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MICRO-HARDNESS STUDY OF RECYCLED CONCRETE

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RESUMEN

En la presente tesis se lleva a cabo un estudio del comportamiento micro-estructural de los hormigones con presencia de áridos reciclados provenientes de los residuos de construcción y demolición (RCD). El nivel de importancia que ha tomado estos últimos años la protección del medio ambiente, la gestión de los recursos y las emisiones de contaminantes; han hecho patente la necesidad de dar una vida útil más longeva a los recursos, sobretodo en construcción.

Para ello, una solución plausible, es la substitución de los áridos naturales por áridos reciclados. Actualmente la legislación española vigente solo permite la substitución de hasta un 20%; una cifra muy limitante fruto de la necesidad de mantener unos límites de seguridad que aseguren las propiedades del hormigón. El propósito de esta tesis es ahondar en la investigación del comportamiento de los hormigones con áridos reciclados en comparación con los hormigones convencionales a nivel microscópico. Para ello, se investiga la zona de inter-fase (ITZ) entre los áridos y la pasta de cemento, y se caracterizan las distintas fases del hormigón. La ITZ está considerada como la zona más vulnerable del hormigón, el punto más débil de la unión del conglomerado, y por tanto la zona que cede en primer lugar ante las cargas.

Se analiza el comportamiento de la ITZ en términos de dureza mediante el ensayo de Vickers para un amplio rango de hormigones con distintas relaciones a/c, distintos porcentajes de substitución por árido reciclado e incluso distintas tipologías de dosificación.

Los resultados se someten a un análisis comparativo y se comentan las particularidades de heterogeneidad que presentan los áridos reciclados, así como los fenómenos micro-estructurales que ocurren en el ensayo de micro-dureza cómo el ISE (Indentation Size Effect).

Por último se encuentra una relación entre la dureza de la pasta del hormigón y la resistencia del mismo a compresión. La misma relación analizada en la ITZ no resulta tan clara. También, y en la misma línea, se revela una relación entre el módulo elástico y la dureza, aunque no de forma clara; parece que la rigidez de los áridos es dominante en esta relación más que la pasta de cemento o la ITZ.

Palabras clave: RCD, Hormigón reciclado, Análisis ITZ, ISE, Resistencia a Compresión, Micro-dureza, ensayo dureza de Vickers.

ABSTRACT

In the present thesis, a micro-structural behavior study of concretes with recycled aggregates, coming from the construction and demolition wastes, is carried out. The crescent importance of the natural environment, the resources management and the polluting emissions; has made clear the need of giving a longer life cycle to our resources, especially in construction.

To do that, one plausible solution, is to change the natural aggregates to recycled aggregates. Nowadays, the actual Spanish legislation only allows the aggregate substitution up to 20%; a very limiting number that explains the ignorance, still living, about the recycled concretes.

The purpose of this thesis is to get deep in the micro-structural behavior research of these concretes that contains recycled aggregates in comparison to the conventional concretes. To do so, the interfacial transition zone (ITZ) between the aggregates and the bulk paste is examined. At the same time the different phases of the concrete are characterized. The ITZ is considered as the more vulnerable zone of the concrete, the weakest point of the conglomerate union, and then, the first zone to break under applied loads.

The ITZ behavior is analyzed in terms of hardness by the Vickers Hardness test. The analysis is done for large concrete typologies with different w/c ratios, different percentages substitution of recycled aggregates and even different dosages methods.

The results are subjected to a comparative analysis and the particularities of the heterogeneity on the recycled aggregates are commented; as well as the micro-structural phenomenon that take place in the micro-hardness test as, for example, the ISE (Indentation Size Effect).

Finally, it has been found a relation between the micro-hardness of the cement paste and the compression strength of concrete. Though, the same relation in the ITZ does not seem to be clear. On the same line, it has shown a relation between the elastic module and the micro-hardness but it is also a bit unclear; it seems that the aggregate's stiffness is dominant in this relation, more than the cement paste or the ITZ could be.

