



CENUȘA ULTRA – REACTIVĂ: UN CONCEPT NOU AL CENUȘII ZBURĂTOARE, CARE CONDUCE LA PRODUCEREA DE ECO – BETON DURABIL ȘI IEFTIN

ULTRA-REACTIVE ASH: A NEW CONCEPT OF FLY ASH LEADING TO THE PRODUCTION OF DURABLE AND CHEAP *ECO-CONCRETE*

ANGEL PALOMO* , OLGA MALTSEVA, ANA FERNANDEZ-JIMENEZ

Instituto Eduardo Torroja (CSIC), Madrid –SPAIN

Coal fly ash can be subject to large variations in characteristics as a function of the type of coal burned, the operation status of the coal power plant and the ash separation technology employed. Good quality fly ash is in demand in the cement industry (and in the concrete plants) due to its ability to partially substitute some Portland cement (typically between 10% and 25%). On the other hand, coal bottom ash, due to its coarser nature, is generally considered as a low value by-product that may at best be used as a partial replacement for aggregates in concretes or as geotechnical fill material. In this paper authors propose a procedure (mechanical-chemical combined procedure) by which to transform regular coal combustion products (fly ashes and/or bottom ashes) into Ultra-Reactive Ashes (URA).

URA is a product with very interesting cementitious characteristics which can become the most important component of a new family of extra-durable and cheap ecoconcretes.

Keywords: Fly ash, chemical activation, mechanical activation, geopolymers concrete

1. Introduction

The steady increase of greenhouse gases (GHGs) as a result of the enormous industrial development that has characterized the last two centuries (especially to the rise in transport since the early 1900s) has driven humanity to the brink of a crisis. Further to present forecasts, unless a remedy is found, GHG emissions will not only fail to decline, but will continue to rise. In fact, the concentration of anthropogenic CO₂ in the atmosphere exceeded, last year (2015) the symbolic 400-ppm (parts per million) ceiling, a level not reached on the planet since the Pliocene Epoch, over three million years ago. Despite the worldwide commitment in place to reduce these emissions, the facts show that in the last five years, in the wake of the crisis, market enthusiasm for fossil fuels has made a comeback [1].

If emissions continue to increase at the present rate, the world will have exceeded the global CO₂ limit estimated for the first half of this century by 2034. Such a scenario could raise CO₂ concentration in the atmosphere to over 1 000 ppm by the end of the century [1-3], with severe consequences for the world climate and the global economy. The Earth's mean temperature could rise in the twenty-first century by 4 to 5.8 °C or more if no measures are taken to halt the upward trend in emission levels. Such a temperature rise will cause, among others, increases in extreme weather-related events (typhoons, hurricanes, tsunamis), the extinction of

over 20-30 % of all plants and animals and a rise in sea level. If humanity wishes to conserve a planet similar to the one on which civilizations developed and to which life on Earth is adapted, we need to reduce emissions to no more than 350 parts per million. The authors of this paper therefore believe that governments and scientists, as well as society at large, must take measures to lower GHG emissions (CO₂ among them) along the lines set out in the Kyoto (1997) and Hague (2000) Protocols and the Copenhagen (2009) and Paris (2015) Conferences on climate change.

Transport accounts for around 22 % of CO₂ emissions, energy generation (heat and power) for 41 % and industry for 20 %. Cement manufacture is indisputably one of the most heavily polluting industries, as it is responsible for 8 % -9% of the planet's total CO₂ emissions. While on the back of the crisis current production has declined in countries such as Spain, constructions and with it cement manufacture continue to grow worldwide. Constructions are a key factor in many economies as a result of the demand for housing and infrastructure, especially in developed nations and emerging economies such as China, India, Brazil, Russia etc.

Total cement manufacture is expected to increase to 6 billT (billion tones) by 2050. Unless preventive measures are taken, in 2050 cement manufacture-induced emissions will stand at 240%-260% of the 1990 value. That means that cement

* Autor corespondent/Corresponding author,
E-mail: palomo@ietcc.csic.es

In the first stage, **destruction-coagulation**, the OH⁻ ions initiate the reaction with the rupture of the Si-O-Si bonds (eq. 1). This takes place by the action of the OH⁻ redistributing the electron density around the silicon atom and rendering the Si-O-Si bond more susceptible to rupture. As consequence, silanol (-Si-OH) and silates (-Si-O-) species are formed. The appearance of (Si-O--Na⁺) bonds hinders the reverse reaction from forming siloxane bonds [26].

