Two methods for extracting alkalis from fly ash and the contribution of these alkalis to the total alkali content of concrete with time

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Abstract

The cement clinker forms the main source of the alkalis in concrete, and the alkali-aggregate reaction (AAR) occurs owing to the interaction between the reactive aggregates and alkalis in concrete. These alkalis are easily soluble and are introduced into the solution during the early stages of the hydration of the cement paste. Additionally, the components in the concrete contain alkalis that can contribute to the AAR over time. These alkalis are generally leached over time in highly humid environments or water. In recent years, the potential extraction of alkalis with time from aggregates containing alkaline components has been extensively studied. However, other components of concrete that also contain alkaline components, such as supplementary cementitious materials (SCMs), have received little attention. The alkali extraction methods studied in this work allow determining the leachable alkalis of the fly ash and their contribution to the development of expansive reactions over time.

In general, SCMs can mitigate the alkali-silica reaction in cement or concrete owing to the partial substitution of the cement clinker, which rapidly releases alkalis, Additionally, SCMs produce a combination of easily soluble alkalis in the hydrated products. The alkali content of SCMs varies depending on their type; but also the substitution percentage differs depending on the type of addition to be effective.

However, the SCMs do not react completely, thereby leaving partially hydrated particles, which contain a certain quantity of alkalis. Over time and in the presence of water, these alkalis may be leached in a similar manner to that of very fine aggregates.

In the present study, two methods for the extraction of alkalis in hot water and alkaline solutions from unreacted SCMs namely, fly ash over time were evaluated. For this purpose, three different fly ash samples using different alkaline solutions, temperatures, extraction times, and other parameters were evaluated. To verify the methods of extraction, have been studied different concretes manufactured with some of the additions studied and exposed to high water environment for several years.

Keywords: *alkali leaching; pozzolanicity; fly ash; concrete; supplementary cementitious materials.*

1. INTRODUCTION

Fly ash is a by-product obtained by electrostatic precipitation or mechanical capture of the dust that accompanies the combustion gases from the burners in thermoelectric plants, which are fueled by pulverized coal [1]. This fly ash is used as a supplementary cementitious material (SCM) to partially replace Portland cement concrete [2]. Notably, fly ash, when used as an SCM, contributes to the properties of hardened concrete through pozzolanic and/or hydraulic activity. Furthermore, fly ash often contributes 15 to 25% of the mass of concrete and a high dosage of 40–60% can be utilized in structural applications [3]. The incorporation of fly ash can strongly affect the properties of fresh concrete and durability of hardened concrete, as well as reduce the potential alkali-silica reactivity in the concrete. The presence of 20-40% wt%. of fly ash in cement is known to suppress the alkali-aggregate reaction (ASR) [4].

Coal fly ash consumes calcium hydroxide from a pore solution and lowers the alkalinity of the solution by forming a C–S–H gel with a low Ca/Si ratio. In addition, this product reduces capillary porosity. Accordingly, the concrete expansion depends on the calcium content of coal fly ash, CaO/SiO_2 ratio [5], and alkalis available over time [6].

The study of the methods for leaching alkalis from SCMs, such as fly ash, can determine the potential contribution of alkalis to the alkali-silica reaction over time. The test conditions, such as the aggregate and cement fineness, solution used for extraction, aggregate-cement/solution ratio, temperature, and test duration greatly varied between reported studies [7]. The aforementioned conditions influenced the rate of alkali leaching and absolute amounts of the leached alkalis. The most aggressive solution used for extraction was a saturated lime solution in the procedure proposed by the Laboratoire Central des Ponts et Chaussées, France [8].

In this study, the leaching of alkalis from fly ash is analyzed using two methods: extraction of alkalis in hot water and alkaline solutions. In the first method, described in [9], the test conditions for the extraction of the alkalis are a water temperature of 100 ºC for 10 min and 24 h of rest [10]. However, the second method used in this study tested the fly ash samples in four different alkaline solutions for 28 and 90 d after conducting the pozzolanicity test for 14 and 180 d based on the concentration obtained by simulating the liquid phase in concrete [9].

2. CHARACTERIZATION OF SCMS

2.1 Samples of Fly Ash

In this study, three types of fly ash from the thermoelectric plants of Anllares, León, Spain (Figure 2.1), Lada, Asturias, Spain (Figure 2.2), and Meirama, La Coruña, Spain (Figure 2.3) were used.

