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TREBALL FINAL DE GRAU

Stabilization of fly APC ashes with Portland cement as encapsulating for their usage as aggregate material. Mechanical and environmental evaluation.

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CONTENTS

1. SUMMARY

The rising generation of waste products signifies a big problem in today's society. This is a direct result of an ever growing population. A possible solution for waste disposal can be found in an incineration plant by means of a revalorization process. This process would not only reduce the volume of waste produced but would function as a power generating system.

The control of waste production involves a cleaning system to purify the resulting gases of the incineration. The cleaning process varies depending on the nature of the waste.

Independently from the type of waste found in the incineration plant, two very different by-products can be obtained: ash and slag. These by-products have properties which resemble those of cement. On the one hand, depending on the cleaning process, the ash obtained can contain a high level of calcium resembling the pozzolanic behavior typically associated with cement; on the other hand, once the slag has been valorized it becomes a fine arid made mostly of concrete, ceramic materials and glass. This composition allows valorized slag to form embankments or to be used as a filler.

Demographic growth has simultaneously caused an increase in CO_2 emissions.

This increase is a result of the necessity to build and join different communities. The creation of new urban nucleus's entails the paving of new roads which consequently produces the need for more construction materials. Nowadays, the cement industry accounts for around 8 to 15 % of total world emissions. For this reason, investigation into the optimization of its use is of great interest.

This investigation project intends to use the properties of the by-products obtained in the incineration process to incorporate the maximum quantity of fly ashes generated in the gas cleaning system, into a Portland cement, which, once mixed with the valorized slag, creates a material that can be used in the layering of roads with small traffic flows. This would contribute to a decrease in the use of cement and would use the by-products obtained from the incineration process, which would in turn reduce CO_2 emissions.

Through compliance with environmental regulations and through the performing of standard tests, different formulations will be studied in order to determine the best way of reusing the highest quantity of ash with the best mechanical properties.

To reach the optimal formulation, different influential factors in the mortar will be determined and will be assigned different values through use of the DoE computer program. Finally, from the results of

the standardized testing an optimal formulation will be found in accordance with its mechanical and environmental criteria.

2. Resumen

El continuo aumento de la sociedad y, como consecuencia directa, la generación de residuos, comporta un gran problema en la sociedad actual. Una solución posible la plantea una planta de incineración, siendo un proceso de revalorización, en el cual no solo se reduce el volumen de forma importante a los residuos sino que también contiene un sistema de generación eléctrica.

Éste tipo de gestión de los residuos precisa de sistemas de limpieza para poder depurar los gases resultantes de la incineración. La depuración se lleva a través de diferentes formas dependiendo de la naturaleza de los residuos. Independientemente del tipo de residuos que tenga una planta de incineración obtendrá dos subproductos muy diferenciados que son las cenizas y escorias. Estos subproductos tienen propiedades afines al cemento. Por una parte, dependiendo del sistema de limpieza, las cenizas contienen un alto contenido en calcio lo que les permite tener un comportamiento puzolánico a fin al cemento. Por otro lado, las escorias unas vez valorizadas son conocidas como Escograva, un árido fino formado principalmente por hormigón, materiales cerámicos y vidrios. Esta composición permite la Escograva formar terraplenes o rellenos.

Paralelamente, el aumento de la población ha provocado un aumento de las emisiones de CO_2, que ha sido consecuencia de la necesidad de edificar y de comunicar diferentes poblaciones. La formación de nuevos núcleos de población obliga a la pavimentación de nuevas carreteras y, consecuentemente, provoca aumentos en las necesidades de materiales para la construcción. Actualmente el sector del cemento contribuye entre un 8 y un 15 % del total de las emisiones por lo que es de gran interés el estudio de la optimización del uso del mismo.

Éste proyecto de investigación pretende aprovechar las propiedades de los subproductos de incineración para incorporar la máxima cantidad de cenizas volantes generadas en el sistema de limpieza de gases a un cemento Portland para que, una vez cuarteado, éste junto con la Escograva supongan un buen material para hacer subsuelos de carretera de bajo rodaje. De esta manera, se podrá contribuir a la disminución del consumo de cemento y aprovechar los subproductos de la incineración, reduciendo así las emisiones de CO_2.

Con el cumplimiento de las normativas medioambientales y realizando ensayos normalizados, se estudiarán diversas formulaciones para determinar que formulación reutiliza la mayor cantidad de cenizas con las mejores propiedades mecánicas.

Para llegar a la formulación óptima se determinarán diferentes factores de influencia en el mortero y se les asignarán valores de importancia a través de un Diseño de Experimentos (DoE). Finalmente, a través de los resultados de los ensayos, se podrá encontrar una formulación óptima bajo un criterio mecánico y ambiental.

3. INTRODUCTION

With the passing of time our society has grown steadily and so have its needs. The increase of urban waste is a direct consequence of the world's urban demographic growth.

Historically, waste was mostly of an organic nature and due to the relatively small amount produced, it presented little effect on the environment. Moving forward in time, with the increase of livestock and agriculture, urban communities emerged and grew and waste began to be amounted in removed areas.

Different solutions have been tried out throughout history. In ancient times the first civilizations along with the vast empires would accumulate waste in large containers which were later buried or covered in earth. With the arrival of numerous epidemics during the Middle Ages, people began to understand the need for upholding hygiene standards, and began tackling waste in different ways. The beginning of the 19th century saw the development of large industries such as metallurgy and construction, which in turn provoked an increase of emissions into the atmosphere.

Towards the end of the 19th century, in answer to the problem of urban waste, the first incineration plant was built in Nottingham, which was shortly followed by the first incineration plant for organic materials in 1885 in the United States.

The correct treatment of urban waste, as well as the need to reduce carbon emissions continues to be a brainteaser for today's engineers. A possible solution would be the incineration of all waste that cannot be recycled or directly reused, although this incineration process still requires its by-products and other waste produced in the combustion, to be comprehensively controlled, these by-products being principally slag and fly ashes.

Slag requires a stabilization process because it is thermodynamically unstable in certain atmospheric conditions. Once it has been stabilized it can be categorized as valorized slag. This enables it to be used in the field of construction.

Fly ash is the other by-product obtained from the burning of waste in one of the incineration stages. The heaviest ash that does not burn is called bottom ash, but is not usually used in construction.

Fly ashes are a pozzolanic material and have a high level of calcium which means they have a cement-like behavior.

Due to this behavior, the possibility of using slag or fly-ashes in the make-up of mortar or concrete is being studied with the aim of improving the final product.

3.1 Experiment design

Experiment design is very useful for the positive outcome of projects. Different factors can be used to control the resulting products meaning teams can develop different processes depending on the services and needs that are trying to be accomplished.