In as much as the hydroxyl groups affect the Al-O-Si bond in the same way, the aluminates in the alkaline solution form complexes, predominantly Al(OH)⁴⁻ (Eq. 2).

In the second stage, coagulation-condensation, accumulation enhances contact among the disaggregated products, forming coagulated structure where the polycondensation takes place (Eq. 3). This reaction is catalyzed by the OH⁻ ions. The clusters formed by the polymerization of silicic acid grow in all directions, generating colloidal particles. Aluminates also participate in the polymerization reaction, substituting isomorphously for silicate tetrahedra. While the alkaline metal catalyses destruction in the first stage, in the following two it is a structural component.

In the last stage, condensation-crystallization, the presence of particles in the initial solid phase prompts the precipitation of product whose compositions is determined by the mineralogical and chemical composition of the initial phase, the alkaline component and the hardening conditions.

2.2. Modeling the fly ash reactions. Development of fly ash cement

Electron microscopy is a very useful tool for monitoring the microstructural development, over time, of the cementitious matrix generated as a result of the chemical activation of fly ash [27]. Additionally the spherical shape of fly ashes facilitates the formulation of a simple conceptual model capable of describing the general process of chemical activation of the ashes in the form of series of consecutive steps [28].

The activation reaction rate, as well as the chemical composition of the reaction products, depends on several factors like, for example, the particle size distribution and the mineral composition of the starting fly ash, the type and concentration of the additives etc. However, the mechanisms controlling the general process of activation are independent of those variables.

The micrographs presented in this paper depict the typical microstructure of the material at specific reaction times.

Figure 1(a) is a SEM image showing some of the characteristic morphology of most of fly ashes. This ash consists of a series of spherical vitreous particles of different sizes (diameters ranging from 200-10 μm). Whilst usually hollow, some of these spheres may contain other particles of a smaller size in their interiors.

In Figure 1(b) the degree of reaction is low-moderate (≈ 35%). Here the spheres are intact or appear within other spheres, depending on the degree of local reactivity. In the early stages the alkaline medium dissolves part of the shells of the cenospheres and plerospheres, exposing the smaller particles (trapped inside the larger ones) to the alkaline medium as well. In this case the reaction product is a silicoaluminate (gel N-AS-H) with a Si/Al ratio between 1 and 1.5.

Figure 2(a) shows the ash particles in a more advanced stage of the reaction (degree of reaction ≈ 55%). In this stage the Si/Al ratio of the main reaction product is on the order of 1.8-2.0; in other words, the Si content is substantially higher than in the gel shown in Figure 1(b). The variation in fly ash reactivity ranges from no appreciable reaction to surface dimpling and finally fly ash particles inside shells, denoting reaction, or simply empty shells, indicative of a full reaction (Fig. 2(a)). This variability, reported in a previous paper (7), suggests either: (i) differences in the granular properties of the fly ash or (ii) limited availability of some fly ash grains for chemical attack.

Figure 2(b) shows system evolution after 90 days (degree of reaction ≈ 70%). Here the matrix has developed into a highly compacted paste, with a Si/Al ratio of 1.71. The fly ash particles that never

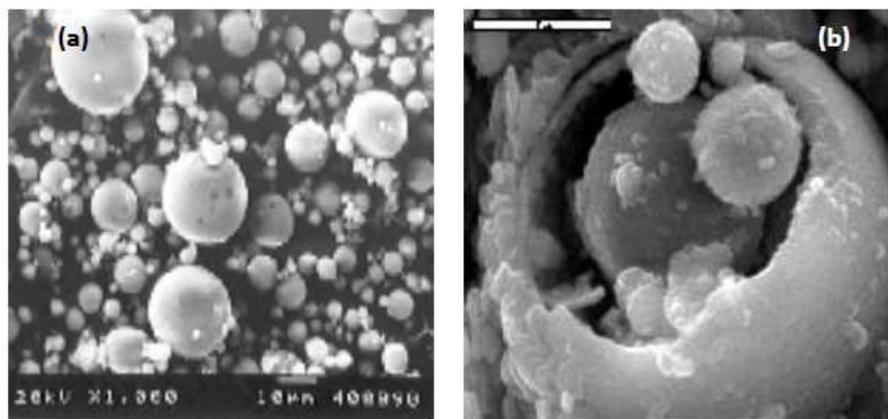


Fig 1(a) - original fly ash;
(b) chemically activated ash (few hours of reaction).

