam pressure	41 bar	41 bar
	Feedwater temperature	253 °C	253 °C
	Main steam inlet temperature	541 °C	541 °C
	Energy yield of the steam boiler	89.42%	89.42%
Condenser	Type	Dual-pressure condenser	Dual-pressure condenser
	Cooling fluid	Seawater in an open circuit cooling system	Seawater in an open circuit cooling system
	Condenser water flow rate	60.408 m^3/h	60.408 m^3/h
Turbine	Manufacturer	Bazán/G.E.E.	data
	Maximum power	577 MW	577 MW
	Number of bodies	4	4
	Number of removals	7	7
	Operating speed	3000 rpm	3000 rpm
Alternator	Manufacturer	General Electric	General Electric
	Power	636 MVA	636 MVA.
Transformer	Manufacturer	Westinghouse.	Westinghouse.
	Power	209.5 MVA	209.5 MVA

The Litoral thermal power plant (Endesa), located in 1,788,547 square metres in Carboneras, Almería, Spain, was built in 1979 to cover the need to increase electrical power. It consists of two generation groups generating 1159 MW of power in all (Table 3). Each of these groups consists of the following equipment: a boiler, a turbine, and an alternator. Group 1 presents a capacity of 577 MW, while group 2, has a capacity of 582 MW. From 1985 to 2021, the installation has generated more than 180,000 GWh. The plant has a Port Terminal for the purpose of unloading coal for the Litoral Thermal Power Plant.

Currently, the coal fired power plants generate the majority of the electricity worldwide and produce the highest rate of CO_2 per kilowatt hour (Table 4) [12].

Table 4. CO_2 emissions from several power generation technologies [12].

Technology	CO_2 Emissions (Kg/MWh)
Pulverised coal-fired subcritical	850
PC-fired supercritical	800
	670

Figure 1 shows a SEM photograph of coal fly ash particles. The hollow spherical particles present lower density than compact spherical particles (high density). They are wastes of power plant coal combustion produced in large quantities.

2.2. Alkali Content, Reactive Silica, Free-CaO, and Fineness Determination

Alkali content was determined by atomic absorption spectrophotometry (AAS) [13]. Reactive silica, free CaO and fineness (residue on 45 μm) were determined according to the standards UNE 80225:2012 [14], UNE 80243 [15] and EN 196-6:2010 [16], respectively.

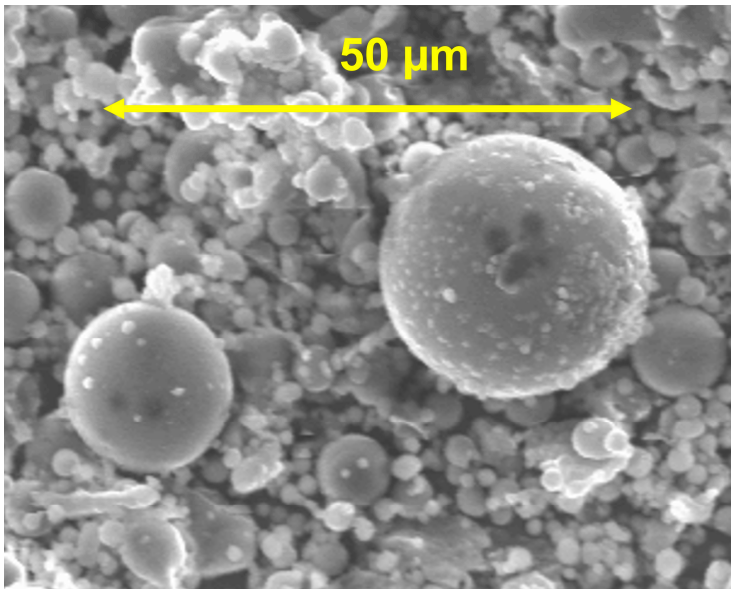


Figure 1. SEM image of coal fly ash particles.

2.3. Coal Fly Ash Chemical Analyses

Coal fly ash average chemical composition is given in Table 5. X-ray fluorescence spectrometry (XRF) was utilized to determine the SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, K_2O, Ti_2O_5, and P_2O_5 content by using a spectrometer Bruker S8 Tigger 4 kW model.