A well planned experiment will not only save process time, but will also distinguish between factors that will affect the experiment and those that will not.

The term 'experiment design' generally englobes all levels in order to determine which experiments will allow us to test out our hypothesis and which will not. This includes everything from choosing the measures to be used to choosing the operations that will be performed [1].

3.2 The incineration process:

The incineration process allows for a reduction of between 70 and 90 % of the volume of the weight of the generated solid urban waste. Although the primordial goal is to reduce weight and volume, the incinerators can also obtain reusable electrical energy from the combustion process.

One of the main differences between the combustion processes in the different incineration plants can be found in the nature of the waste they receive and the previous treatment of this waste. Some examples of these pretreatments are:

- Composting to eliminate pathogens.
- Pressing to expel humidity.
- The grounded down waste increases the area of exchange and as a result improves combustion efficiency.

The following diagram shows different parts of a combustion line of waste.

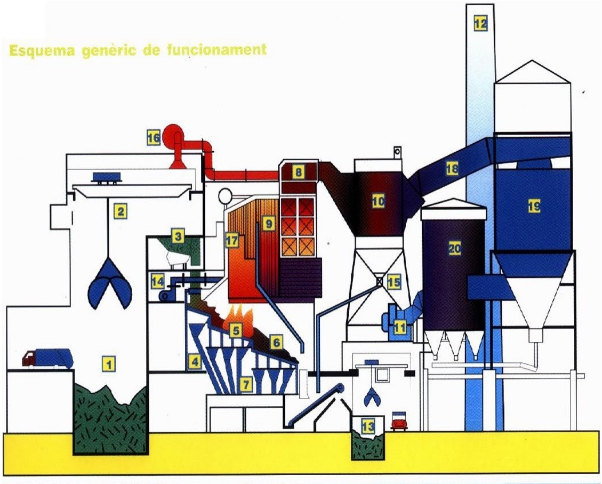


Figure 1: Layout of incineration plant

1 Garbage pit
2 Garbage crane
3 Distributor
4 Drying grill
5 Main grill
6 Final grill
7 rimary vent

11 Circulation fan
12 Chimney
13 Slag pit
14 Secondary ventilator
15 Ash transporter
16 Air combustion ventilator
17 Natural as burner

8 Air-Vapor preheater
9 Boiler
10 Electrostatic filter
18 Conduct reactor inlet
19 Reactor
20 Sleeve filter

Reception pit:

The reception pit is where the garbage trucks dump their load. Once the trucks are weighed at the entrance they dump their loads in the reception pit.

This pit should be designed to withstand 3 days accumulation. It also has to withstand the leachate from the waste during rainy seasons. This means the material from which the pit is built is of the utmost importance from an environmental perspective.

The waste will try to be homogenized before the process of incineration. The bad smells will be collected from the pit and will be sent through a ventilation process and then to the furnace.

Furnaces:

A crane will collect the contents deposited in the pit and will transport it to a conveyor belt which will take it to the furnace, where the combustion will take place. The input of oxygen is controlled throughout this process.

There are various types of furnaces

Rotating furnaces:

They consist of a cylindrical furnace, laid out horizontally and with a built in rotation system. These furnaces tend to be slightly sloped to make sure the waste is transported and rotated, which increases its contact with primary air.

The proceeding gases from the furnace are then conducted towards a postcombustion chamber, to make sure they reach the highest necessary temperatures in order to completely destroy any organic components.

Postcombustion furnaces and chambers are usually built like adiabatic chambers with a refractive ceramic covering.

The advantage of rotating furnaces lies in the fact that they're a closed system, meaning they can deal with both harmful/toxic waste and food waste.

Nevertheless, this technology is being used less and less for waste processing because of the difficulty of complying with emission rules and because of its limited capacity.

Grill furnaces:

Incineration grills consist of a structure in the form of stairs or mobile rollers that are in charge of helping the combustion process through movement. Insomuch that, as waste is mixed together, air is injected through the inferior part of the grill.

The mobile grills have to be controlled in regards to the amount of injected air and the waste that travels through it. Different types of grills exist which include mobile roller grills or mobile grills.

Fluidized bed furnaces:

These furnaces, instead of having a grill system, have a cylindrical combustion chamber, whose inferior part has a conic form. Limestone sand is deposited in this inferior part, and is kept in constant movement since it is fluidized by the injected air.

Types of fluidized bed furnaces:

- Bubbling bed.
- Circulating fluid bed.

The difference between the two is the speed of the injection. In the case of the circulating fluid bed the speed is 20 times faster which makes substrate particles move towards the combustion chamber. These particles have to be recuperated later on through means of a cyclone.

In the case of the bubbling bed the air is not injected so rapidly since it is done through a double fluidification process. These types of beds are used in installations with a power of up to 100 MW. When a plant needs higher thermal input it uses circulating fluid beds.

The use of any sort of refractory sand bed allows the temperature to be raised in the combustion chamber and also the use of reagents such as lime which is directly added to the chamber in order to achieve the desulphurization of the gases.

Each system has its advantages and disadvantages, the balance of which depends on the explicit situation. The main factors which are used to learn about the behavior of furnaces are:

-Adapting to the changing characteristics of waste: calorific power, humidity and ash content.

-Ease of operation: mobile elements, starting and stopping.

-Energy consumption: energetic needs for correct functioning.

-Contamination in the exhaust gas stream: purifying techniques, energy recovery systems.

3.3 Gas treatment systems:

During the incineration process of urban solid waste, gases are generated with a high level of toxic and contaminating agents. In order to control and regulate these emissions, the European Union issued the Directive 2000/76/CE which establishes the legal limits of atmospheric emissions for incineration plants.

Therefore, it is fundamental to equip the installations with controllers and technology that will clean the air that is emitted into the atmosphere.

In continuation, the particle separation systems of the incineration plants shall be explained.

3.4 Separation of particles

Fly ashes are considered to be particles along with the fine ash found in the furnace, the reagents. These by-products are formed as a result of other cleaning processes and condensing.

The most widely used equipment in the cleaning of gases are:

Cyclones:

This equipment is used to separate the solid particles suspended in air, gas or liquid. Rotation and gravity are used to separate solid and fluid mixtures. A high speed air flow is established in the cylindrical or conic container, otherwise known as a cyclone. The air flows in a helical pattern travelling from top to bottom.

Venturi washers:

It is a highly effective wet scrubber, particularly suited for particle matter that is sticky, inflammable or corrosive. A venturi washer has a neck, where the gas is prepared to be cleaned, and a centrifugation separator that separates dust attached to water drops from the gas flow.

The advantages of this washer are that they have low inversion and maintenance costs, they have a simple design and installation process and are highly effective at collecting fine particles. The disadvantage is that they consume a lot of water, which increases the cost of operation.