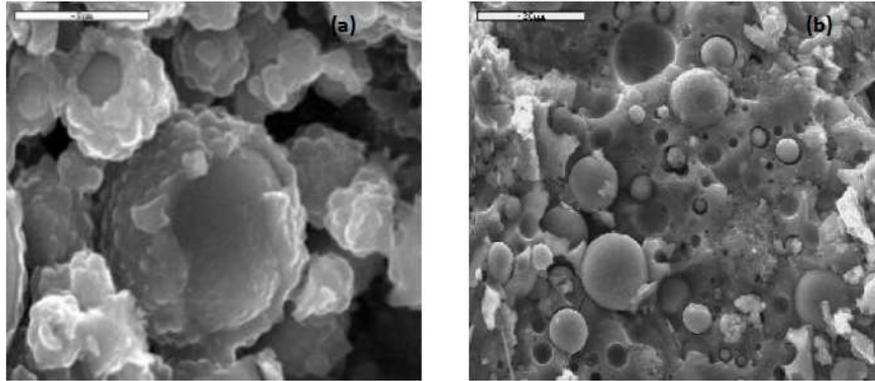


Fig. 2 - (a) ash chemically activated for long time (24 hours); (b) very long chemical attack (90 days) .

reacted are embedded in the matrix, which bears the semispherical imprints of some of the grains that did.

From the standpoint of reaction mechanisms, the specific chemical activation of a fly ash can be well explained through two well defined steps. In the first step (**nucleation**), the glassy component in the fly ash dissolves in the alkaline medium created by the additives, favoring the formation of a certain amount of a cementing gel (N-A-S-H gel) [26]. During nucleation, gel composition is significantly affected by thermodynamic and kinetic parameters.

The exact composition and structure of this N-A-S-H gel depends essentially on the size, structure and concentration of the ionic species present in the medium, as well as synthesis duration and temperature and the pH of the mixture.

The second stage, known as **growth**, begins when the nuclei reach a critical size and the crystals begin to grow. Due to the low “*water/fly ash*” ratios prevailing under experimental conditions, this stage is extraordinarily slow. Consequently, the final result of the reaction between the fly ash and water (with additives) is an amorphous material with cementitious properties that might be considered like a *zeolite precursor* [15].

The hypothetical evolution of this precursor to form an orderly zeolitic crystal would entail depolymerisation of the gel structure.

A transmission electron microscope picture of the fly ash chemically activated with NaOH 8M for 7 days at 85°C is shown in Figure 3. The spherical morphology of some fly ash particles becomes evident through this powerful technique of observation. The most interesting features to be remarked from Figure 3 are those extracted from the observation of the rests of a large spherical fly ash particle that underwent an intense and long reaction process (7 days at 85°C). The mentioned rests include a semicircular crust of about 50-60 μm thick, probably partially permeable. In the inner part of that big particle some small particles (25-35μm diameter) have been arrowed. They are embedded into the sodium aluminosilicate gel (“N-A-S-H gel”) produced during the reaction process.

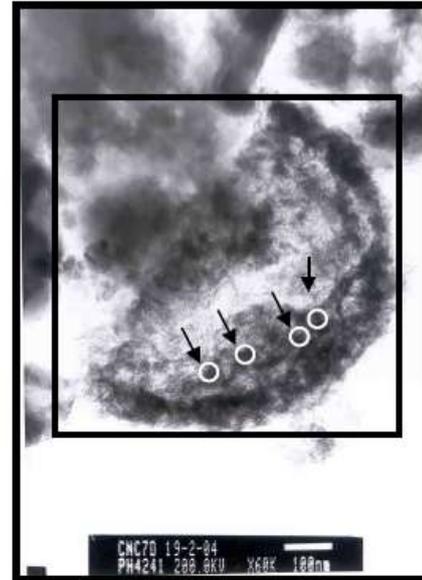


Fig. 3 - TEM picture of a chemically activated fly ash sample. Curing conditions: 7 days at 85°C.