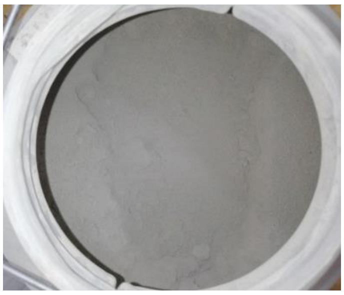

Figure 2.1: Fly ash from Anllares

Figure 2.2: Fly ash from Lada

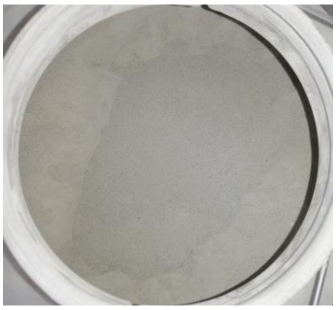

Figure 2.3: Fly ash from Meirama

2.2 Mineralogical composition

The major crystalline compounds that constituted the fly ash samples were determined using an X-ray diffractometer (Bruker Model D8, advance diffractometer with a 2.2 kW copper anode X-ray tube).

The crystalline and amorphous compounds present in the fly ash samples were quantified by analyzing the X-ray diffraction patterns obtained using the Rietvelt Topas refinement program. Table 2.1 lists the percentages of the crystalline and amorphous compounds present in the three types of fly ash.

Table 2.1 Crystalline and amorphous phases present in the three types of fly ash

Compound	Anllares Fly Ash	Lada Fly Ash	Meirama Fly Ash
Amorphous	87.8 %	59.3 %	72.9 %
Mullite	6.8 %	21.5 %	15.7 %
Quartz	4.0 %	15.8 %	9.3 %
Anorthite	0.9 %	2.7 %	1.4 %
Anhydrite	0.3 %	0.0 %	0.6 %
CaO	0.2 %	0.7 %	0.1 %

Table 2.1 reveals that the fly ash samples mostly possessed amorphous mineralogical composition with a few crystalline components such as quartz, mullite, anorthite, and CaO, which were present in very small quantities. The fly ash with the least quantity of amorphous compounds and thus, the lowest pozzolanic activity was the one obtained from the Lada plant.

2.3 Chemical composition

The chemical compositions of the three types of fly ash were analyzed using the X-ray fluorescence technique with a wavelength dispersion X-ray spectrometer (Bruker S8 Tiger). The alkali content was determined using the inductively coupled plasma technique; the percentage of CO_2 was determined by loss on ignition in accordance with the UNE-EN 196-2 standard [11]. Table 2.2 lists the percentages of the most stable oxides present in the fly ash samples.

Table 2.2 Chemical composition of the fly ash samples

Compound	Anllares Fly Ash	Lada Fly Ash	Meirama Fly Ash
SiO_2	52.40 %	59.67 %	54.65 %
Al_2O_3	23.39 %	20.12 %	21.86 %
Fe_2O_3	6.77 %	7.02 %	6.88 %
CaO	5.65 %	1.67 %	6.04 %
CO_2	3.94 %	4.97 %	5.35 %
K_2O	2.39 %	1.93 %	1.43 %
MgO	1.94 %	1.58 %	0.05 %
Na_2O	1.40 %	1.18 %	1.16 %
TiO_2	0.91 %	0.90 %	0.87 %
P_2O_5	0.58 %	0.16 %	0.69 %
BaO	0.22 %	0.16 %	0.23 %
SrO	0.11 %	0.05 %	0.16 %
SO_3	0.11 %	0.09 %	0.11 %
MnO	0.05 %	0.04 %	0.05 %
Rb_2O	0.04 %	0.09 %	0.05 %
ZrO_2	0.03 %	0.02 %	0.17 %
Cr_2O_3	0.03 %	0.27 %	0.13 %
NiO	0.02 %	0.02 %	0.02 %
ZnO	0.02 %	0.02 %	0.02 %
Cl^-	0 %	0.03 %	0.05 %
CuO	0.01 %	0.01 %	0.02 %
Na_2O_e	2.97 %	2.45 %	2.10 %

In addition, the insoluble residue, reactive silica, and reactive calcium oxide were analyzed according to the EN 197-1 standard [12], as shown in Table 2.3.

Table 2.3 Reactive calcium oxide, insoluble residue, and reactive silica content in the fly ash samples

Compound	Anllares Fly Ash	Lada Fly Ash	Meirama Fly Ash
CaO reactive	4.4 %	0.6 %	2.2 %
Insoluble residue	29.4 %	29.8 %	24.7 %
Reactive silica	37.6 %	47.4 %	36.6 %

According to the EN 197-1 standard [12], siliceous fly ash must contain at least 25% of reactive SiO_2 and less than 10% of reactive CaO. Table 2.3 shows that all three fly ash samples complied with these requirements.

2.4 Pozzolanicity

The pozzolanicity values of the fly ash samples were determined according to the EN 196-5 standard [13]. The test was conducted at 7, 14, 90, 180 and 270 d, although the standardized test indicated that the test period should be 7 and 14 days.

Figure 2.4 shows the pozzolanicity graph of the three types of fly ash at different times.