Sleeve filters:

Sleeve filters are an equipment that use fiber filters. Combustion gases are circulated through and these filters retain the solid particles. The filter is made up of various fiber sleeves deposited over metal baskets. These sleeves should be designed around the thermal conditions they will be exposed to and around the presence or non-presence of corrosive compounds. The size of the pores will determine the minimum size of retained particles.

3.5 Elimination of acid gases: SO_x, HCl, HF.

Depending on the nature of the waste to be incinerated in the combustion process, different gases are produced with variable concentrations. These gases are then cleaned through various methods.

Wet scrubbing process:

This type of cleaning requires two stages of scrubbing. As was explained previously, this process consists of a chamber that is injected with water spray, sometimes additivated, counterflowing against the gas so that particles will stick to it.

During the first stage gases are cooled down until they reach their saturation temperature, when the halogen compounds are absorbed. The acid ions react with calcium hydroxide and form their respective salts

During the second stage of the cleaning process water spray is injected into the different levels to counter flow against the incoming gas. Different reagents can be added to the water, and they are calcium hydroxide, calcium carbonate or sodium hydroxide. Thus, all SO_2 becomes $CaSO_3$.

Dry wash process:

This process is based on the injection of a neutralizing compound into the gas flow. Lime is released into an absorber. An absorber is used because this facilitates the neutralization reaction as well as allowing for the collection of the by-products.

Semi-dry wash process:

This process is similar to the dry wash, but instead of releasing lime into the gas flow, the solids are ground down by other means

The previous technologies allow us to obtain good results in the elimination of acid gases from the gas flow. The semi-dry process allows us to lower the consumption of reagents in comparison with the dry wash, and these two processes do not generate waste water as happens in the wet scrubbing process. It has to be taken into account that this waste water has to be treated before being discharged.

3.6 Issuance of waste:

The APC ash collected from the gas purifying system, due to its high content in metal and leachate, has to be treated before being discharged into a class T3/33 waste container.

The generated slag is stabilized in a water base, and, by means of a conveyor belt and a set of sieves, the large particles are eliminated. Following the stabilization and homogenization processes, the slag can then be used in the field of construction.

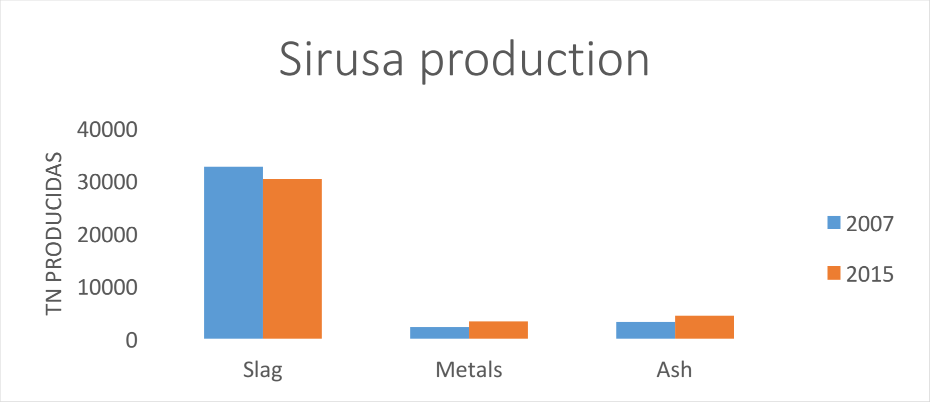
3.7 The Tarragona Incineration Plant (SIRUSA.SA)

SIRUSA in its origin was conceived as a smart solution, a supra-municipal and intercounty solution to the problem of urban waste and over-flowing landfills. It was a brave option for energy recovery from the transformation of waste, during a time of much opposition and social controversy surrounding the theme of incineration.

After the agreement of the constitution of the Commonwealth the location of the plant was chosen in an industrial polygon close to road junctions that unite the various municipality owners of the plant (Tarragona, Reus, Salou, Cambrils,Vila-Seca,Vall,la Canonja y Constantino), in accordance with the criteria for sustainable mobility.

The success of its handling is due to the compiling of strategies and policies to tackle key future challenges. These policies have three main focuses: to anticipate possible legal changes, alternative proposals for plant needs and the search for cooperative alliances with other businesses and public administration bodies.

During the 25 years of service, from the initial activity in January 1991, the path SIRUSA has taken reflects very smart criteria, constantly focusing on reducing, reusing and recycling concepts such as responsibility and investigation. For this reason, SIRUSA is a global reference, not only for experts, workers and politicians, but for its overall management.



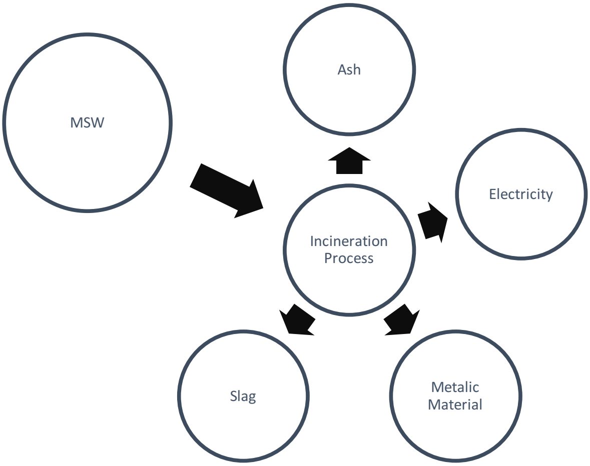
Graph 1: Sirusa production years: 2007 and 2015.

Table 1. Sirusa emissions 2015

Emission value into atmosphere 2015	Limit	Emission
Particles (mg/Nm^3)	10	5.72
NO_x (mg/Nm^3)	200	92.50
CO (mg/Nm^3)	50	13.91
HCl (mg/Nm^3)	10	4.77
SO_2 (mg/Nm^3)	50	12.15
NH_3 (mg/Nm^3)	10	5.79
TOC (mg/Nm^3)	10	1.12
HF (mg/Nm^3)	1	0.10
Hg (µg/Nm^3)	0,05	0.0006
PCDD/PCDF (ng/Nm^3)	0,1	0.00937
Cd+Tl (mg/Nm^3)	0,05	0.0038
Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V (mg/Nm^3)	0,5	0.0455

On the one hand, the data collected from SIRUSA in graph 1 shows a decrease in slag production, but an increase in the amount of ash and ferrous material in regards to 2007. On the other hand, we can appreciate the fact that SIRUSA's emissions from 2015 were much lower than the established limit.

3.7 Incineration waste.



The data issued by ACEVERSU in 2007, shows that for every 1000 kg of solid urban waste the incinerator produces 25kg of ferrous material, 30 kg of ash, 230 kg of slag and obtains 430 KW/h of electrical energy.