Figure 4 contains a descriptive diagram of the chemical activation of fly ash. Figure 4(a) shows the initial chemical attack at one point on the surface of a particle, which then expands into a larger hole, exposing smaller particles, whether hollow or partially filled with other yet smaller ashes, to bi-directional alkaline attack: i.e., from the outside in and from the inside out (Fig. 4(b)). Consequently, reaction product is generated both inside and outside the shell of the sphere, until the ash particle is completely consumed (Fig.4c). The process involved in this reaction is **dissolution**. At the same time as the chemicals (dissolved in water) penetrates the smaller particles housed inside the larger spheres, the interior space of the latter starts to fill up with reaction product, forming a dense matrix.

One of the consequences of mass precipitation of reaction products is that a layer of these products covers certain portions of the smaller spheres. This crust prevents their contact with the medium (Fig. 4(e)). Ongoing reactions within the bulk of the matrix consolidate such crusts,

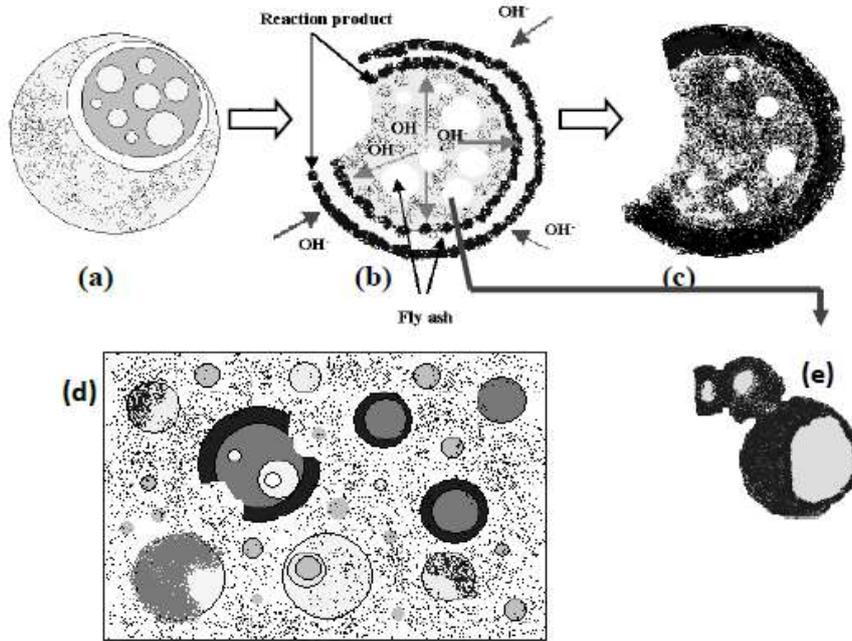


Fig. 4 - Descriptive model of the chemical activation of fly ash [28].

with the concomitant effect on the pH gradient across the fly ash reaction product. As chemical activation continues, the unreacted fly ash buried under reaction product may not be affected by the very high pH associated with the additives (activator), thereby reducing the reaction rate. In this case chemical reactions are governed by a **diffusion mechanism**. The variation in the degree of reaction at different times (45% at 5h, 55% at 24h and 70% at 90h) may suggest variable permeability of the layers of hydration product.

Moreover, the processes described are not uniform throughout the gel but vary locally from one point in the matrix to another, depending on the distribution of particle size and the local chemistry (e.g. pH). Several morphologies may co-exist in a single paste: unreacted particles, particles attacked by the alkaline solution but which maintain their spherical shape, reaction product and so on (Fig. 4(d)).

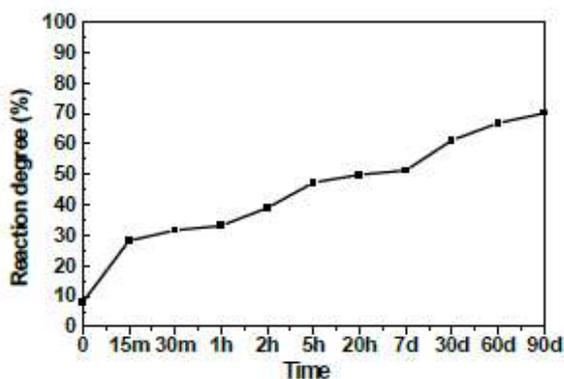


Fig. 5 - Evolution of the reaction degree of a fly ash activated with a 8M NaOH dissolution. Curing temperature: 85°C

Finally, in Figure 5, the values of the degree of reaction of a chemically activated fly ash have been

plotted versus the time. Results show, as expected, that the degree of reaction is continuously increasing with time. It should be especially remarked the high degree of reaction reached during the first hours of reaction.