Table 5. Average chemical compositions of the tested coal fly ash (%).

Parameter	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Ti_2O_5	P_2O_5	LOI	IR [1]	Cl^-
Content (%)	50.5	28.9	4.7	5.0	1.8	0.21	0.8	1.56	0.76	3.6	71.3	0.001

[1] Insoluble residue determined by the Na_2CO_3 method (European standard EN 196-2).

Insoluble residue, IR, loss on ignition, LOI, and chloride content determination were performed according to the European standard EN 196-2 [13]. Table 5 shows that the coal fly ash collected for this research program, which is a common by-product of a low-lime bituminous coal combustion, meet the European standard EN 450-1 [17].

3. Results and Discussion

3.1. Alkali Content over the Years

Figure 2 shows the alkali content results obtained in 765 coal fly ash spot samples taken for 10 years at the Carboneras coal-fired power station. The alkali content refers to the content of Na_2O and K_2O in cement. In almost all cases, the percentages were lower than 2% and most of the samples displayed percentages lower than 1%.

The necessary condition for the initiation of the alkali–silica reaction in concrete is that the Portland cement must contain a high level of alkali. Normally, alkali–silica reaction is due to the reactivity between hydroxyl (OH^-) ions generally associated with alkalis (Na_2O and K_2O) in the concrete constituents, such as Portland cement, and silica minerals in the concrete mix, which can result in the expansion and microcracking of concrete [18].

When reactive aggregates are used, the pozzolanic blended cements with low alkali content should be used [18]. Pozzolanic constituents reduce the Ca/Si ratio of C-S-H gel, and this allows more alkalis to be incorporated in the calcium silicate hydrates [19]. Some national standard specifies that the alkali content in Portland cement, calculated by Na_2O + 0.658 K_2O, should not exceed 0.60%. Therefore, the coal fly ash alkali content in blended cements should be as low as possible. The Na_2O-equivalent of coal fly ash in Figure 2

ranges from 0.35% to 2.53%, with an average value of 0.79%. Despite being the same coal origin, the Na_2O-equivalent results for coal fly ash showed a relatively high degree of dispersion, ranging from 35% to 2.53%. This fact reflects the variability in the coal and burning conditions over the time.

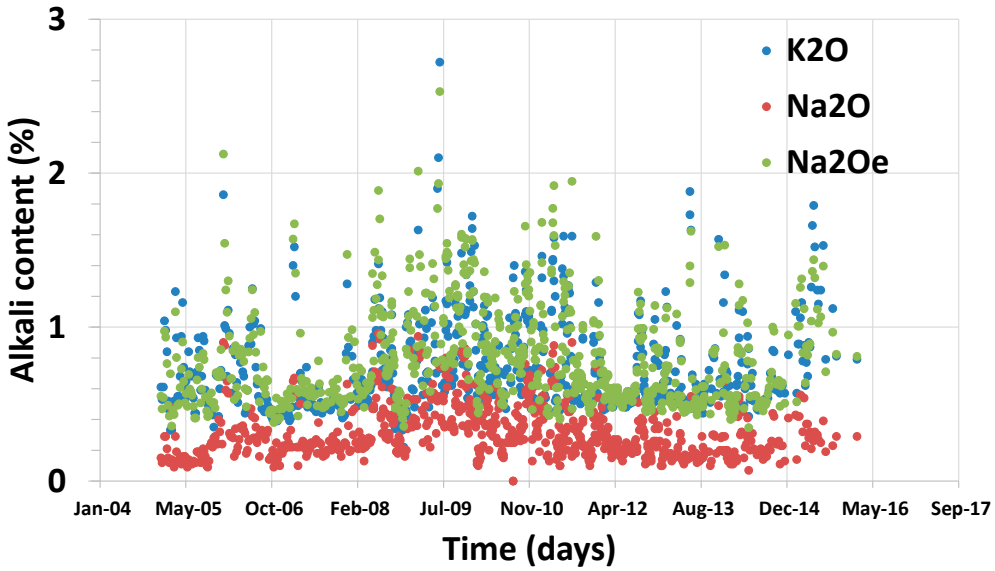


Figure 2. Maximum, minimum, and average values of Na_2O, K_2O, and Na_2O_e in coal fly ash.