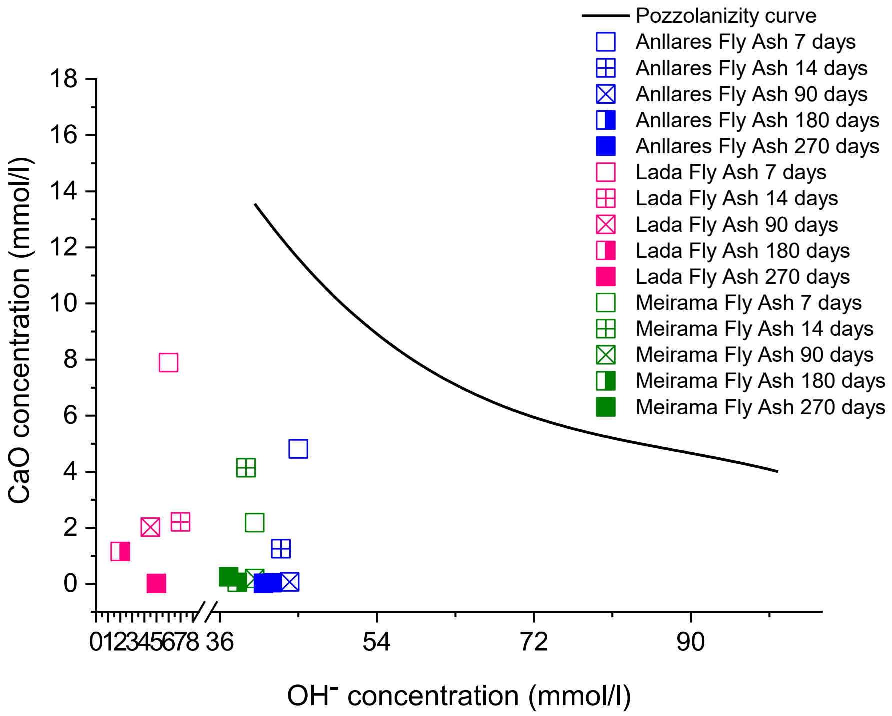

Figure 2.4: Pozzolanicity of the fly ash samples at different times

All tested fly ash has developed pozzolanic activity since the first test age.

3. TESTING METHOD

The extraction of alkalis from fly ash was analyzed to evaluate their possible contribution to the porous phase of concrete once hardened and in contact with moisture. For this, two methods were implemented: (i) the extraction of alkalis in hot water, which simulated the potential leaching of alkalis during the hydration process of the cementitious paste (Method 1) and (ii) extraction in an alkaline medium (Method 2), which simulated the potential extraction of alkalis from the porous phase of concrete.

In both methods, the contents of the alkalis were determined using an inductively coupled plasma (Varian model 725-ES). The alkalis were expressed as % Na_2O_e as follows:

$$\% \, Na_2O_e = \% \, Na_2O \cdot \% K_2O \cdot 0.658 \tag{1}$$

The result obtained from the alkali extraction was expressed as a percentage of the alkali leached with respect to the total percentage of alkalis as follows:

$$\% \text{ Extracted alkalis} = \frac{\%Na2Oe \ (Leached)}{\% \ Na2Oe \ (total)} \cdot 100 \tag{2}$$

In some cases, these results may be negative, such as those obtained using Method 2; this phenomenon may be associated with the combining of alkalis owing to the saturation of the extraction solutions.

3.1 Method 1: Extraction of alkalis in hot water

This test simulated the alkali extraction that occurs during the initial phase of the concrete mix. The test method involved mixing a sample of each fly ash with deionized water with a liquid: solid ratio of 10:1 at a temperature of 100 ºC for 10 minutes. All results were obtained as duplicates. The samples were filtered after 24 h of rest, and their pH values and conductivities were measured. Subsequently, the contents of the extracted alkalis were determined using the inductively coupled plasma technique.

3.2 Method 2: Extraction in alkaline solutions

This test method involved developing the pozzolanicity test described in the UNE 196-5 standard [13] to apply to the fly ashes in this study. A proportion of each type of fly ash was weighed, mixed with water, and stored in an oven at 40 ºC for 14 d; in this study, the extraction test duration was extended to 180 d. Finally, the solution in contact with the fly ash was removed and the calcium and hydroxyls were measured. Subsequently, the solids recovered from the pozzolanicity test were removed, crushed, and placed in contact with the alkaline extraction solutions for 28 or 90 d. This methodology was applied to each sample of fly ash, and the tests were performed in duplicates. The values shown in the graphs are the weighted averages of the values obtained, which are represented as the relative variation of the leached alkalis with respect to the total alkalis in the fly ash samples. The main test conditions are listed in Table 3.1.

