INCIDENCE OF CATALYTIC CRACKING SPENT CATALYST (FCC) ON PROPERTIES PHYSICAL-MECHANICAL CHARACTERISTICS OF HIGH-PERFORMANCE CONCRETE

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Abstract

In recent years, due to technological progress, the requirement for high-performance concrete has led to research into the improvement or substitution of petrochemical residues in concrete mixtures. The objective of this investigation was to design a 55 MPa concrete with the use of Lafarge Reinforced Cement, Holcim Type HE Cement and Chimborazo Type HE Cement with the replacement of the cement by exhausted catalyst at 2.5%, 5%, 7.5% and 10% in order to reduce the environmental impact generated in the cement production and manufacturing process. Finally, it was concluded that the use of spent catalyst is feasible in the field of high-strength concrete because it improves mechanical properties such as resistance to compression, traction, bending and elasticity modulus, as well as increases durability, generates protection against attacks. by carbonates, sulfates and damage caused by chlorides

Keywords: High Performance Concrete, Fcc Depleted Catalyst, Durability, Compressive Strength, Tensile, Bending, Modulus of Elasticity.

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1. Introduction

In the field of construction, concrete is a fundamental element due to the advantages it presents when preparing different civil works. This mixture is made up of cement, water, aggregates and additives. The quality of the concrete reached the granulometry of the particles, quality of the fine and coarse aggregate, type of cementitious material, dosage, mixing and curing process [1].

The cement is composed of two mineral raw materials: limestone with a high content of calcium oxide and clay with a high content of silicon oxide, which are taken to a special kiln, where the temperature reaches approximately 1400°C; The minerals are not melted, but if they are combined, after obtaining this mixture, they are crushed in order to produce a binder material with great fineness for use in construction. The pure portland cement obtained has a final composition as shown in **Table 1.**

Table 1. Composition of Portland Cement

Chemical element	Compound	Porcentage
Calcium	CaO	64,0%
Silicon	SiO2	21,0%
Iron	Fe2O3	2,5%
Aluminium	Al2O3	5,5%
Magnesium	MgO	2,4%
Sulfur	SO3	4,0%
Sodium	Na2O	1,5%
Potassium	K2O	1,2%
Titanium	TiO2	1,0%

Note: [2].

The use of pozzolanic materials in the manufacture of cement is essential due to its potential to react with hydrated lime, which allows greater efficiency in pastes and mortars, where it presents an improvement in mechanical properties, decreases permeability, increases durability, these positive characteristics can be significant in the long or short term, which helps us to have a better performance and development of the concrete in the different civil works.

From another point of view, the catalyst for catalytic cracking (Fluid Catalytic Cracking, hence the acronym FCC), is extracted from the oil industry from fluid bed catalytic rupture units; In Ecuador there are 5 refineries, each year the amounts of industrial waste obtained from the cracking unit are large; the same ones that have a high toxic content, and by not giving them further use, they become a potential environmental and biological threat.

This petrochemical residue can be used as a pozzolanic material in the production of high-performance concrete. The addition or substitution of this element plays a similar role to silica fume, fly ash, and calcined clay, thus allowing the reduction of CO_2 emissions present in the production of cement, and economically, as it is a disposable material, it will reduce the cost in the construction of large-scale works.

2. Methodology

For this project, the design of a high-performance concrete was proposed with the substitution of petrochemical waste from the Fcc unit in a percentage range of 2.5% to 10% in the cement. These percentages were selected based on the investigation "Obtaining Concrete and Mortar from the exhausted catalyst of the fluidized catalytic cracking unit of the Esmeraldas Refinery as pozzolanic addition" where the optimal percentage varies between 5% to 15% for traditional concretes. [3]. This replacement aims to improve the mechanical properties of concrete and reduce environmental pollution. According to the ACI 211.4R-08 Regulation, a Type I Concrete was proposed for dosing, where the compressive strength varies between 50 - 74.99 MPa, in addition the materials used for the mix design are observed in Table 2. shown below:

Table 2. Materials for the mix design

Materiales	**Procedencia**
Cement	Holcim Type HE. Chimborazo Type HE Armaduro Lafarge
Fine Aggregate	Pifo
Coarse Aggregate	Pifo ½”
Additive	Rheobuild 1000

Note: [4].