Keywords: CDW, Recycled concrete, ITZ Analysis, ISE, Compressive Strength, Micro-hardness, Hardness Vickers test.

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Chapter 1

INTRODUCTION

1. Sustainability: Ecological, economical and social vision

In a world of constant changes, of straightforward evolution through technologies, innovation and social intercommunication, is a paradox that nobody has come up with the key solution for stopping excessive biological/industrial demands of resources.

The last decades, our planet has become a place where human population has grown unstoppable, where under-developed countries start to reclaim their ethical position in the world as fast as they grow up, and where the developed ones have been increasing their consumption and wasting of ultimate technologies whose consequences are rarely predictable.

As a result, amount of emissions of CO_2 (or whatever the green house gases) has been sent to the atmosphere inducing and maximizing the global warming process and all other pollution associated problems. When we focus our attention on which processes produce mostly of these undesirable impacts we can summarize them on a few principal actors. According to the IEA (International Energy Agency), the most contributing emisor of CO_2 is the fuel combustion with an approximately 87% of the whole emissions [24]. Complementarily, the land uses and the industrial processes only join the 13% remaining.

However, that 87% has a large list of contributors as the Fig.1shows.

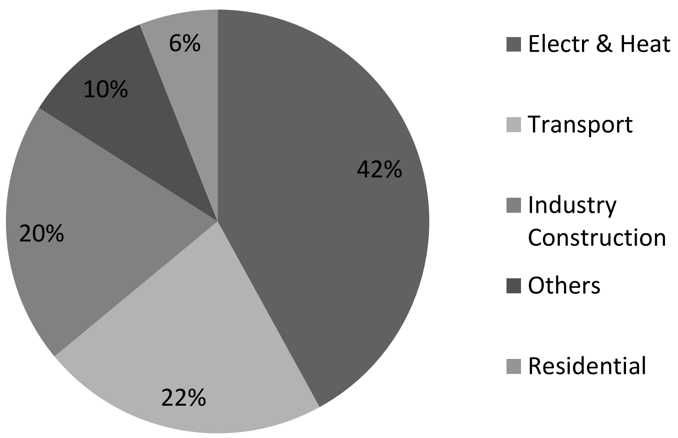


Figure 1: Fuel CO_2 contributors [24]

As one can see the major contributor on fuel CO_2 emissions is that resulting of the electricity generation and heating systems of buildings. However, the Industry Construction waste of energy mashes an incredible part of the emissions up to 20% of them. That is a non-depreciable value if society wants to reach a true state of sustainability.

There is a lot to do within the next years to reduce the wasting of resources and, more than trying to cut off the fuel delivered products (like oils, gas, etc.), people have to pay attention on optimizing these highly industrial consumption processes as cement making or, even more focused on the thesis' topic, the natural aggregate production.

For example, the cement making not only consumes a lot of energy resources but also contributes in the CO_2 emissions. Some statistics tell that for each ton of cement an average number of 0,7-0,8 tons of CO_2 are emitted at the atmosphere.

The latter aspect has an evident impact on the concrete related CO_2 emissions. The rudimentary procedures of natural aggregate production, by means of explosives and heavy machinery as well as a huge consumption of electricity on running the crushers' engines, in order to obtain acceptable aggregate sizes is one of the first steps that construction industry can improve.

Moreover, obtaining natural aggregate has another huge impact that we have to take into account: the natural one. Obtaining new natural aggregates from the nature, society enhance the destruction of their environment and, in fact, accelerate the resources consumption of earth.

Mixing and using recycling aggregates coming from demolition waste materials (i.e: used concrete) on new construction projects must be the gateway to the energy and emission reduction. Following that way we could give a second life to all these materials that other way would go to the dump. The reutilization will be an important thing on the near future because of its benefits in all three-block presented above: environmental, economic and social.

The so called 'waste valorisation' plays (and will play) an important role on what-to-do with wasting materials.