Table 3.1 Test conditions for Method 2

Conditions	Pozzolanicity test (P)	Extraction test in alkaline solutions (A)	Temperature
1 (P14-28A)	14 days	*28 days*	20 ºC
2 (P14-90A)		*90 days*	
3 (P180-28A)	180 days	*28 days*	
4 (P180-90A)		*90 days*	

Four alkaline solutions were used for extraction with different concentrations of K, Na, and Ca. The solution containing Na^+, K^+, and Ca^{2+} were named D(Na), D(K), and D(Ca), respectively. The solution containing all of the three cations, which simulated the concentration of the aqueous phase of the concrete proposed in [3], was named D(Ca-Na-K). The composition and characteristics of the extraction solutions are listed in Table 3.2.

Table 3.2 Test solutions

Solution	Composition	pH	Conductivity
D(Na)	1 M NaOH	13.88	30.9 mS
D(K)	1 M KOH	13.99	81.1 mS
D(Ca)	$Ca(OH)_2$ saturated	12.35	8.0 mS
D(Na-K-Ca)	0.1 M NaOH + 0.6 M KOH + $Ca(OH)_2$ sat	13.85	119.7 mS

After the duration of the test, the pH values and conductivities of the filtered liquid samples were measured and the alkali ions were analyzed using an inductively coupled plasma.

4. RESULTS

4.1 Test method 1

Figures 4.1 and 4.2 represent the variation in the pH values and conductivities owing to the contact between the fly ash samples and deionized water in Method 1.

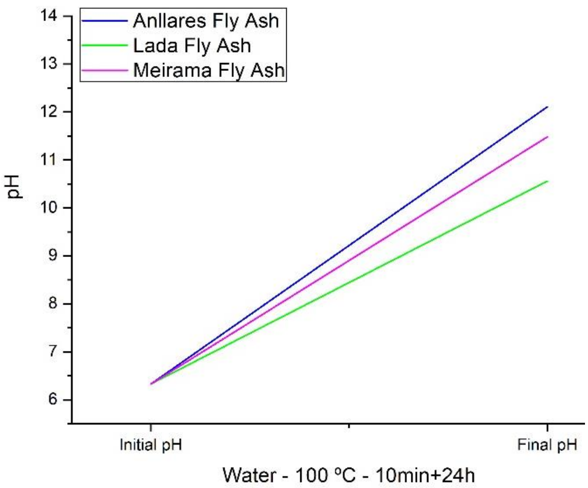

Figure 4.1: Variation in the pH of water containing the fly ash samples at 20 ºC for 24 h

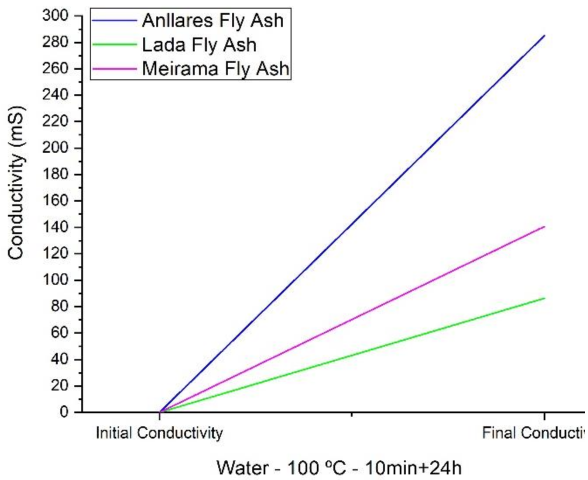

Figure 4.2: Variation in the conductivity of water containing the fly ash samples at 20 ºC for 24 h

The smallest increases in the pH and conductivity were observed in the solution containing the Lada fly ash. Therefore, we concluded that the Lada fly ash was the sample that leached the least amount of alkalis. The extracted alkalis, expressed as % K_2O, % Na_2O, and % Na_2O_e were determined, and the values were represented as the weighted average of the values obtained from each sample. The percentages of the leached alkalis are displayed in Figure 4.3.

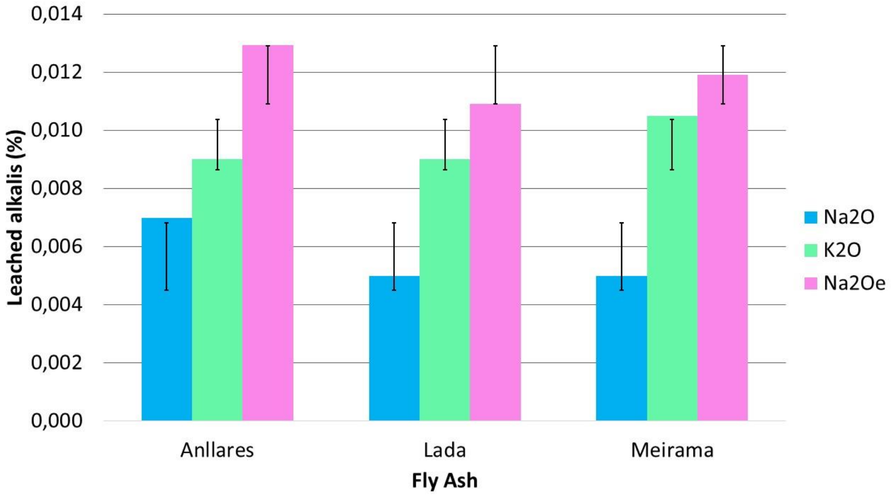

Figure 4.3: Alkalis leached from the different fly ash samples

As observed in Figure 4.3, leached K was the main contributor to the extracted alkalis and the proportion of the leached K was substantially higher than that of Na. This was because the K content in the fly ash sample was higher than the Na content. However, the fly ash obtained from Lada leached the smallest quantity of alkalis among the three samples.