3. Mechanical activation of fly ashes

Fly ash, initially, was used in the construction sector as a partial replacement of the mass or the volume of the hydraulic cement, the most expensive component of concrete in order to reduce the cost. However, the results of further studies on fly ash concrete showed that the fly ash could impart beneficial properties to the concrete. The results of research in 1930's served as a foundation to adopt the early specification, methods of testing and use of fly ash in concrete, and led to better understanding of the behavior of fly ash concrete.

For more than 70 years, fly ash has been used successfully in Portland cement concrete as a mineral admixture. And in the last three decades, fly ash has been used as a compound of blended cement. Intergrading Portland clinker, fly ash, and calcium sulfate produce Portland-fly ash cement. Under most specifications the amount of fly ash in the cement is limited to 30%-40%, but typically an addition of about 15%-25% may be considered more practical.

But..., too many fly ashes are produced nowadays in the world..., and the global level of utilization is still low ($\approx 50\%$).... And at the same time the level of responsibility of electricity companies for the management of wastes is increasing.... One report carried out at University of Oklahoma in 2006 (for the Oklahoma Department of Transportation) established that by using the disposed fly ash at the

USA in that moment (10 years ago), a four-lane highway (with 600 lb/yd³ binder) could have been built around the whole perimeter of the United States. Nowadays (10 years later), disposed fly ash has obviously increased significantly. On the other hand just by comparing the expensive and energetic process of producing Portland cement with the enormous amount of available land fill fly ash, would be enough to demonstrate the economical benefits of using fly ash in concrete. **Replacing fifty percent of Portland cement with fly ash could reduce the cost of concrete up to 30 percent (the environmental benefit cannot be valued just with money).**

Mechanical activation of fly ashes is not, in fact, a new idea that researchers have recently applied in technical projects in order to improve the performance of ash-blended cements or ash-blended concretes. Many authors in many laboratories all around the world have tried to stimulate reactivity of ashes in concrete or blended cements by increasing the ash specific surface area.

However, when checking carefully the existing bibliography on this topic everybody will realize that not all written papers reach the same conclusions in the evaluation of the effect of mechanical activated ashes on the cement or concrete performance (usually a positive effect). It is likely due to the fact that authors of papers and reports are analyzing very different systems (different ashes with different physical, chemical and mineral characteristics and also different grinding conditions).

In this sense two very simple reflections should always be kept fresh in mind:

- Grinding is a complex operation (very complex). Technically speaking the efficiency of grinding is affected by a huge number of factors (shape and dimensions of mill; power applied to the

grinding operation; grindability of materials inside the mill; type, dimensions and nature of grinding elements etc.,etc., etc.). More and better knowledge is needed about grinding.

- Fly ash is a complex material.....It is well known that fly ash contains small particles that are collected from the exhaust of coal power plants. Fly ash particles are hot when they are collected..... while fly ash is cooling the small particles tend to adhere to the surface of larger particles. Grinding of fly ash can change the topography of the fly ash particles by removing the small particles adhering to the surface; and cleaning the fly ash topography by removing the small particles creates a larger available reaction surface area overall. As a general rule higher reaction surface area is an important factor to shortening the setting and hardening time of concrete.

On the other hand the spherical particles of fly ash are formed upon cooling the melted material in the furnace with a predominantly glassy structure. The particles that are formed in the coldest part of the boiler (consequently not formed at the highest possible temperatures) tend to be more irregularly shaped, because of reduced amount of melted material present.

In summary, it seems obvious that by using a fly ash with a very high specific surface area the reactivity of particles should increase, but it is not so obvious how to reach the optimal specific surface area of ashes taking into consideration not only the expected technical results (good performance of cement or concrete) but a realistic economical framework.