Slag:

According to the catalog of waste in Catalonia (CRC) slag and none-fly ashes are categorized with the waste code 190101. (CER 190112) and are classified a non-special waste. On the 15th of February 1996 the environmental department defined slag as: "Industrial waste principally of an inorganic nature that is left in a furnace following the thermal process and the separation of the iron fraction".

Slag is a very important by-product of the incinerator because it represents between 80 and 95% of the solid waste obtained in an incineration plant.

The incineration process considerably reduces the volume and mass of waste. There is around 100 and 150 thousand tons of slag produced in Catalonia every year. Between 250 and 420 kg of slag obtained for every ton of waste incinerated. Slag has the appearance of a granular material, with a maximum size of a variable particle, a greyish color, wide particle size distribution, and a high level of humidity.

Different studies have shown that slag produced from incineration has a continuous particle size distribution in its heterogeneity. A slight divergence of values can be observed in the bigger fractions, but for the medium fractions, in the same sieve opening there can be differences of up to 50%.

- Synthetic ceramics.
- Natural ceramics.
- Glass.
- Fusion products.
- Non-burnt material.
- Ferrous metals.
- Non-ferrous metals.

The slag obtained after incineration does not cease to be reactive or pollutant. The best way of reducing this behavior is by aging it. There are different factors that take part, such as the pH, humidity conditions and the temperature. As a result, small mineralogical and physical changes can be observed that affect the stability of the metal in the slag.

4. OBJECTIVES

The aim of this study is to reduce CO_2 emissions and as a result to reduce the amount of cement used in mortar. Accordingly, the objectives are the following:

- Elaborate a formulation with the highest possible ash contents that still maintains the necessary mechanical properties.
- Find out the best ratio between the two factors depending on the mechanical properties of the formulations.
- Carry out a leachate analysis on the best formulation obtained from the study.
- Determine the viability of using the formulated mortar as a base for roads with little traffic flow.

5.CHARACTERIZATION OF MATERIALS

5.1 Fly ashes

Fly ashes are defined, according to the Spanish regulation UNE-EN 450-1:2006+A1:2008, as "a fine dust made up of mostly spherical particles, crystalline, caused by the combustion of ground down waste, with or without co-combustion materials, that have pozzolanic properties and that are fundamentally formed by SiO_2 y Al_2O_3; the contents of reactive SiO_2, as is defined and described by the EN 197-1 regulation, constitutes at least 25% of its mass.

Figure 2: Fly ashes. (http://www.silotransport.cz/en/fly-ash)

Fly ashes are used as complementary cement-like materials[2],[3] in the production of mortar for the Portland base. A cement-like material, when used in conjunction with cement, it contributes to the resistance properties of the material, whether it be through hydraulic or pozzolanic activity. Previous studies [4],[5],[6] have shown that the amount of incorporated ash into cement is limited by the salt quantity, especially of chlorides.

The potential of using fly-ashes as a substitute material for concrete has been studied since the beginning of the last century, but was not put into use until nearly half a century later.

Fly ashes are a product of incinerators and energy generating plants. A large amount come from waste incinerators where unburnt waste is taken to a combustion zone in a furnace, while the gases are collected overhead.

Fly-ashes form a pozzolanic material. Following their definition ash creates 3 reactions that take place in close sequence: a) formation of gel due to the metallic oxidation, b) formation of ettringite when the ash is saturated with water, c) hydration of the oxide calcium and oxide magnesium [7].

Chemical properties.

The fluorescence of X rays (FRX) allows us to determine in a semi-quantitative way the presence of the most numerous elements that the sample contains, expressed in the way of the respective oxides that are most stable. As can be observed in the table 2, the quantity of each compound is expressed by its percentage.

Table 2: Fluorescence X ray results

Compound	medium Wt (%)	Element	medium Wt (%)
CaO	48.345	**Ca**	34.57
Cl	8.85	**Cl**	8.85
SiO_2	6.64	**Si**	3.11
SO_3	6.24	**S_x**	2.5
K_2O	4.33	**K**	3.59
Na_2O	4.28	**Na**	3.18
Al_2O_3	4.02	**Al**	2.13
MgO	1.73	**Mg**	0.05
P_2O_5	1.36	**P_x**	0.6

TiO_2	0.86	**Ti**	0.52
Fe_2O_3	0.79	**Fe**	0.55
ZnO	0.72	**Zn**	0.58
PbO	0.12	**Pb**	0.11

As was mentioned earlier, due to the gas cleaning system, the main component of this type of ash is calcium. In the gas currents of SIRUSA, they use a type of dry wash, so that in the neutralization of the gas with lime, the main components obtained are lime, chloride and Sulphur

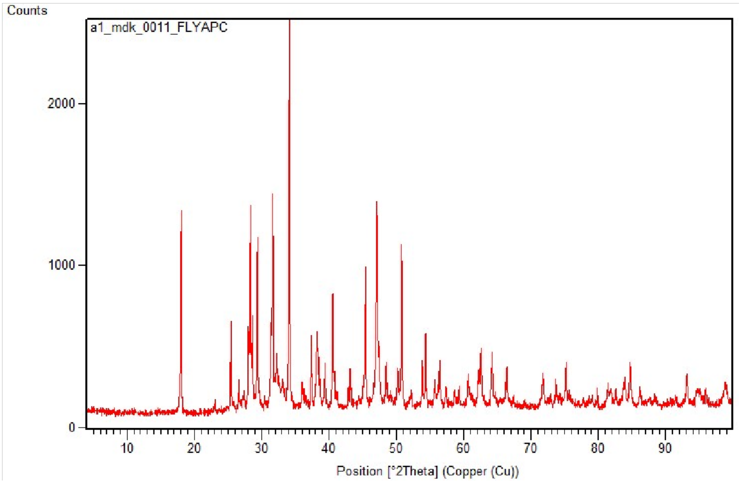


Figure 3: DRX results.

In the case of APC ash, the resulting components from the DRX testing are NaCl, KCl, $CaCO_3$, CaO, CaCl(OH), $CaSO_4$, $Ca(OH)_2$, MgO. These phases have to have a similar outcome in the DRX testing of the mortar. The resulting salts are caused by the chloride derivatives from the combustion.