4.2 Test method 2

Figures 4.4–4.7 show the variations in the pH values of the different solutions containing the fly ash samples that were analyzed in this study.

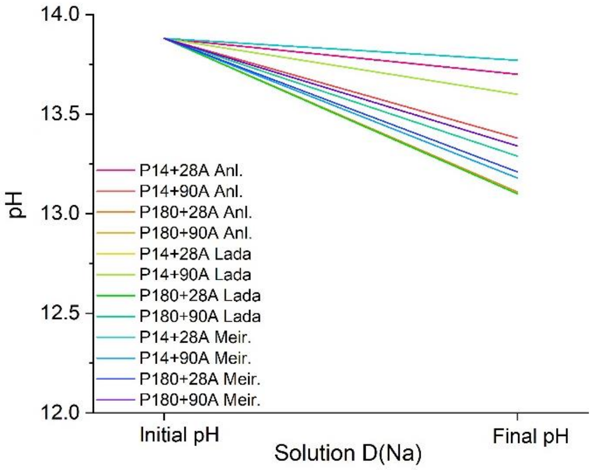

Figure 4.4: Variations in the pH of the D(Na) solution containing the fly ash samples under different conditions

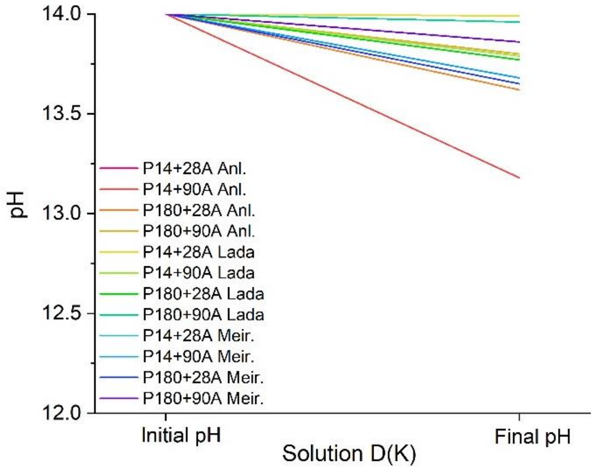

Figure 4.5: Variations in the pH of the D(K) solution containing the fly ash samples under different conditions

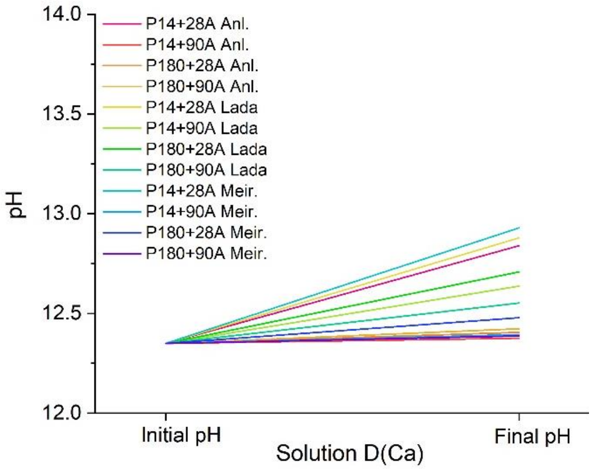

Figure 4.6: Variations in the pH of the D(Ca) solution containing the fly ash samples under different conditions

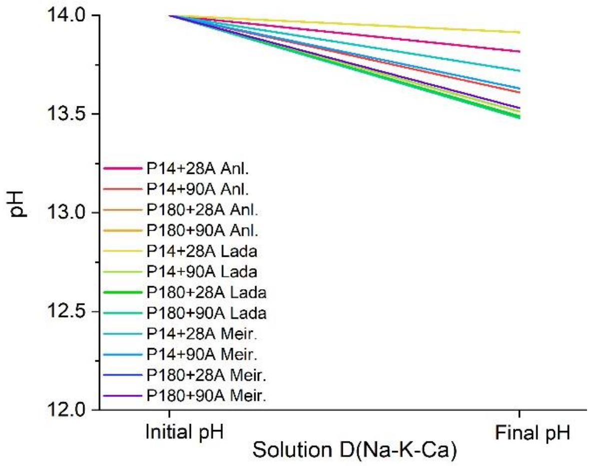

Figure 4.7: Variations in the pH of the D(Na-K-Ca) solution containing the fly ash samples under different conditions

In general, the pH of the solutions decreased owing to the combination of the three cations. However, the pH of the D(Ca) solution increased for all the samples owing to the extraction of the alkalis and low initial pH of the solution. Figures 4.8–4.11 show the variations in the conductivities of the different solutions containing the fly ash samples.