4. Mechano-chemical activation of fly ashes

Both procedures already described for the ash activation have evidenced that individually speaking (chemically and mechanically) the

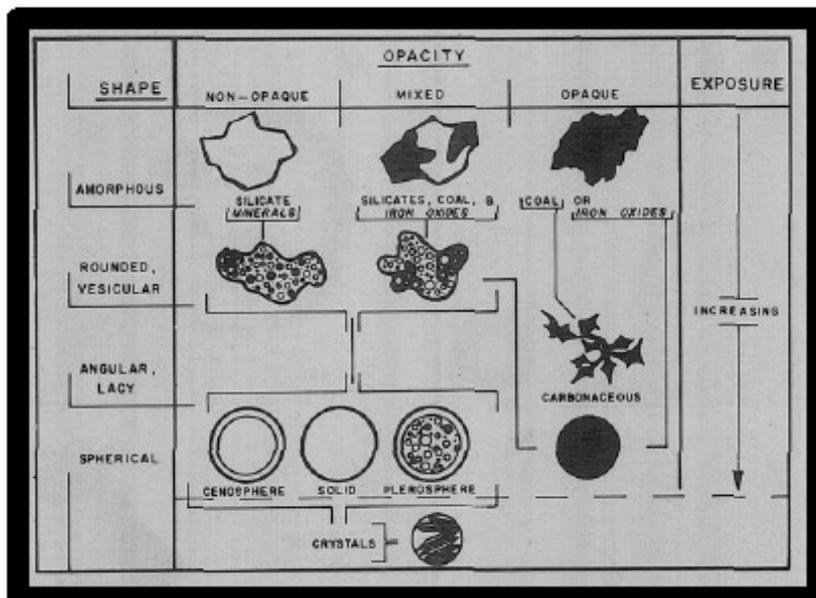


Fig.6 - Fly ash morphogenesis scheme illustrating probable relationship of opacity to particle composition, and relationship of particle shape to exposure in combustion chamber (Picture taken from [29])

application of any of them can improve the performance of ash blended cements and/or ash blended concretes. It seems very obvious that the next stage is to try to advance with both procedures simultaneously.

A deep study of the physical and morphological properties of four fractions of size classified coal fly ash was reported by Gerald L. Fisher et al. in 1978. Volume average diameters of the four size fractions were 2.2, 3.2, 6.3 and 20 μm , respectively. Authors compared the size distributions of the four fractions with isokinetically collected samples. Density variations and results of three standard particle sizing techniques were discussed in terms of particle size and morphological properties. The most important conclusion extracted from this investigation was that relative abundance of the 11 morphological particle types within each size cut appeared to be particle size dependent. In that context authors found that the finest fraction was composed of 87% nonopaque solid spheres and 7.9% cenospheres in contrast to the coarsest fraction composed of 26% nonopaque solid spheres and 41% cenospheres. The density variation with particle size was explained in terms of the relative abundance of predominant particle types. On the basis of morphological appearance, a coal fly ash morphogenesis scheme was developed by the authors (see Fig.6).

Authors of this paper developed the idea of the stimulation of reactivity of ashes just by making that all particles (solid spheres as well as cenospheres and plerospheres) could get in intimate contact with chemicals (solid additives) in the moment that particles were submitted to a mechanical process of grinding. **The ultimate objective of this type of activation is to generate an optimal distribution of particles (solid spheres, cenospheres, plerospheres etc.) with enough reticular defects in the surface (especially reactive points) and consequently capable to reproduce in practice the model described in Figure 4 just by putting in contact the ashes with water.**

4.1 Hybrid Cements

Hybrid cements are complex cementitious blends basically made with traditional Portland clinker (20% - 30%) and mecano-chemically activated ash (65% - 75%). Reaction products of hybrid cements are intricate mixes of different gels (the type of product formed depends largely on the reaction conditions) [15].

In 2007 Palomo *et al.* [16] reported the results of a research project on hybrid cements containing 30% Portland cement clinker and 70% fly ash. The characterization studies of the hardened matrices showed that in all cases the reaction products consisted of a mixture of amorphous gels (C-S-H + N-A-S-H). Another remarkable finding of these authors was that the chemical activation of the ash at ambient temperatures is accelerated by the

presence of Portland cement. It might be explained by the heat released during OPC hydration reactions.

Summing up, prior studies have shown that the co-precipitation of these two gels in hybrid cements is possible, although recent research has revealed that the two products do not develop separately, as two separate gels, but that they interact, undergoing structural and compositional change in the process [23].

Consequently, the compatibility of the two cementitious gels, C-S-H/C-(A)-S-H (the main reaction product of ordinary Portland cement hydration) and N-A-S-H (the main product of the chemical activation of aluminosilicate materials), may have important technological implications for future cementitious systems in which both products might be expected to precipitate.