2.1. Characterization of the aggregates

Based on the ACI 211.4R code, the respective mix design was carried out, in order to determine the appropriate proportions and take as a reference the guidelines established by the Ecuadorian Regulation NTE INEN 2010, to carry out the respective tests on the stone aggregates and the different types of cements used in the investigation.

2.1.1. Loose and compact density of aggregates

For the preparation of the Loose and Compact Density test for Fine and Coarse Aggregate, the NTE INEN 858 (2010) standard was used, where a 2.8 m3 mold was used, considering that it is based on the ½ "aggregate. Below, Table 3 shows the results obtained for the aggregates from the Pifo Quarry.

Tabla 3. Masa Unitaria Agregados de Pifo

Aggregate	**Compacted unit mass (g/cm^3)**
Fine aggregate	1.70
Coarse aggregate	1.42

Note: [4].

2.1.2. Coarse aggregate specific weight

The relative density or specific weight of the coarse aggregate consists in the use of a regulated basket, where the sample of the aggregate is placed, in order to introduce it into water and thus obtain the volume. [5]

2.1.3. Fine aggregate specific gravity

By using a pycnometer calibrated with distilled water, the fine aggregate sample is added and the voids inside the container are removed.[6]

Tabla 4. Unit mass Pifo aggregates

Aggregate	**Specific Weight(g/cm^3)**
Fine aggregate	2.55
Coarse aggregate	2.62

Note: [4].

Table 4 shows the results obtained from specific weights for the aggregates (fine and coarse) from the Pifo Quarry.

2.1.4. Absorption capacity

Property of the aggregates, where the water completely occupies the voids produced in the internal structure of the aggregate, after being exposed to saturation conditions for 24 hours, the calculation of this value is defined by equation (1) proposed by the NTE Regulation INEN 857 and 858.

$$\boldsymbol{C.A} = \frac{W_{SSS}-W_S}{W_S} * 100 \quad (1)$$

Where:

CA: Absorption capacity [%]
Wsss: Mass of the Aggregate in the SSS State [g]
Ws: Mass of oven-dry aggregate [g]

2.1.5. Moisture Content

Based on the NTE INEN 857 and 858 Regulations, moisture content is defined as the amount of water trapped within the pores of the aggregate, this property varies according to the environmental conditions where the material is stored. The percentage of humidity is fundamental in the design of the mix, because it can modify the water/cement ratio, improving the properties of the concrete. This property is calculated using equation (2) given below:

$$\boldsymbol{C.H} = \frac{W_h - W_S}{W_S} * 100 \qquad (2)$$

Where:

C.H: Moisture Content [%]
Wh: Wet aggregate mass [g]
Ws: Oven-dry aggregate mass [g]

2.1.6. Fineness modulus

This value is found by adding the retained percentages accumulated in the series of sieves that comply with the 2 to 1 ratio, this sum is divided by 100, in order to obtain the value that indicates the thickness of the aggregate (which means that between the coarser the aggregate, the higher the modulus of fineness result) [7].
Below is a summary in Table (5) of the data obtained from the fineness modulus for the aggregates (fine and coarse) that will be used in the design of the high-strength concrete mix.

Table 5. Modulus of fineness of aggregates

Aggregate	Fineness modulus
Fine aggregate	3.17
Coarse aggregate	6.73

Note: [4].

2.2. Cement density

According to the NTE INEN 156 (2011) regulation, the density of cement is defined as the relationship between mass and volume, where it is calculated using the Le-Chatelier jar method, which must be filled with gasoline to a point in the lower part of the neck between 0 and 1 cm3, weighed the cement is introduced in minimum quantities with the purpose that it does not adhere to the walls of the bottle, once all the cement has been introduced a stopper is placed and in position inclined the air is released until there are no voids in the surface of the liquid [5]. Table 6 details the data obtained on the density of the cement for each of the cements to be used in the design of the mix.