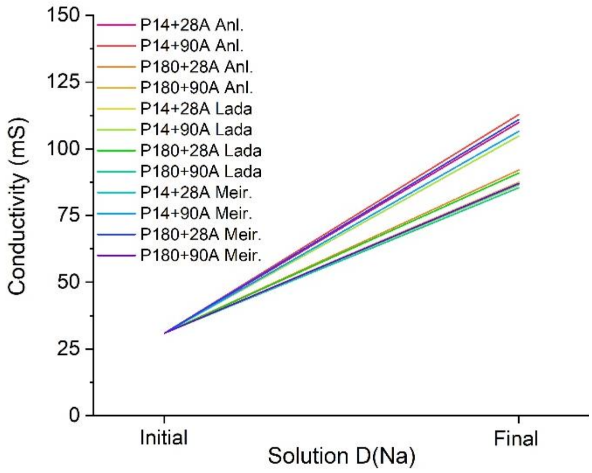

Figure 4.8: Variations in the conductivity of the D(Na) solution containing the fly ash samples under different conditions

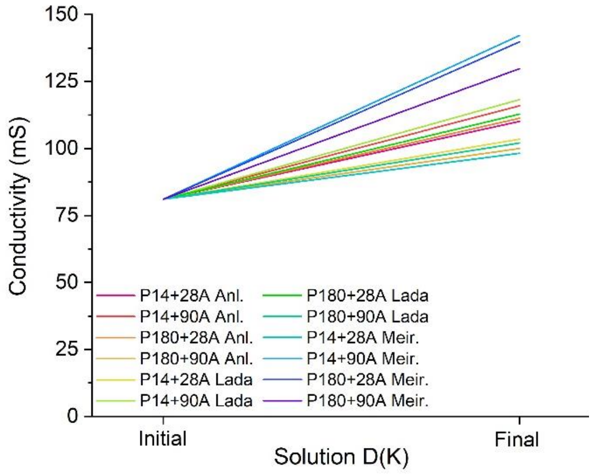

Figure 4.9: Variations in the conductivity of the D(K) solution containing the fly ash samples under different conditions

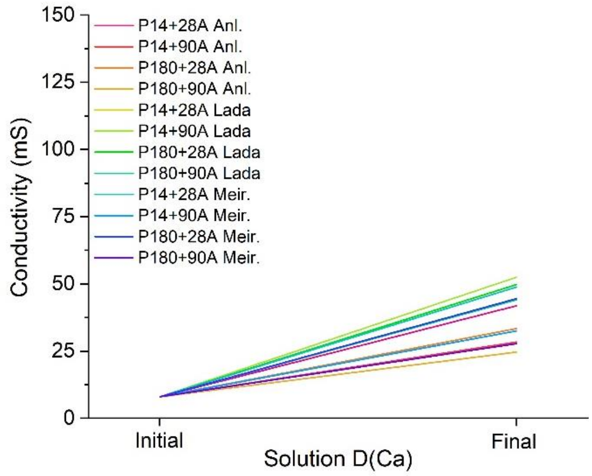

Figure 4.10: Variations in the conductivity of the D(Ca) solution containing the fly ash samples under different conditions

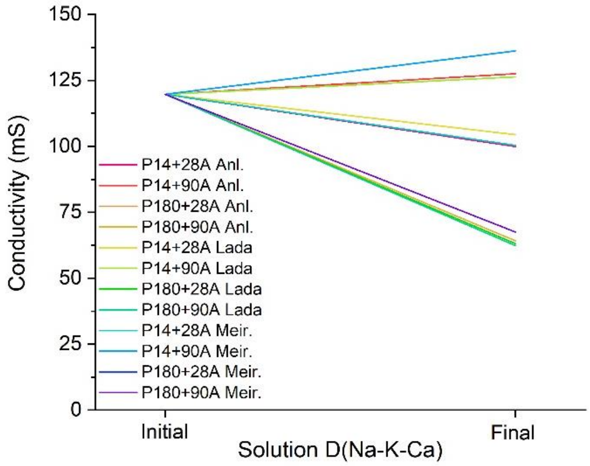

Figure 4.11: Variations in the conductivity of the D(Na-K-Ca) solution containing the fly ash samples under different conditions

In general, the conductivities of the test solutions increased because of the increase in the ions. However, in the D(Na-K-Ca) solution, a combination of ions was produced and, therefore, the conductivity decreased. The extraction of alkalis in the different alkaline solutions exhibited two different behaviors. Firstly, the fly ash samples in contact with the D(Na), D (K), and D(Na-K-Ca) combined some of the alkali ions present in the solution and, therefore, the alkali concentration in the solution decreased, which was expressed as % Na_2O_e. Figures 4.12 and 4.13 show the percentage decrease in Na_2O_e after 14 and 180 d of the pozzolanicity test, respectively, in D(Na), D(K), and D(Na-K-Ca) solutions.