Coal fly ashes are utilized worldwide to manufacture blended cements and concretes. This pozzolanic constituents provides enhanced properties including better durability in attacking environments, long-term mechanical strength, and a lower hydration heat [2,5]. These properties are affected directly by the alkali content in the coal fly ash [20].

3.2. The Na_2O-Equivalent Relationships

Figure 3 shows the relationship between the Na_2O-equivalent and K_2O, reactive silica, 45 μm residue and free lime in coal fly ash. Increasing Na_2O percentage will increase K_2O content. In addition, increasing Na_2O-equivalent percentage will increase reactive silica amount. It was suggested that alkali content in coal fly ash mainly depends on reactive silica amount [20]. By contrast, when the 45 μm residue or free lime in coal fly ash are linked to the Na_2O-equivalent, there is no clear equation between both variables.

It is well-known that knowing the relationship among variables will guide further analyses. A weak relationship seems to exist between Na_2O-equivalent and reactive silicon. Accordingly, with the rise in reactive silicon a higher alkali content is expected. Nevertheless, the knowledge of one parameter cannot be used to deduce the other.

Itskos et al. found a considerable deviation in the coal fly ash chemical composition. Therefore, they believed necessary an intense monitoring in terms of its possible utilization, i.e., effective homogenization. In addition, not only alkalis content but also variations of CaO, SiO_2, and SO_3 contents of the coal fly ash are decisive for its utilization as a constituent in Portland cement [21].

An early acceleration of Portland cement constituent's hydration by alkali has been found [22], leading to a shorter induction period [23]. Alkalis increase the initial and second heat evolution peaks of Portland cement hydration [24]. The acceleration effect of the alkali can be attributed to the increase in the pH value of the concrete pore solution, and the subsequent $Ca(OH)_2$ solubility decrease. Furthermore, alkalis enhance the calcium silicate dissolution and the formation of $Ca(OH)_2$, as well as a faster rate of nucleation and crystallization of hydrates, but suppresses the formation of ettringite, $(CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O$ [22]. The high silicon concentration in the concrete pore solution promotes the C–S–H gel generation [25], showing a higher compressive strength at

early age [26]. By contrast, hydration becomes decelerated, and the mechanical strength of concrete is negatively affected with advancing age [22,27]. However, the compressive strength decrease in cement-based materials is related to other factors, which need further research. Accordingly, the mechanism is not yet clear.