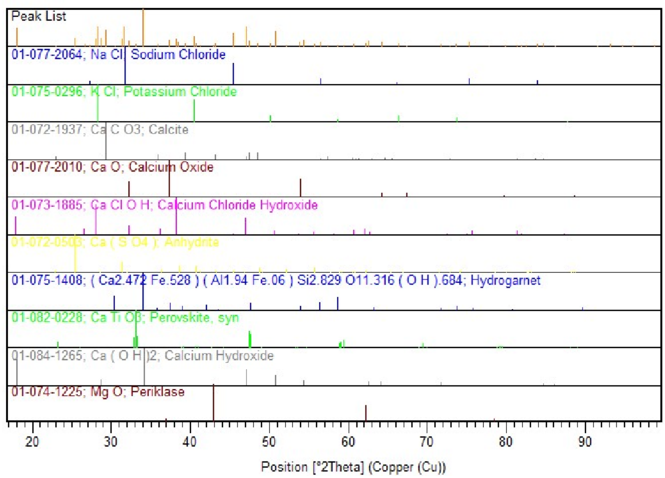
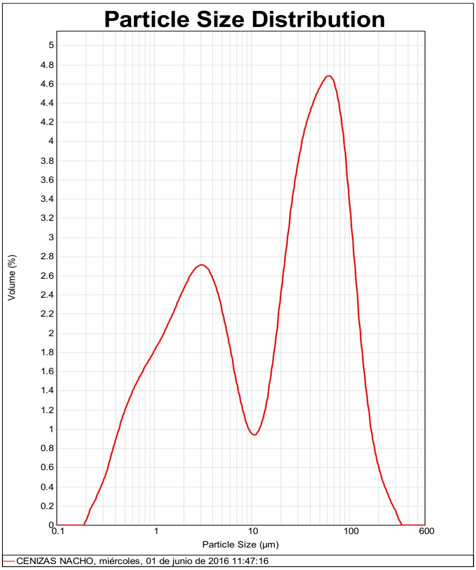


Figure 4 FRX results.

Older studies have shown that a possible optimization of fly-ashes resides in a pre-wash, which in the following study has not being undertaken for budget reasons. The washing of the ash is done. to extract the maximum content of chlorides and Sulphur [8].

Granulometric distribution

The particle size distribution of ash is a result of the type of utensil used in its collection. In the case of SIRUSA, a sleeve filter is used which means that the particle size distribution will be adapted to this. This analysis has been done, in a dry environment, without being diluted, as can be observed in Figure 4.



Graph 2: Granulometric distribution APC

As can be seen in the figure, the maximum size of the APC ashes is 60 µm.

All the granulometric test follows UNE-EN-1015-1 for those which particle sizes is below 2.

Leachate potential

According to the “ *Agencia Catalana de Residuos*”, APC ashes are catalogued as hazardous waste meaning that all the resulting ash in Catalonia has to be deposited in specialized and controlled containers.

As is indicated in the regulation, testing has been done on particles with an inferior size of 4mm, on a 100 g sample with a solid-water ratio of 1:10 that is stirred constantly at 3 rpm during a 24h period.

According to the catalogue of waste in Catalonia (CRC), dust and fly-ashes are categorized with the waste code 190103.(CER 190113) and are classified as special waste, which requires them to undergo a stabilization process.

5.2 Cement

Cement is a conglomerate hydraulic, or in other words, an inorganic material that has been finely ground down, which, when mixed with water, forms a paste that sets and hardens by means of reactions and hydration processes and that, once hardened, retains its resistance and stability below water.

When dosed and appropriately mixed with water and aggregate it should produce a concrete or mortar which retains its workability for a sufficient amount of time, which will reach a certain level or pre-established resistance and should present a long-term stability of volume.

The hydraulic hardening of cement is mainly due to the hydration of the calcium silicates, although the hardening process can also be influenced by other chemical compounds, such as aluminates. The sum of the proportions of reactive calcium oxide (CaO) and reactive calcium silicon dioxide (SiO2) will be at least 50% of the overall mass, when the proportions are in accord with the European legislation EN 196-2.

A CEM I 52,5R type Portland cement is used in the process, which is commercialized by the business Ciments Molins, SA.

Table 3: Properties of cement SuperDragon CEM I 52,5 R (Ciments Molins, 2015)

	Usual value	**ications according to regulation**
Clinker (%)	98	min. 95-max. 100
Minor component (%)	2	min.0-max.5
Loss due to calcination (%)	2,5	max. 5.0
Sulphur, SO (%)	3,4	max. 4.0
Chlorides, Cl- (%)	0.04	max. 0.10
Insoluble waste (%)	0.7	max. 5.0
Specific surface Blaine (cm/g)	4,600	-
Expansion Le Chatelier (mm) start	0.5	max. 10

Setting (min)	110	min. 45
Final Setting (min)	170	max.720
1 day Compression (Mpa)	27	-
2 day Compression (Mpa)	40	min.30.0
7 day Compression (Mpa)	52	-
28 day Compression (Mpa)	61	min. 52.5

5.3 Centipor Retard:

The additives in mortar are products that are capable of being dissolved in water. They are added during the mixing process or directly to the formulation of the mortar. An additive allows different properties to be incorporated which can influence everything from the malleability to the mechanical properties of the mortar.

The most common additives in the industry are: retarders, accelerators, water reducers, defoamers and fluidizers.

For this Project we decided to use a retardant additive (Centripor Retard 225). This type of additive is a chemical substance which slows down the initial setting of the mortar, increasing its workable time. The use of retarders can also influence the amount of water needed for mixing.

6. METHODOLOGY

6.1 Formulations

The influence of different factors in the mechanical properties has to be analyzed. These factors depend on the ratio between the amount of ash and cement content and the influence of the ratio between water and the total solid content. The quantity of additive is fixed at 1% over the total weight of the cement.

In this way, the matrix is as follows on table 4:

Table 4: Formulation matrix

	-1	**0**	**1**
APC/OPC	30/70	50/50	70/30
W/S	0.3	0.4	0.5
Additive		1% Cement	

By introducing the number of experiments that we want to do along with the matrix, the program will give the corresponding formulations with the different weight of ash, cement and water.

Once the testing is done and the resulting values introduced a plan is obtained of the tested values of the materials. In the present study the aim is to incorporate the maximum quantity of ash while maintaining resistance to high compression. These factors will be the most important in the designing of new experiments.

The properties that were analyzed by the program were: consistency, flexural strength, and resistance to compression

6.2 Mixing of mortar.

The mixing of mortar was done in a regular cement mixer. The mixing of cement was decided to be done as follows:

The mixing of mortar is done following the regulation for the mixing of floor mortar UNE-EN 1015-2 which specifies that it will be mixed for a minute at a low revolution speed, it will be hand-mixed for a minute and finally, mixed rapidly for the last minute.

First, all the cement is mixed with all the water and all the additives. It is done in this way so ensure that all the water will react with the cement. Once the first mixing is done, all the ashes are added for the hand-mixing process and protocol is continued to be upheld

Thus, part of the excess water from the reaction with the cement will be for the encapsulation of the ashes.