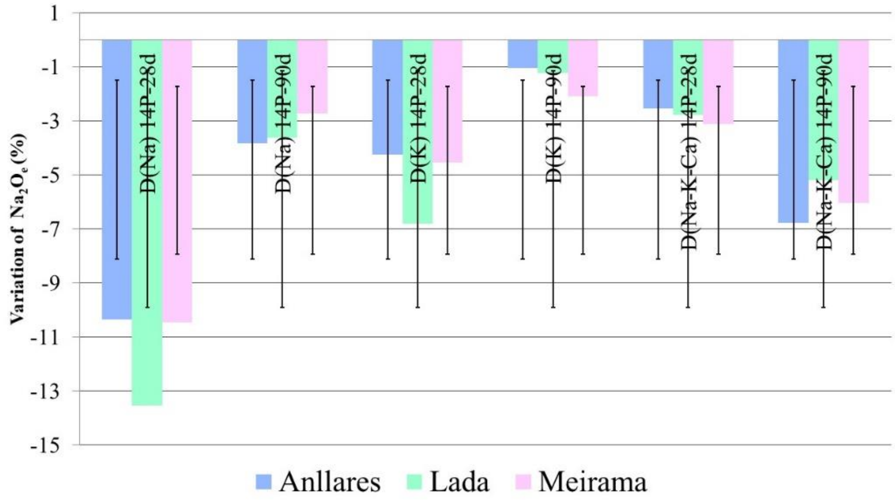

Figure 4.12: Variations in the percentages of Na_2O_e in the alkaline solutions after 14 d of pozzolanicity test and 28 - 90 d of tests in D(Na), D(K), and D(Na-K-Ca) solutions

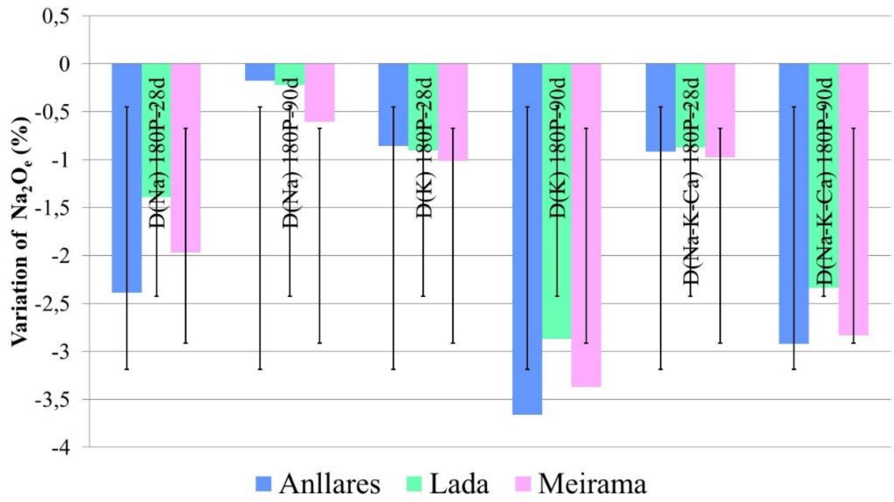

Figure 4.13: Variations in the percentages of Na_2O_e in the alkaline solutions after 180 d of pozzolanicity test and 28 - 90 d of test in D (Na), D (K), and D (Na-K-Ca) solutions

A much higher quantity of alkali ions was observed when the pozzolanicity test lasted for 14 d than when this test lasted for 180 d. This was associated with the low degree of hydration of the fly ash sample within 14 d. However, after 180 d of the pozzolanicity test, the fly ash samples reacted further and the absorption of alkali was low.

The fly ash samples in contact with the D(Ca) solution leached alkali ions even though the observed behavior of this solution was similar to that of the other solutions. As the duration of the pozzolanicity test increased, the samples leached minor quantities of alkalis, which were expressed as % Na_2O_e. Figure 4.14 shows the variations in the percentages of Na_2O_e in the D(Ca) solution after 14 or 180 d of pozzolanicity tests and 28 or 90 d of tests in the alkaline solution.