Tabla 7. Cement Density

Cement type	**Density (g/cm^3)**
Holcim Tipo HE	3.024
Chimborazo Tipo HE Armaduro Lafarge	3.014 3.028

Note: [4].

2.3. X-ray fluorescence

The exhausted catalyst analysis was carried out by means of the X-ray fluorescence spectroscopy assay, which consists in the use of a secondary or fluorescent emission generated by exciting the exhausted catalyst sample by means of strong X radiation [8]. The purpose of this test is the quantitative and qualitative analysis of the chemical elements existing in the sample, as detailed in Table 7, the S8 Tiger Series 2 machine was used, equipped with a rhodium tube and beryllium window, it also presents a greater sensitivity. and high resolution in the analysis of light and heavy materials, guided by the new HighSense technology.

Table 7. Spent catalyst chemical analysis

Element	**Percentage (%)**	**Oxide**	**Percentage (%)**
Al	27,89	Al_2o_3	52,7
Si	26,3	Sio_2	56,25
La	2,19	La_2o_3	2,56
Ti	0,72	Tio_2	1,2
Fe	0,66	Fe_2o_3	0,94
Na	0,32	Na_2o	0,43
Mg	0,26	MgO	0,43
P	0,16	P_2o_5	0,37
Ca	0,1	Cao	0,14

K	0,08	K_2o	0,1
V	0,08	V_2o_5	0,14
Ni	0,05	NiO	0,06
Zn	0,03	ZnO	0,04
Ce	0,03	Ceo_2	0,04
As	0,02	As_2O_3	0,02
Ba	0,01	Bao	0,02
Si	0,1		
Cl	0,03		

Note: [4].

2.4. High performance concrete mix design

The design of the high-performance concrete mix was carried out based on the results obtained in the laboratory, through the use of the ACI 211.4R-08 standard, developing step by step to obtain the final dosage [9]. Below, the dosage is summarized in Table 8 including the humidity correction and the final water adjustment to make the master mix.

Table 8. Final standard dosage

Final Dosage		
Material	Weight (Kg)	Dosage
Cement	563,513	1,000
Coarse aggregate	707,616	1,256
Fine aggregate	794,473	1,410
Water	200,289	0,355

Note: [4].