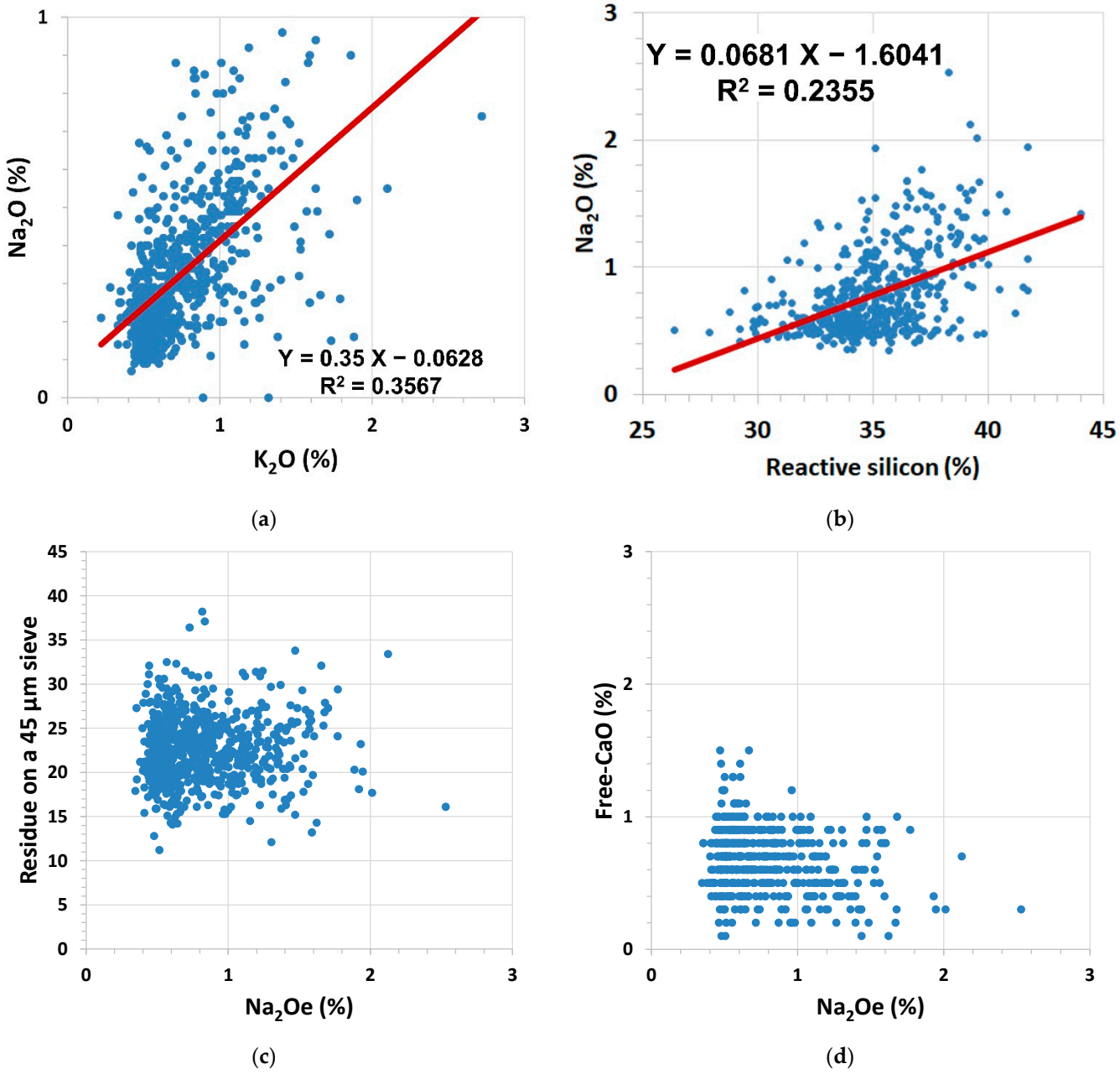


Figure 3. Relationship between the Na_2O-equivalent and: (**a**) K_2O; (**b**) reactive silicon; (**c**) 45 µm residue; (**d**) Free lime.

3.3. Reactive Silicon versus 45 µm Residue Relationship

Figure 4 plots the relationship between reactive silicon and 45 µm residue. No correlation was found between these two variables. According to reference [28], the average fineness (and standard deviation) on 45 µm, was 22.5% (3.7%), and the minimum, maximum and average values are 26.40%, 44.00%, and 34.95%, respectively (Figure 3b). It is assumed that the coal fly ash retained on a 45 µm sieve is an indirect indicator of the residues on the 63 µm, 90 µm and 200 µm mesh sieves [28].