1.1. Environmental aspects of waste valorization

The increasing demand of products, infrastructure, transport, etc., of our society has doomed nature in a way that it cannot support higher level pressures in what respect to its exploitation. Thereby, in Spain, the last year's consumption of materials has grown in a linear form and in a close relation with PIB. (Fig.2) That tendency has been only stopped by the irruption of the financial and economical crisis.

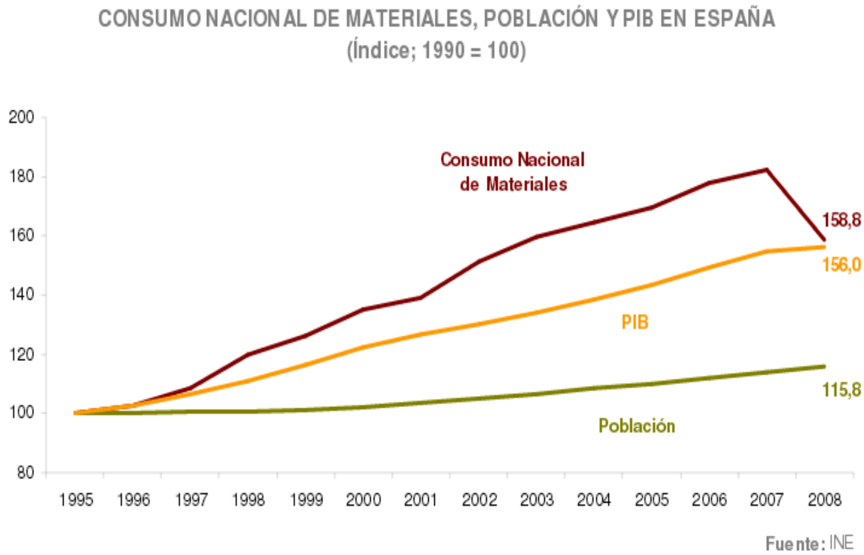


Figure 2: National consumption of materials [INE].

The natural resources consumption has many impacts. Firstly due to his extractive process which causes huge terrain erosion and pollution and secondly because the vast majority of the exploited materials are non-renewable (Renewable vs. Non-renewable argument). That is why valorisation takes importance, even so in the construction sector, which is the biggest consumer of certain typology of materials.

Environmental valorisation (substitution of new materials for these that otherway will be considered wastes) allows reaching two main objectives:

- Give a second life to wastes avoiding a bigger erosion on territory
- Avoiding that all these wastes could fill the dump

Additionally, the waste revalorization contributes in other forms to the environment's maintenance. In example enhancing reutilization contributes on obtain lower associated consumptions of the extractive processes (such as energy, water, fuel, etc.) that are related with extraction or impurity cleaning of raw materials.

Environmental valorisation results in a rational management of resources and in an added protection of environment which calls for better preservation.

Waste → **Valorisation**
- Waste minimization
- Raw materials conservation

→ Resources management
Sustainable growth
Environment protection

1.2. Economic aspects of waste valorization

At economic level is fundamental to get a profitable process which makes valorization an interesting business to put money in. Otherwise it's going to be impossible to create a market which spreads the waste recycling procedures.

The main thing that makes valorization interesting is that is cheaper to transport (in general) wastes to a recycling plant than to transport them to a dump because of their high fees (although it depends on the dump) and costs associated in environmental and social terms. Also because material's revalorization can mean benefits if they are again attractive for the market and its uses and applications.

In general, as Centro de Estudios y Experimentación de ObrasPúblicas (CEDEX) from Ministerio de Fomento explains [12], the raw materials from nature has a slightly higher price than the recycled ones. That is a key point for the viability of reutilization politics.
But what it's really important to get is strong normative that makes really profitable the use of recycled materials. Rules that improve the demand and its insertion to the market by, for example, delivering energetic certificates or eco-tags.