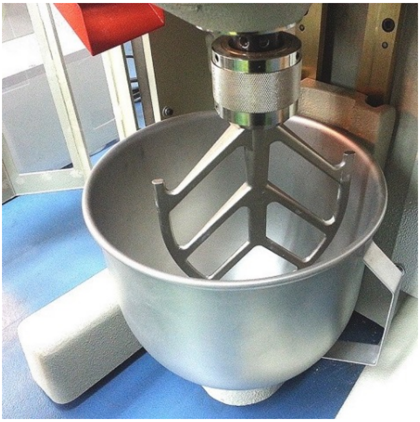


Figure 5: Planetary mixer.

6.3. Determining the fresh density

To determine the fresh density of the mortar we used a recipient, whose volume we knew, and a set of scales. For the testing to be representative, the recipient is filled without putting pressure on the cement so as to not compact it and the table that supports it is hit 5 times, once each second. Shortly after the excess content is collected, and is also weighed in the recipient. The blows are dealt to evacuate any air that might be trapped in the recipient due to the way the cement was introduced or for the way it was mixed.

6.4 Determining the consistency:

To determine the consistency a flow table and a cylinder is used. The cylinder is placed in the center of the flow table, after being wet with a wet cloth, and is then filled with the fresh mortar. It is slumped 5 times. The cylinder is then removed, and the mortar is slumped 5 times once again. After a quick interval it is slumped for a final 5 times.

Figure 6: Shaking table, Material Laboratory UPC ETSEB

6.5 Making of test tubes

Once the mortar has been mixed it can be put into polystyrene molds (16x4x4cm). Once these molds are full they are put on a shaking table be vibrated twice for 5 seconds. Later, with the help of a trowel they are spread out, and are weighed to later determine the water that is evacuated in the following hours.

The shaking table serves to ensure a homogenous weight in the three test tubes of mortar and to evacuate all the introduced air during the mixing process.

6.6 Hydraulic retraction

The contraction of the mortar from water evaporation is produced after having finished the setting time. If the retraction from the drying process is intense it causes a volumetric change capable of creating important tensions in areas that are prevented from being misshapen. If the adherent value of the mortar is surpassed, it causes the edges of the cracks to arise and curl up.

It is important to control the retraction of the mortar once it is hard because dryness can also cause cracks.

6.7 Flexural strength of mortar.

Flexural strength is an important parameter in the characterization of the mechanical properties of mortar. After 7 days of curing, the flexural strength of all the test tubes was evaluated.

To do this we need a mechanical testing machine designed for the test tubes used for mortar. This type of machine has a mobile head that can be replaced with different ones, depending if we are doing flexural or compression testing.

This testing follows the UNE-EN 1015-11

Figure 7: 3-Point flection test. DIOPMA, Laboratory of Materials

6.8 Mortar resistance to compression.

Resistance to compression is one of the most important properties of mortar. This resistance is evaluated after 7 and then 28 days. The same test tubes are used for testing compression and flexing, but two compression values are obtained for each flection value.

To carry out the testing of the compression the same machine is used to test flexing, but the head is switched to a compression head.

This testing follows the UNE 80-101-88/EN 196-1 regulation.

Figure 8: Compression test UNE-196-1. DIOPMA Laboratory of Materials

6.9 Resistance to abrasion. The Los Ángeles test.

In order to determine the abrasion resistance a set of sieves is needed that fulfill the regulations dictated by the UNE 7.050. We also needed a Los Angeles testing machine as well as an abrasive load that consisted of 11 balls with an approximate diameter of 48.8 mm and a weight between 390 and 455 g.

For this test, 10 kg of material is introduced into the chamber of the Los Ángeles machine and it is allowed to spin 500-1000 times depending on the particle size distribution.

The result of the test is the difference between the original mass of the sample and the mass after testing once it has been put through the same sieve.

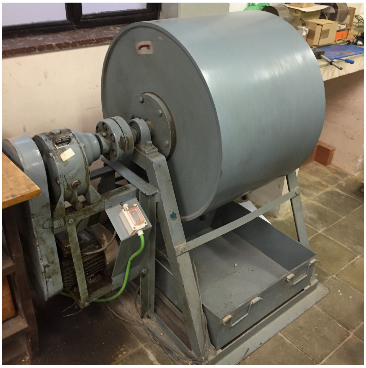


Figure 9:Abrasive testing machine LA

Figure 10. Mortar after LA testing

7. RESULTS AND DISCUSSION

This part is a presentation of the results obtained from the testing of the different formulations of mortars.

Formulations:

Below are the formulations carried out to determine the best ratio of cement-ash-water.

Table 5: Formulations

Run	APC (%)	W (%)	Run	APC%)	W(%)
1	30.0	32.5	**15**	70.0	45.0
2	40.780	35.0	**16**	60.0	40.0
3	52.236	40.7	**17**	40.800	35.2
4	50.0	45.0	**18**	52.200	38.1
5	35.0	33.8	**19**	50.0	37.5
6	70.0	35.0	**20**	70.0	42.5
7	55.0	38.8	**21**	40.800	35.2
8	40.780	35.0	**22**	70.0	42.5
9	70.0	40.9	**23**	70.0	42.5
10	70.0	35.0	**24**	60.0	40.0
11	60.0	37.7	**25**	70.0	42.5
12	70.0	45.0	**26**	55.0	38.8
13	30.0	32.5	**27**	70.0	42.5
14	55.0	35.0			

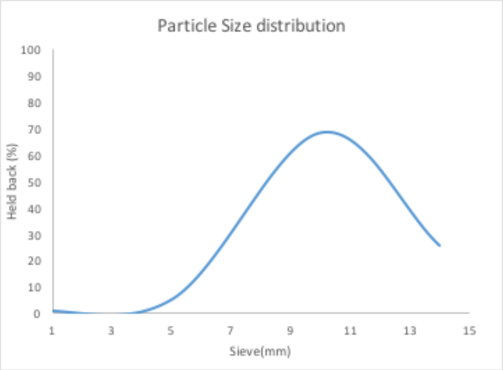
As was stated earlier, our priority was to incorporate the maximum quantity of ash while maintaining good mechanical properties. To do so, we formulated 16 initial proposals.

After obtaining the mechanical results we made 12 new proposals whose expected values were focused towards the optimal plain of interaction factors.

Particle size study.

In the previous section we commented on the particle size distribution that the ash presented. In continuation are the results of the formulation with the optimal results.

The following values were obtained after a 28 day curing process, after the standardized testing with the Los Ángeles machine and subsequent grinding.



Graph 3: Particle size distribution before LA test

Consistency

Accordingly, here is the data of the tested consistencies of all the formulations.