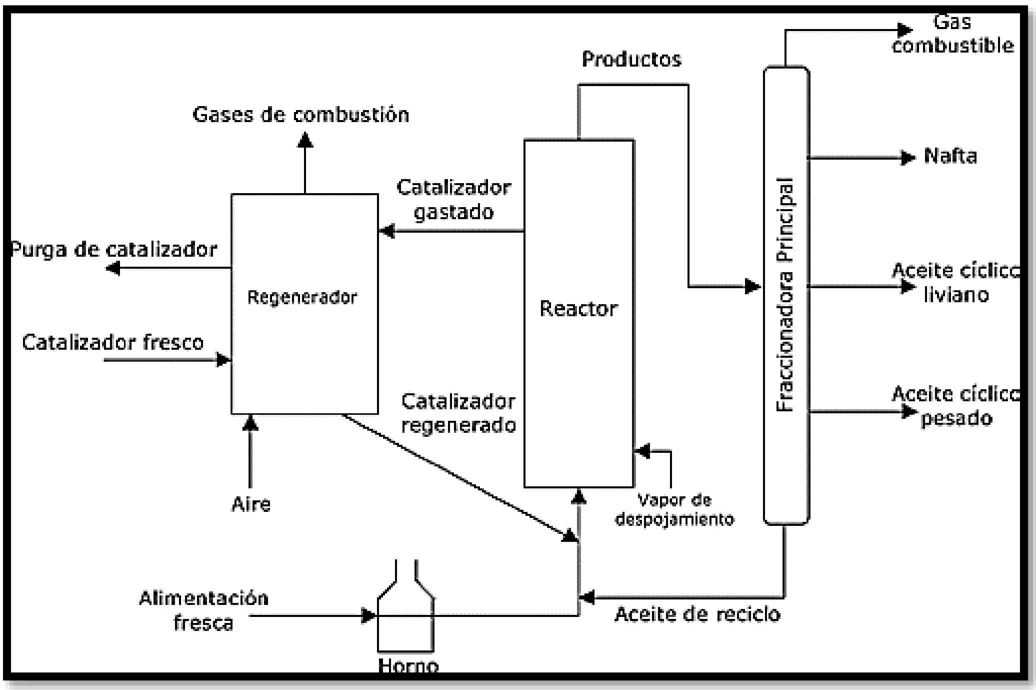


Figura 1. Catalyc Cracking unit [10].

Figure 2. Depleted catalyst sift

Figure 3. Cylinder curing well

Figure 4. Adding wáter and superplasticizer to the mix**Results And Discussion**

3. Results

3.1.1. Compressive strength

For the Compression Resistance tests we are guided by the ASTM C39 Regulation, and the method of maximum normal deviation MND that is based on the number of specimens tested, standard deviation and the average, this statistical model allows us to establish the nominal limit of maximum and minimum variation in order to validate each of the values obtained in the tested specimens, discarding the cylinders that are not within the established range.

According to the results, at 5% of exhausted catalyst there was a notable improvement in mechanical properties, for Holcim Type HE Cement a compressive strength value of 69.94 MPa was obtained, for Chimborazo Type HE Cement of 71.42 MPa and for Lafarge Armor Cement of 60.60 MPa, complying with the value proposed in the design, the exhausted catalyst generating a benefit in the compressive stress by substituting a percentage of cement at 5%.

3.1.2. Flexural strenght

The Flexural Strength or Modulus of Rupture is tested based on the NTE INEN 2554 Regulation, since there is no standardized material, the standard deviation should not differ by more than 16% for tests carried out by the same operator and the same mix.

The calculation to obtain the Modulus of Rupture (Mr) is carried out if the failure is within the middle third or outside it using the equation:

$$\boldsymbol{Mr} = \frac{\boldsymbol{P\ x\ L}}{\boldsymbol{b\ x\ d^2}} \quad (3)$$

Where:

Mr: bending stress of the tested beam (MPa)

P: Maximum load applied on the beam to be tested (N)

L: length of the tested specimen (mm)

b: calculated average of the base (mm)

d: calculated average height (mm)

For each of the beams with the different types of cements, the failure was shown within the middle third with a representative value at 5% of exhausted catalyst for each of the cements tested, resulting in the modulus of rupture for the Holcim Type Cement. HE of 6.89 MPa, Cement Chimborazo Type HE of 7.10 MPa and for Lafarge Armor Cement of 6.24 MPa.

3.1.3. Tensile strength

Based on the ASTM C670 Standard, the indirect tensile test was performed for each of the cylindrical specimens, where the values calculated for two or more test tubes properly made with similar materials should not vary by more than 14% in relation to the average of tensile strength.

To obtain the tensile strength of each cylinder made with exhausted catalyst, it is calculated using Equation (4) shown below:

$$\boldsymbol{fti} = \frac{2\,x\,P}{\pi\,x\,d\,x\,h} \quad (4)$$

Where:
Fti: Tensile stress of concrete (MPa)
P: Breaking load (N)
d: Cylinder diameter (mm)
h: Cylinder length (mm)

According to the tests carried out, the value of tensile strength for Holcim Cement Type HE with substitution of the cement by exhausted catalyst at 5% obtained is 5.26 MPa, presenting a considerable variation in relation to Chimborazo Cement type HE (5% catalyst exhausted) of 4.61 MPa and Lafarge Armor Cement (5% exhausted catalyst) of 3.94 MPa.