Another important mission for economic valorization tasks is to achieve the cheapest transport costs we can. It's significant to point out the relevance of having the recycling plant close to the location where the construction takes place. At the same time it is quite suitable to do a previous classification of wastes in the construction rather than in the recycling plant because of the added costs related. It is also important to avoid the materials' contamination because their cleaning treatment can truly be very expensive.

Valorization is economically adequate because having dumps on the territory becomes an added cost to the public funds as they indirectly carry extra investments on environmental compensations and public health (noises, dust, air pollution, etc.).

1.3. Social aspects of waste valorization

From the social point of view, valorization has been, and in fact is, one of the main supports to achieve sustainable process and products that we all consume. The separation of wastes depending on their typology and the recycling treatment are possible thanks to the environmental awareness acquired these last decades.

The valorization of waste contributes on waste disposal that arrives to the dumps. Dumps that doesn't consume only soil but have associated serious health problems for society. Hence, valorization contributes on rising life quality levels for people and, in addition, helps to get a bigger sustainability of the whole system by reducing money and energy consumption in a notable manner.

The increasingly awareness of people about the hazards of waste management has also helped the growing of a new business world which is profitable for society doubly: Firstly because it enhance the sanitary management and secondly because it generates new jobs. A recently so-called win-win relation.

1.4. The waste

RCD (Wastes from construction and demolition), as are known in the constructive argot the wastes from excavations, constructions and demolitions (whether from buildings or civil works) that present a heterogeneous composition that might be treated if they final disposition are valorization. The composition might contain from inert material to potentially toxic material which make its management fundamental. This management has to ensure sustainable solutions for RCD because they are one of the main problems of construction in terms of volume and time-consuming elimination.

Paying attention to their potential composition, RCD from construction have many different types of material such as concrete, ceramics, mortar, gypsum, metals, paper, plastics, wood and others being the percentage of each one different depending on the kind of origin they have. It is important to point out the existing differences between the purity of the RCD according to their source (new work or demolition). In the latter one the materials tend to be mixed forming composites what difficult their separation.
With much less presences there are highly poisonous materials like amiant or heavy metals that must be treated with priority in order to avoid that they pollute all other RCD which would mean a decreasing valorization opportunities.

In terms of composition, CEDEX has obtained the following results shown on Fig.3

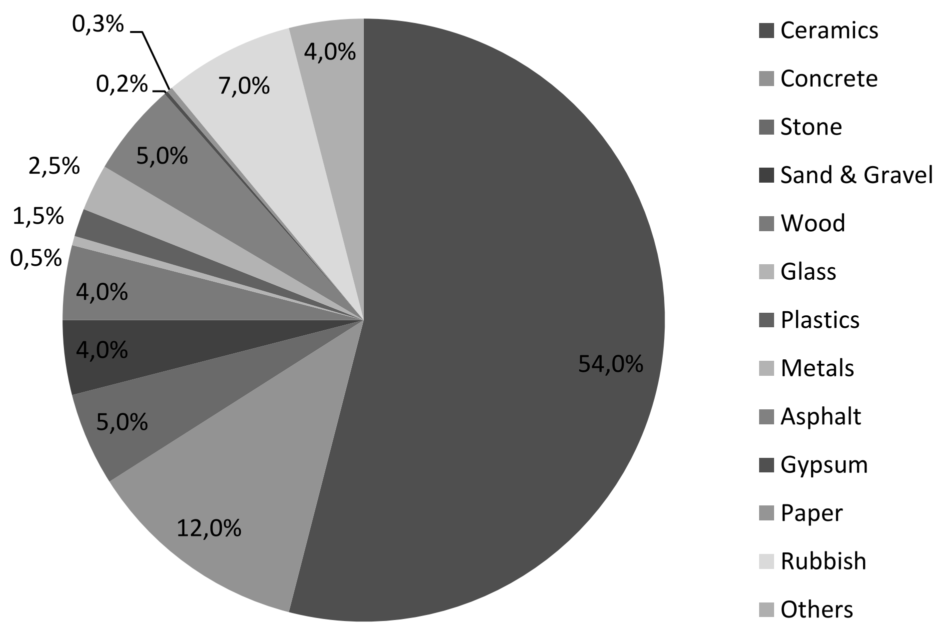


Figure 3: RCD medium composition [20]

These results from the 2010 period reflect the huge percentage of inert materials that exists in RCD. Especially ceramics which come, in fact, from buildings' demolition while the concrete sources are civil engineering works in general. With such a great amount of petrous original materials it is not weird to think that valorisation as secondary materials is a priority.