Recent studies carried out for the same authors in mechanically and chemically activated "binders" (70% FA +30% OPC mixtures) at short and long term (28 and 365 days respectively) showed that the C-S-H/N-A-S-H mix of gels precipitating did not precipitate in a pure state, but rather that their composition was affected by the presence of dissolved species. After one year of hydration, unreacted ash and cement particles co-existed in the cementitious matrix with secondary phases such as carboaluminate hydrates, along with a (N,C)-A-S-H /C-A-S-H gel mix with a tendency to form C-A-S-H gels.

The mechanical strengths development of these cements can reach more than 20 MPa at 2 days and more than 50 MPa at 28 days; and setting times were of 180 minutes for the initial and 250 minutes for the final.

4.2. Concrete with URA

Once explained the basic reasons of the great reactivity of the "mechanically –chemically" activated ashes it is also important to clarify that by using Ultra Reactive Ashes (URA) to make concretes, has not any negative effect on concrete (no negative effects in the concrete making process and no negative effects in the durability of concrete).

With respect workability, fly ash has lower unit weight than Portland cement. Therefore, when the same volume of cement is replaced with fly ash (assuming the w/c ratio is constant), the amount of paste will increase. This higher volume of the paste provides more plasticity and cohesiveness to the concrete.

The spherical shape fly ash particles serve as ball bearings in the mix and reduce the friction between the particles and between concrete and pumping line. Fly ash concrete is more cohesive and less prone to segregation and bleeding during pumping. Thus, pumping a fly ash concrete requires less energy and longer pumping is possible.

If additionally fly ash has previously been mechanically-chemically activated, this higher volume of paste will also provide a better packing of particles in the final hardened material.

All extra effects provided by the mechanical-chemical activation will have a very interesting and positive consequence in early mechanical strength development of concrete. We cannot forget that **normal fly ash concrete** (with not activated ash), in general, develops lower strength at early age than **regular OPC concrete** (with no ash at all in the concrete mixture).

In a study made at Madrid (by the authors of this paper) using a fly ash supplied by a North American power plant (Roxboro) we applied this concept of mechano-chemical activation of ashes in order to prepare a new ash concrete.

Firstly, and with the objective of observing the effect of grinding on the morphology of the ash particles a SEM study was carried out. Figure 7 contains 2 pictures of the ash before grinding. In Figure 8 pictures correspond to the same ash sample but after grinding together with chemicals. Magnification of pictures is always the same in order not to generate confusion when valuing the grinding effect.

The grinder used in this study was a cylindrical steel ball mill with a diameter and depth of sixteen inches. The ball mill spun around a horizontal axis. The optimal revolution rate, weight of balls, and fly ash load for each grinding time was previously established and then kept constant throughout the entire study.

Secondly we established a procedure for the preparation of concrete samples with both ashes (original ash and mechanically-chemically activated ash).

The main concrete characteristics were previously defined like it is done in many concrete plants (ready mix concrete) all around the world:

- Plastic Slump (Abrams cone) 3 - 4 cm
- Compressive strength at 28 days 20-30 MPa.

Concrete composition:

- Sand/gravel/binder \approx 3/3.5/1

- Water/binder \approx 0.52 (sometimes we had to modify this ratio in order to obtain the required slump)

The procedure followed to prepare the concrete samples (15x15x15) cm³ can be observed in Figure 9. Mechanical strength was determined in a testing device SUPEZCAR 150T as described in the European standard UNE-EN 12390-3: 2003.

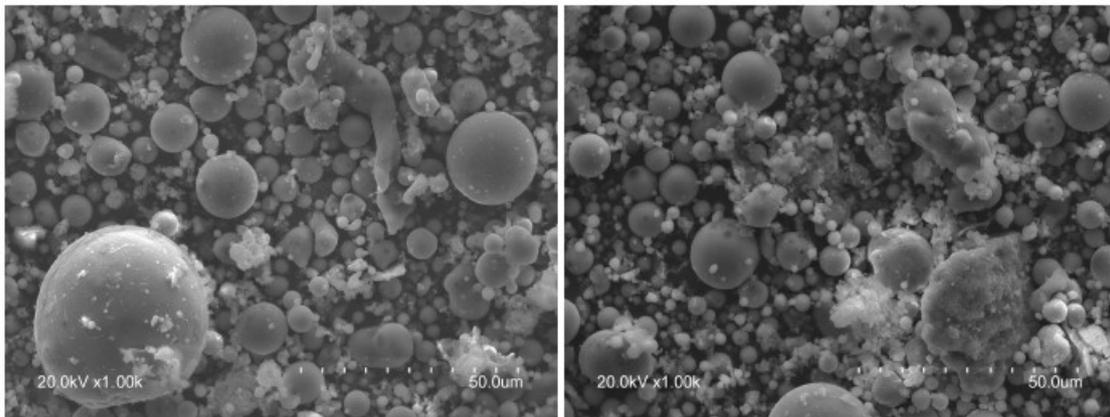


Fig. 7 - Original ash (supplied by the Roxboro power plant).