3.1.4. Elasticity modulus

The modulus of elasticity calculated for the different types of cement, presented an increase for the replacement percentages of exhausted catalyst at 2.5.5 and 7.5 %, being the most representative result of the petrochemical waste in Cement Chimborazo Type HE with 36908.41 MPa, for For Holcim Type HE Cement, the result was 36,517.01 MPa and finally for Lafarge Armor Cement, 32,074 MPa.

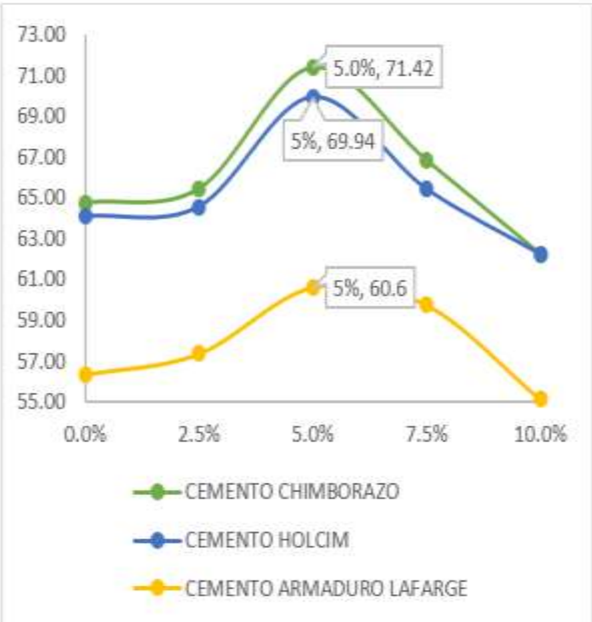


Figure 5. Compressive strength results

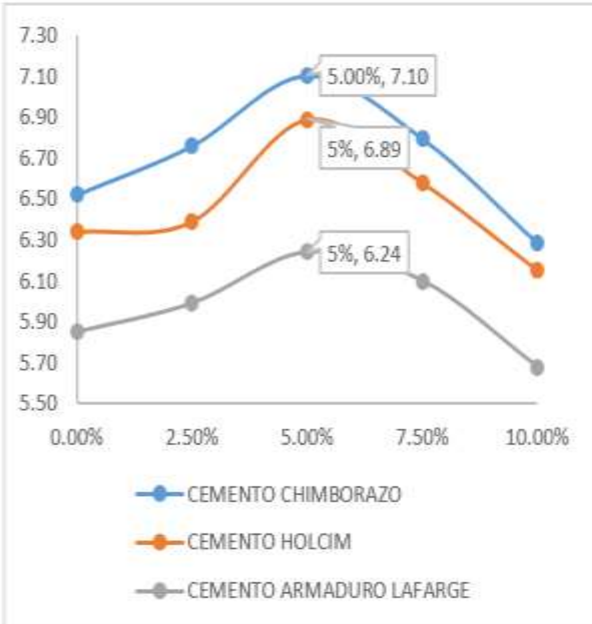
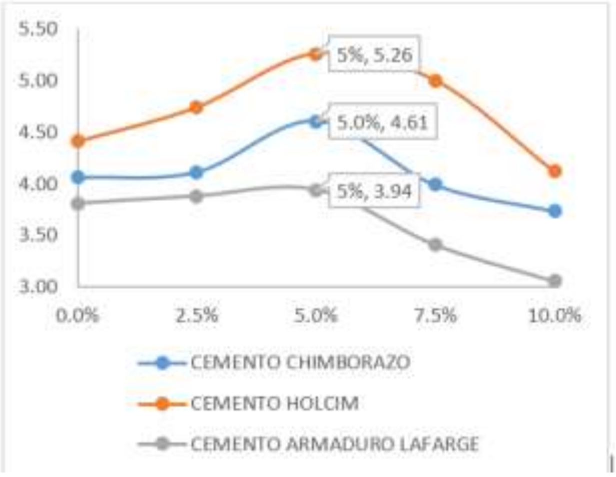
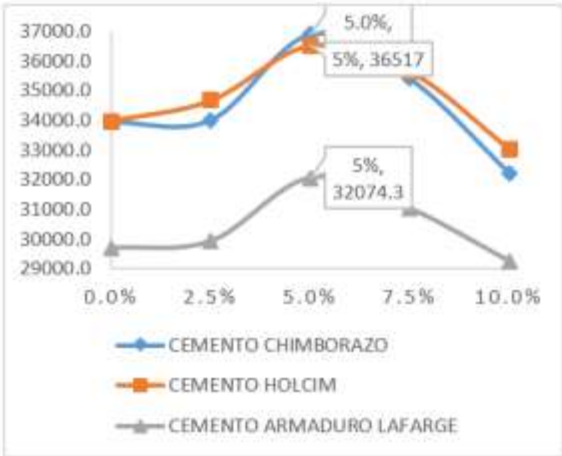