But RCD valorisation depends, in a great manner, of the regulatory existing instruments as well as the market factors and raw materials prices. Moreover, valorisation process is affected by the dumps rivalry whose prices can make the materials' second life not feasible.

It is very important to take into account that because of RCD are a mix of essentially inert materials they are subject to be dumped illegally. A fact difficult to quantify but approximately possible with accurate data as the Asociación Española de Gestores de Residuos de Construcción y Demolición (GERD) did. They found that more or less a ratio of 40-50% of the total RCD might be dumped illegally.

Despite of the fact that Spanish state has been affected by a big economical crisis that reduces the construction activity during the 2008-2011 period, Spain has produced an important volume of RCD as shown on the following Tab.1.

Table 1: RCD estimated generation in Spain (GERD) [20].

	2008	2009	2010	2011
CCAA Partial controlled management (Tn/yr)	20.732.455	18.017.690	15.549.902	10.315.794
CCAA Inhabitants ratio (Tn/Inh/yr)	0,61	0,43	0,39	0,29
National Approx management (Tn)	28.732.891	20.015.666	18.214.765	13.463.609
% Estimated illegal production	35	40	45	50
Total production estimated ratio (Tn/Inh/yr)	0,83	0,6	0,56	0,43
Spain's estimated production (Tn/yr)	38.789.403	28.021.933	26.411.409	20.195.413

But in spite of have a huge volume of RCD Spain already has a poor recycling/reutilization percentage that only represents about 5% from the whole volume generated. That's because the abundance of natural existing resources in the country with reduced prices don't allow valorisated materials to compete with yet.[1]

In contrast there are many European countries like Deutschland, Denmark, Holland or Estonia that reached a high recycled percentage around 80%, becoming eurozone leaders. In the other hand there are countries like Spain, Greece, Portugal or Italy with very low valorization rates [19]

1.5. The legislation role

The last years, and specially the 00-08 period, have meant a high increment of materials consumption and wasting resources due to the unstoppable fever of building-infrastructure construction. That phenomenon has translated to an uncontrolled dumping of tonnes and tonnes of construction rubbish to the natural environment.

Nevertheless, the growing of material industry, associated to these expansive years has supposed the birth of new requirements of waste management who has translated, at the same time, to the expansion of treatment plants for RCD (construction & demolition wastes from now) and social awareness.

All these concerns have lead to the redaction of regulatory laws that provide to the society, to the government and to the companies a frame of obligations and rights in their activities' development.

In Spain the normative and legislative background of wasting management is led by the law 22/2011 (28th July of 2011) [7]of *'de residuos y suelos contaminados'* where is set the correct steps to follow to face the management. That law, which derogate the law 10/1998 (21thArpil of 1998) [6], put all of its efforts on the modern conceptions of wasting valorization and reuse. Simultaneously, the law plans specific programs to reduce the waste generation and improve impacts on human healthcare. In addition, it regulates the waste's transport from the construction zones to the dumps or treatment plants.

The 5th and 6th article from the Chapter 1 of the same mandatory law declare when and how the waste have to be seen as new material ready to be used after a valorization process. Furthermore, it also specifies when the waste is potentially dangerous or not according to the European List of Waste published by the European Commission on their decision 2000/532/CE [17] and re-published by the Spanish government on their ministerial order MAM/304/2002 [9].

In the case that concerns this thesis, one can find from the mentioned list of waste a detailed inventory of construction and demolition materials on its chapter 17th and, more focused, the codes related to each material (for example concrete has the following code: 17 01 01).