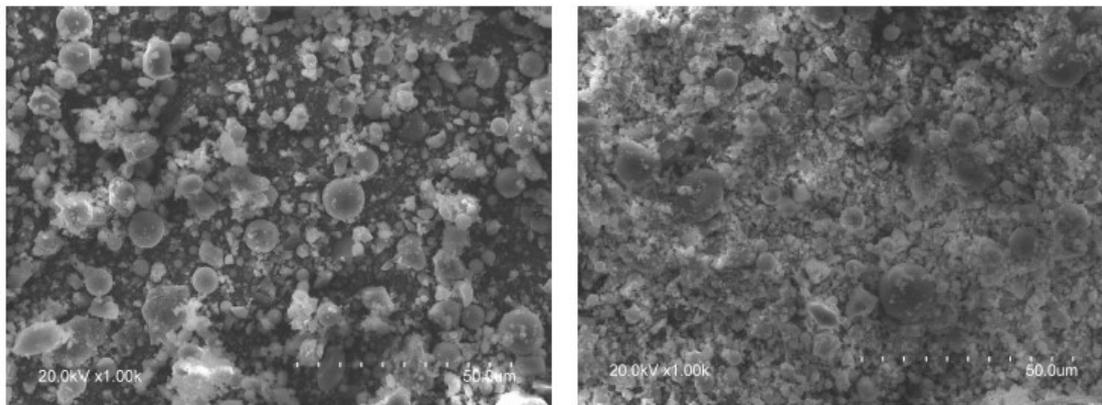


Fig. 8 - Ash after grinding.



Fig. 9 - Procedure of preparation and testing of concrete cubes (EN 12390-3: 2003)

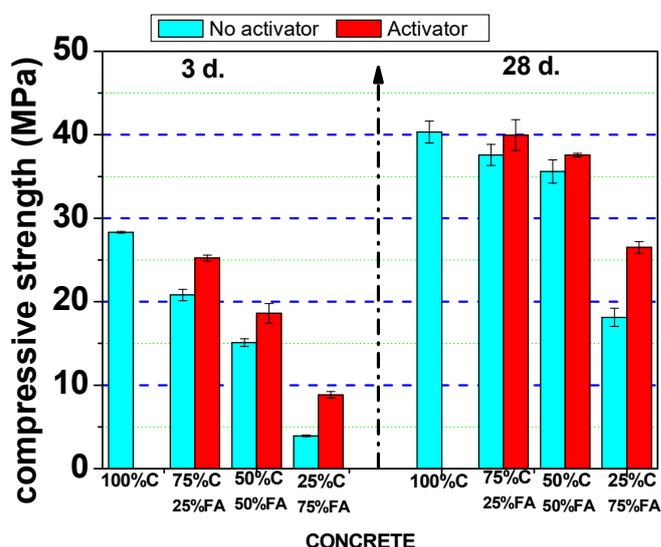


Fig. 10 - Mechanical strength evolution of concretes with different levels of replacement "OPC-UltraReactiveAsh".

*Light blue bars correspond to the different concrete samples prepared with the original ash (no previous activation of the ash). And red bars correspond to the same concrete samples (same level of replacement of Ordinary Portland Cement) but with Ultra Reactive Ash.

By observing the results plotted at Figure.10 we rapidly discover that mechanical strength development of concrete cubes at 3 days and 28 days is very relevant...Even with levels of replacement of 75% of OPC by URA, concrete cubes (at room temperature) can develop near 10 MPa after 3 days and between 20 – 30 MPa after 28 days.

5. Conclusions

Mechanical-chemical activation of ashes can become a very serious alternative for the massive utilization of ashes in cement and/or concrete. This procedure has very interesting advantages:

- It is economically profitable
- It is environmentally friendly
- It helps to improve the performance of concrete

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