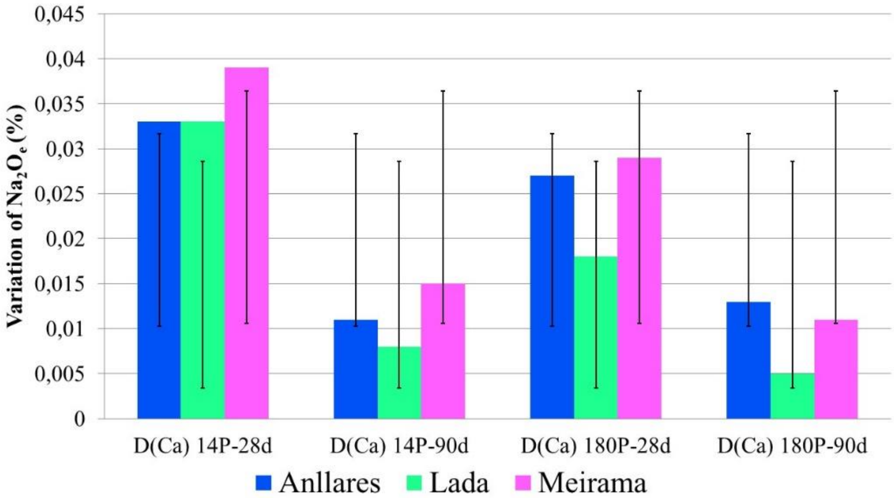

Figure 4.14: Variations in the percentages of Na_2O_e in the D(Ca) solution after 14 or 180 d of pozzolanicity test and 28 - 90 d of tests in the alkaline solution

In solutions that only contained a single ionic species, such as the D(Na) and D(K) solutions, the behaviors observed after the tests were attributed to the presence of a combination of alkalis owing to ion exchange processes. The D(Na-K-Ca) solution behaved in a similar manner, which resembled the composition of the porous phase of concrete. In this solution both species were combined, thereby rendering it less favorable for alkali leaching. In contrast, the D(Ca) solution resulted in a small quantity of leaching; this was the only solution in this study that was capable of extracting alkalis from the fly ash samples. Furthermore, the quantity of the extracted alkali reduced with the increase in the duration of the pozzolanicity test.

Additionally, we observed that long durations of testing resulted in a combination of alkalis from the fly ash samples; therefore, the extraction over 90 d of testing was much lower than that over 28 d. According to the results, different percentages of extracted alkalis were obtained depending on the conditions and the type of tests performed. Table 4.1 shows the percentages of alkalis obtained in each solution containing the fly ash samples.

Table 4.1 Extraction of alkalis from the fly ash samples in the different test solutions

Fly ash	**Extraction solution**				
	H_2O–100 ºC–10 min	D(Ca)14P-28 d	D(Ca)14P-90 d	D(Ca)180P-28 d	D(Ca)180P-90 d
Anllares Fly Ash	0.013 %	0.033 %	0.011 %	0.027 %	0.013 %
Lada Fly Ash	0.011 %	0.033 %	0.008 %	0.018 %	0.005 %
Meirama Fly Ash	0.012 %	0.039 %	0.015 %	0.029 %	0.011 %
Total Alkali extraction	0.036 %	0.105 %	0.034 %	0.074 %	0.029 %

In the extraction test after 14 d of pozzolanicity, the fly ash samples were considered to be unreacted and, the test after 180 d of pozzolanicity was the most suitable for extracting the largest quantity of alkalis from the SCMs. Here, the extracted alkalis were considered to have come from the porous phase of concrete and, therefore, can be available to develop the AAR reaction. However, for reliability reasons, 28 d of leaching was considered appropriate for the test design because larger quantities of leached alkalis are achieved under this condition.

5. CONCLUSIONS

The potential contribution of fly ash to alkalis in concrete is evident mainly owing to the high alkali content of concrete. The two alkali extraction methods were described to evaluate the potential contributions of alkalis to concrete. Method 1 provided information on free alkalis in the solution at the early stages, and the results allowed us to evaluate the potential contribution of alkalis from fly ash. In contrast, Method 2 describes a scenario, in which the alkalis were chemically conjugated and only in the case of the extraction solution D(Ca), relatively high quantities of alkali were extracted. This phenomenon occurred mainly because the excess alkaline ions in the remaining extraction solutions resulted in a combination of the leachable alkalis by electrostatic and chemical interactions, thereby causing small quantities of alkalis to be leached. However, solutions containing alkalis, D(Na), D(K), and D(Na-K-Ca) produced a combination of alkalis without resulting in any additional extraction. The most promising results in terms of the efficiency of alkali leaching from fly ash were observed in the case in which the fly ash samples were subjected to 14 d of pozzolanicity test and 28 d in contact with the alkaline solution D(Ca), this solution produces a high pH but does not produce reaction products. In general, this solution produces a greater extraction of alkalis by ion exchange and avoids the inconveniences presented by solutions with a concentration more similar to that of the porous phase of concrete D (Na-K-Ca).

This methodology can provide a fast and economical technique for evaluating the extraction of alkalis from fly ash, which is one of the most widely used SCMs today and contributes to superior mechanical performance of concrete.

6. REFERENCES

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