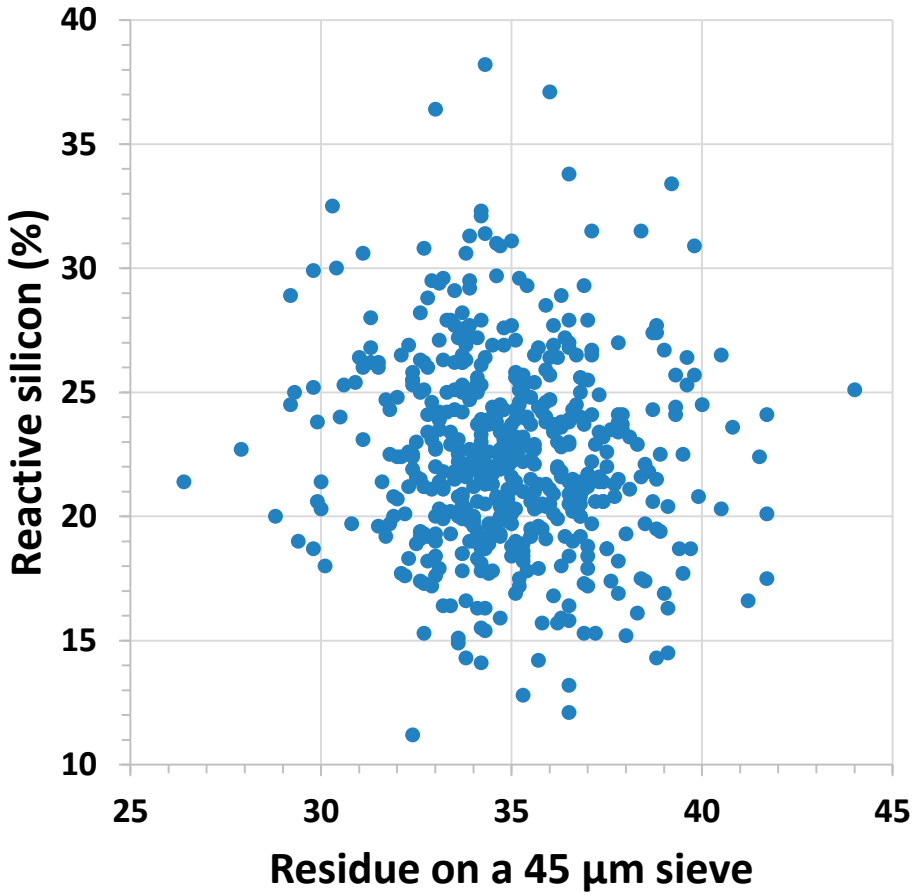


Figure 4. Relationship between reactive silicon and 45 µm residue.

Although no overall connection was found in this study between reactive silicon and 45 µm residue, it is well-known that the finer the coal fly ash is and the higher reactive silicon content in it, the more effective it becomes in terms of mechanical strength and durability [29,30]. This enhancement in the mechanical properties with the fineness increase has also been found in other pozzolanic materials [31].

Furthermore, the lack of relationship found between reactive silicon and 45 µm residue suggests that the reactive silicon is uniformly distributed in the coal fly ash regardless of its particulate size.

We know well that active silica is the fraction of the total silica which is involved in the pozzolanic reactions producing calcium silicate hydrates with a low Ca/Si ratio (C-S-H gel) to which the strengthening of blended cements is attributed. An empirical correlation between compressive strength, fineness and soluble silica of coal fly ash has been reported [32]. Reactive silica is a non-crystalline phase, present in the amorphous part of the coal fly ash, which is proportional to the compressive strength gain in blended cements [33]. In addition, it has been reported that total silica in coal fly ash can vary from 32% to 42% over 10 years [21].

4. Conclusions

Evaluation of the Na_2O, K_2O, reactive silica, 45 µm residue and free lime content in 765 coal fly ash samples taken for 10 years was performed. The findings are concluded as follows:

1. The Na_2O-equivalent of coal fly ash ranged from 0.35% to 2.53%, with an average value of 0.79%. These values should be taken into account producing concretes made with potentially reactive aggregates in order to mitigate the alkali–silica reaction (ASR);

2. There is a positive correlation between Na_2O and K_2O of coal fly ash and there is only a weak relationship between the Na_2O-equivalent and reactive silica. Therefore, the mathematical relationship between the two variables is such that knowledge of one key cannot be used to deduce the other;
3. Conversely, this study confirms no correlation between the reactive silicon and the 45 μm residue. In addition, non-correlation between the Na_2O-equivalent content and the 45 μm residue or the free lime in coal fly ash were found;
4. The most significant performance characteristics of coal fly ash in concrete are the particle size (percentage retained on a 45 μm sieve), reactive silica content and the Na_2O-equivalent amount. They should be determined independently since a weak or non-correlation was found between them.

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