The Spanish law is complemented by the Royal Decree (13thFebruary of 2008)[8] whose main purpose is to regulate the production and management of waste materials from the construction and demolition. In the same direction, the decree specifies the responsibilities and obligations of the different stakeholders of the management process and, moreover, specifies the maximum quantity of admitted material without a properly division of fractions at the construction place.Tab.2. (Separation is a key process in order to reduce costs of revalorization).

Table 2: Maximum quantity of material without division [8]

Type of material	Quantity (Tn)
Concrete	80
Bricks & Ceramics	40
Metals	2
Wood	1
Glass	1
Plastics	0,5
Paper & Paperboard	0,5

Without loss, the law 22/2011 also looks at the development plans and strategies from the different 'Comunidades autónomas' due to the existing transferred competences. As it is specified at the 14th article these strategies must be (and must avoid conflict) in harmony with the related master plan in force.

That plan takes shape below the umbrella of PNIR (Plan Nacional Integradode Residuos) for the 2008-2015 [10]period whose objective is to reach a decrease on waste generation and to ensure a correct treatment of them (valorisation, reuse, prevention, elimination).

The PNIR also wants to collect reliable information to fill the government's database in order to bring up better statistics and tendencies that help to improve the master plan and its processes.

Finally, the PNIR takes into account the valuable benefits of investing in I+D+i to find new applications for RCD and to enhance the existing techniques. More concretely, the 12^{th} point of the PNIR makes reference to the RCD justifying the need of waste management on the strong and booming construction activities that generate in 2004 approximately 40 million tonnes of waste in Spain. Far from the peaks that are supposed for the 'best' construction years in Spain. According to the plan's estimation only 3 million tonnes went directly to valorisation plants to be used as a recycled aggregate. Figure that pretends to motivate and improve during its in force period until reach an ambitious ratio of recycled RCD: 35% in 2015.

That rate won't be reachable without the complicity of the different technical regulations as PG-3 (Mandatory for roads, embankments and bridges in Spain) or EHE-08 (Mandatory for any concrete structure).

Accurately, engineers already have the possibility of use recycled aggregates in their embankments according to the article 330 of PG-3 ('Terraplenes') on its paragraph related to the material properties: *'it might be used products from industrial or human handling sources to build embankments if only they are in accordance with physical and chemical requirements.'*

The concrete instruction EHE-08 goes in the same direction about the recycling concerns. It specifies on its Annex nº15 [30] the use of recycled crushed concrete to form new structural concrete. The regulation states only a maximum substitution of natural aggregate to recycled aggregate up to 20 %(in weight from the total natural aggregates' big fraction). That works like this because modern industry has very reliable information about the strength properties developed by this kind of mixing aggregates in concrete. Not so in higher ratios of substitution. Then, more tests may be needed to complement the accepted methods.

EHE-08 forbids using recycled aggregates on concretes with higher strength required than 40N/mm and on pre-stressed concrete. The instruction also rejects those recycled aggregates whose roots are concrete with pathologies or different from concrete uses such as road pavements, for example. In addition aggregates must be bigger than 4mm diameter. Due to their special properties (higher needs of water or higher porosity and bigger deformation), recycled aggregates are subjected to another restrictions of use. For example they are limited to a maximum rate of 7% of absorption and a maximum rate of impurities (ceramics, wood, asphalt, etc.).

Chapter 2
OBJECTIVES

2. Main objective

The main purpose of this thesis is double. Firstly, it wants to study and pay attention to the behaviour of such an important zone as it is the interfacial transition zone (ITZ) and to resume that it is a critic point in the resistance mechanism of concrete. To do that is going to be characterized the transition zone between the aggregates and the bulk paste of concrete by testing different types of concrete (conventional and with recycled aggregate added) with also different ratios of water/cement.

In order to follow this purpose is going to be used the Vickers micro-hardness test. A non-destructive test which will provides us to know the hardness associated to each element of the concrete and to bear out at microscopic behaviour that concrete has a slightly decreasing hardness capacity in the ITZ.