Table 6: Consistency results

Run	Flow (mm)	Run	Flow(mm)
1	96.310	**15**	138.575
2	103.745	**16**	116.800
3	183.080	**17**	106.655
4	194.445	**18**	110.180
5	95.750	**19**	108.06

6	101.445	**20**	110.595
7	125.105	**21**	96.240
8	131.210	**22**	107.95
9	121.735	**23**	98.155
10	88.085	**24**	116.800
11	147.545	**25**	68.920
12	134.420	**26**	125.105
13	99.265	**27**	98.155
14	90.960		

As can be seen in the formulations, consistency is not a factor that is affected by the amount of incorporated ash, which varies from 30 to 70 % of ash. Throughout, the consistency remains constant.

On the other hand, the amount of water used could be observed to considerably influence the formulations. In a formulation with 70% ash, the consistency increased by 25% when going from a content of 35 to 45 % in water weight over the total solid (1,500 grams).

As can be seen in the plan obtained through the program, interaction of the different factors is related. An increase in the amount of water and a reduction of the of the ash contents considerably increases the consistency.

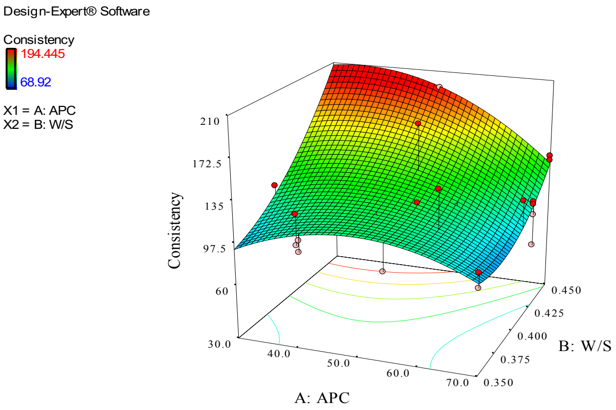


Figure 11: Consistency results DoE

The function that describes the plan is shown in the following Equation:

$$Flow\ (mm) = 590 + 13APC - 4545{,}88W - 18{,}94APC\ W - 0{,}06APC^2 + 7827{,}73W^2$$

The computer program gives feedback of the property influence through different influential factors. It gives us a function of quadratic fit that allows us to obtain a likely outcome without having to physically do an experiment.

Flexural Resistance.

As was mentioned previously, the resistance to flection is an important mechanical property of concrete. Quite often, the measuring of flexural properties serves to analyze the capacity of our mortar to evacuate air. A mortar containing no antifoam, as in the case of this study, has the tendency to retain air, so if it has problems evacuating, it leaves small vacancies in the form of pores and cracks will subsequently form going downwards as a result of the flection.

The results obtained for the formulations are as follows:

Run	Flexural(MPa)	Run	Flexural (MPa)
1	4.176	**15**	1.592
2	4.279	**16**	2.089
3	3.444	**17**	3.4553
4	3.116	**18**	2.9176
5	5.235	**19**	3.7318
6	1.242	**20**	1.3297
7	3.014	**21**	5.2757
8	4.450	**22**	1.4092
9	1.168	**23**	1.4658
10	1.333	**24**	2.0891
11	2.382	**25**	1.9552
12	1.256	**26**	3.014

13	5.756	**27**	1.465
14	2.492		

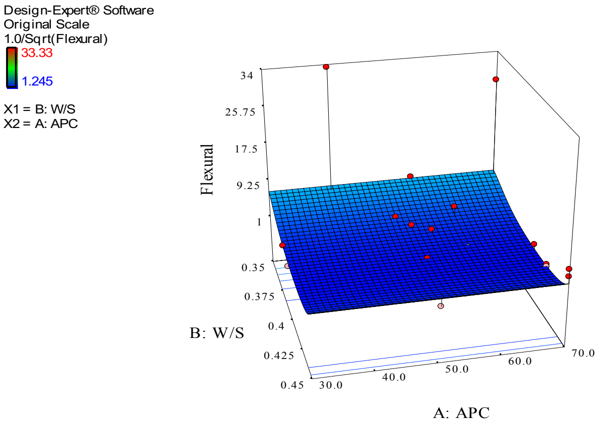


Figure 12: Respuesta Flexión DoE.

The function that describes the plan is shown in the following Equation:

$$\frac{1}{\sqrt{Rf}} = 118{,}52 - 945{,}68W + 2503{,}58W^2 - 2188{,}75W^3$$

It is possible to observe from the equation or from the diagram itself how the ash does not influence the flexural resistance. The flexural resistance decreases in tests with a higher water content.

The capacity to evacuate water that has not reacted with cement is very important. If water is not evacuated quickly it can leave air bubbles in the mortar which can lead to the development of cracks. This can be solved by incorporating antifoam in the mortar which helps evacuate the air quicker and, in turn, avoid cracks.

Resistance to compression.

As was mentioned previously, resistance to compression is the most characteristic property of mortar. For every formulation three cubic test tubes with standardized dimensions were prepared to be tested following the UNE 80-101-88/ EN 196-1 regulation.
Next are the results of the resistance to compression, obtained over a 7 day period.

Table 8: compression results.

Run	Compressive (MPa)	Run	Compressive (MPa)
1	18.031	**15**	3.145
2	22.901	**16**	3.884
3	10.595	**17**	19.798
4	9.046	**18**	8.661
5	17.711	**19**	11.198
6	3.001	**20**	3.000
7	6.780	**21**	18.129
8	21.612	**22**	3.225
9	2.483	**23**	2.841
10	2.456	**24**	3.884
11	5.998	**25**	6.298
12	2.492	**26**	6.780
13	26.301	**27**	2.841
14	7.023		

The function that describes the plan is:

$$Log\ (Rc) = 5{,}267 - 0{,}011APC - 15{,}823W + 0{,}248APC \cdot W - 0{,}001APC^2$$

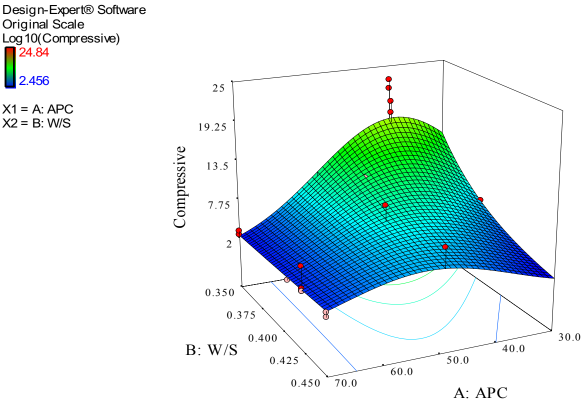


Figure 13: Compression results DoE

The test tubes that contain a higher water and ash content have a lower compression value. The higher resistance to compression is found in the formulations with maximum cement content.