Figure 6. Rupture modulus results





3.2. Discussion

According to the research "Reuse of waste catalysts from the petrochemical industry to replace cement", the concrete made with replacement of exhausted catalyst presented a compressive strength 15% higher than that of concrete without substitution, the bleeding of the mix was reduced and the heat of hydration at 10% and 15% substitution percentages is similar to concrete without substitution since this petrochemical waste is exothermic. In comparison with the results obtained in our research, it can be confirmed that the addition of spent catalyst in the high-performance concrete mix improves the physical-mechanical properties [11].

Regarding the modulus of rupture, the Chimborazo Type HE Cement with replacement of 5% of exhausted catalyst obtained a higher value in relation to the other cements used in the investigation, a deviation of 12.11% was presented in relation to the Lafarge Armor Cement, this result reiterates that concretes made with IP Pozzolanic Cement generate lower resistances compared to Special Type HE cements.

- Based on the results of Tensile Strength, it was analyzed that Holcim Type HE Cement with 5% exhausted catalyst substitution obtained the most representative value in relation to the other test pieces tested, therefore, by adding minimum percentages of residue petrochemical in the mix, the mechanical properties will be optimized, improving the performance in relation to the master mix.

The modulus of Elasticity obtained for Lafarge Reinforcement Cement at 5% was 32074.32 MPa with a Poisson's Modulus of 0.201, presenting a decrease of 13.10% in relation to Chimborazo Type HE Cement, the experimental equation obtained for Lafarge Reinforcement Cement in based on its composition IP pozzolanic type resembles the equation given by the NSR-98 Regulation, so the addition of exhausted catalyst in low percentages in the concrete mix increases the Modulus of Elasticity corroborating the results obtained in the Thesis "New Contributions in the Development of Cement Materials with Used FCC Catalytic Cracking Residue "where the value of Modulus of Elasticity for high-strength concrete with the addition of petrochemical waste ranges between 34.5-39 GPa, exceeding theoretical values [12].

4. Conclusions

The studies carried out based on the elaboration of high-performance concrete are diverse, however, in the country few proposed topics have been found that evaluate the mechanical properties of concrete with the replacement of exhausted catalyst. In this titling project, high-performance concrete Type I (50 - 74.99 MPa) with 5% exhausted catalyst replacement and Type HE Chimborazo Cement presented the best behavior of mechanical properties, since adding catalytic residue to the mix reduces the amount of empty spaces in the concrete and in turn prevents exudation, generating favorable results with an increase of 10.30% in Compressive Strength, 13.41% in Tensile Strength, 8.94% in the Modulus of Rupture and 8.73% in the Modulus of Rupture. Elasticity compared to the standard dosage. High-performance concrete made with 5% exhausted catalyst for the 3 types of cement has low permeability, therefore, this addition protects against attacks by carbonates, sulfates, and damage caused by chlorides in the steel reinforcement. With the increase in impermeability, the durability of the concrete increases, due to the fact that the catalytic residue helps to close the capillary ducts, giving greater cohesion in the mixture, in order to prolong the useful life of civil works.

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