By comparing the values from the technical sheet of the cement used, it could be observed that after 7 days, a cement formulation with a complete cement content presented a compression value of around 50 MPa, while the formulations with a lower ash and water content presented half the compression values. This happens for various reasons:

-The granulometric curve can be very similar to the Füller model which allow us to predict better mechanical properties.

- The formulations done with a lower percentage of water cause better mechanical properties because there are less likely to be any problems evacuating this same substance. In this manner, we achieve a total hydration of the cement.

-Pozzolanicity. This is defined as the capacity of certain materials to react with lime or calcium hydroxide proceeding from the hydration of Portland cement, which, when in contact with water or at room temperature, forms hydrated products with conglomerate properties.

Mortar retraction.

The changing dimensions of the test tubes was followed. During the curing process the test tubes lose water and often they expand or shrink depending on the system that forms them.
To elaborate this study, the dimensions were measured after a 24 h period, 7 days.

Table 9: Shrinkage results

Run	Shrinkage (mm/mm)	Run	Shrinkage (mm/mm)
1	0.001	**15**	-0.003
2	0.003	**16**	-0.007
3	-0.002	**17**	0.003
4	-0.004	**18**	-0.003
5	0.002	**19**	-0.005
6	-0.006	**20**	-0.003
7	-0.007	**21**	0.000
8	0.001	**22**	-0.006
9	-0.001	**23**	-0.001
10	-0.009	**24**	-0.007
11	-0.014	**25**	-0.002
12	-0.002	**26**	-0.007
13	0.002	**27**	-0.001
14	-0.003		

Results of optimal formulation.

To determine the optimal formulation, we decided to prioritize the incorporation of the maximum amount of ash while maintaining the maximum resistance to compression. Thus, we did not prioritize as highly the consistency or the flexural resistance, and so reached a formulation with an ash content of 54%, with a water quantity of 35% in relation to the cement. The following table is a summary of the values discovered from experiments and the values predicted by the computer program.

Table 10: Comparison of consistency results from the experimental testing with the DoE

	Consistencia		
Test Tubes	**DoE**	**Test**	**Starndar desviation**
1	116.996 ± 19.230	78.325	27.344
2			
3			
4		91.165	19.696
5			
6			
7		80.720	17.697
8			
9			

Table 11: Comparison of Flexural strenght results from the experimental testing with the DoE

	Flexión		
Test tube	**DoE**	**Test**	**Standard desviation**
1	6.854± 2.880	2.473	3.203
2		2.062	3.493
3		2.375	3.272
4		2.553	3.146
5		3.014	2.820
6		2.552	3.147
7		2.388	3.263
8		2.396	3.257
9		2.250	3.361

Table 10: Comparison of consistency results from the experimental testing with the DoE

Table 12:Comparison of compression results after 7 days with DoE

	Compression (7 days)		
Test tube	**DoE (mm)**	**Test (MPa)**	**Standard desviation**
1	11.065 ± 1.318	8.878	1.546
2		8.167	2.049
3		8.633	1.720
4		7.621	2.435
5		7.174	2.752
6		8.106	2.093
7		7.240	2.705
8		6.627	3.138
9		7.774	2.327

Table 13: Comparison of compression results after 28 days with DoE

Compresion (28 days)			
Test tube	**DoE (mm)**	**Test (**MPa**)**	**Standard deviation**
1	11,065± 1.318	14.071	1.74
2		14.457	2.020
3		14.249	1.873
4		12.462	0.609
5		13.274	1.183
6		13.519	1.357
7		10.163	1.0164
8		15.120	2.488
9		12.183	0.412

As we can see in table 13, with the pass of time compressive streght fits better the model. Although we have no lat of fit desviation still significant once we evaluate the optimal formulation insde our range .

Testing results from LA abrasion.

Table 14: LA results.

m (g)	**1500**	
Sieve (mm)	initial weight (g)	Final weight(g)
13.35	384	80
9.42	1023	654
4.94	78	514
0	15	252
Total	1500	1500
Coef LA	36%	

Generally, the arids with an LA coefficient superior than 50% are described as bad quality arids and so cannot be used in the construction sector. Those with an inferior value of 20% constitute high performance arids and are usually used for roads with heavy traffic flows. In our case, we have obtained a medium-type arid, meaning it can be used for roads with little traffic flow.

The before and after particle size distribution of the LA tests are shown as follows.

Table 15: Particle size results before and after LA testing.

sieve (mm)	**pass (g)**
2	471.7
1	6.8
0.5	2.4
0.25	1.1
0.125	5.7
0.063	6.6
0	5.7

Mortar		**Mortar + LA**	
tamiz (mm)	**paso (g)**	**tamiz (mm)**	**paso (g)**
14	384	**14**	80
10	1023	**10**	654
5	78	**5**	514
0	15	**0**	250

Leachate testing results.

Table 16: Results from leachate testing

pH	**12.4**
k(ms/cm)	22.1
Cl^-	7616
Zn	0.95
Pb	0.19
Ni	0.04
Cu	0.01
Ba	6.78
As	0.02
Mo	0.21
Hg	<0.001
Cr total	<0.001

The results are expressed in ppm and we can observe a high content of chlorine. A prewashing of the ash would help reduce the chlorine content in the mortar and, as a result, in its pH.

8. CONCLUSIONS

Once the 27 proposals were analyzed and the results of the testing incorporated into the computer program, we were able to obtain a formulation which focuses on the resistance to compression, but that also contains the maximum amount of ash. This formulation is made up of an ash content of 54%, a water-solid ratio of 35% and an additive fixed at 1% over the weight of the cement. The interaction model obtained from the computer program presents no lack of fit with the data obtained from testing.

The results from the testing in each study present deviations from the values obtained from the computer program. Nevertheless, if these are compared with the 28-day curing process, the deviations are reduced.

There is a dependency between the water and ash content that is reflected in the data obtained from the compression and consistency testing.

The lesser content of water allows the cement to be completely hydrated along with part of the ash content, as a consequence, there is less evacuation of water during the curing process, something that causes a better mechanical resistance and a medium retraction of 0.002 (mm/mm).

The results from the leaching analysis reflect a high content of chlorine in the mixture. This means it is potentially a contaminating material and from an environmental point of view, it would be inappropriate for use in construction. As was mentioned previously, a study should be undertaken of the washing of fly ashes in order to reduce this chlorine content.

From the abrasion testing with the LA machine we were able to determine if the aggregate was accurate, in concordance with the regulation for use in civil engineering construction.

According to regulation, the maximum abrasion (AASHTO T-96) for an aggregate in a sub-base layer should be of 50%, and 45% for a base layer, which means that our material could be used together with Portland cement in slabs for bridges, sub-base layers, or base layers.

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12. ACRONYMS

APC : air pollution control
W: water
OPC: Portland cement.
LA: Los Ángeles machine