Secondly, it wants to resume if there are any significant differences between using natural aggregates, or natural aggregates mixed with recycled ones, in terms of resistance and behaviour. A key point in future uses in order to enhance reutilization of materials from demolition.

The micro-hardness characterization is going to be useful either to discover a new behaviour patron for the ITZ in different concretes as well as to put a basis for establish a strong relation with a destructive test like the uniaxial compression test. That relation may be useful to know the approximately macroscopic strength of, for example, a beam from a structure, starting with an accurate hardness value from a little piece of concrete.

That will provide us profitable information of the resistance without having to destroy large pieces from civil or architectural structures to test them in a different ways at the laboratory.

2.1. Specific objectives

To sum up, the specific objectives are enumerated in the following points:

- Characterize the different aggregates and cement pastes (by w/c ratio)
- Show the hardness behaviour in the aggregates-cement paste transition by the Vickers Hardness test
- Show the differences between using natural aggregates or recycled aggregates in concrete by examining them in the ITZ

- To study the possible existent relations between the ITZ and the concrete properties.
- Establish if there is any relation between the compression strength and the hardness values of the cement paste.
- Proof if the elastic modulus has any relation with the hardness values of the cement paste and the ITZ.

Chapter 3

STATE OF THE ART

On the following chapter is evaluated the current knowledge state of concrete. The reader will find essential information to understand what the concrete is, which composition it has and how the chemical fundamental processes affect it in order to reach a final stable state.

At the same time the chapter presents (and focuses in) the existing differences between the use of natural aggregates and the recycled ones. The production procedures and their properties are examined.

Is also analyzed and defined the concrete transition zone between aggregate and bulk paste due to its importance on this thesis. Finally are defined the carried tests to study the bulk paste and the interfacial transition zone paying special attention to the Micro-hardness Vickers Test.

3. Concrete

3.1. What is concrete?

Concrete is a hydraulic conglomerate composed by water, aggregate (sand and gravel) and a binder which nowadays is cement. In conjunction all this elements develop a reaction hydration chain that lead into a metastable final result able to maintain its petrous consistency even below water.

This consistency gives to the concrete a very valuable compression strength capacity for structural uses. Therefore, depending on the demanding conditions it's possible to find concretes with different densities classifying them commonly in three groups: heavy (more than 3200kg/m^3), normal (2400kg/m^3) and light (1800kg/m^3).

It is important to mention the water/cement (w/c) relation and its influences on the concrete resistance characteristics. Insufficient water can produce the hydration reactions to stop. Water excess can lead into a serious increase of the porosity what will affect the whole behavior of concrete.

The concrete, formed by aggregates that can have varied sources either through natural or artificial crushing, or through third materials valorization, has a key quality that makes it very useful: Its malleability, its capacity to take different shapes and adapt to the constructive demands. That quality is due to the setting process (as is known the loss of concrete plasticity). The setting period between the hydration start and the hardness can be adjusted by adding accelerators or retardants.

But concrete has not ever been as we know actually. Its origin goes back to the Roman Empire ere when the romans discovered for the first time one binder able to resist the time and the weather, what is called pozzolanic cement. Formed by volcanic grounds with high silica and alumina contents when they merge with lime they obtained good quality cement.

Until the beginning of the XIX century concrete was not truly developed. It was Joseph Aspdin and James Parker who, in 1824, patented new cement: Portland cement. It was obtained mixing argillaceous limestone and calcined coal. Soon it started to be introduced, used and industrialized all over the world. The researches carried by Vicat, Le Chatelier and Micháelis gave the ultimate push to its extensive and intensive use.

Nowadays the main research lines are based on the recycled materials use, on the reutilization of demolition or construction wastes and on the others wastes. It is also widely studied the micro-structural characteristics of concrete in order to find better processes or to identify improvements on its strength, durability or properties.

The concrete's macrostructure is composed by aggregates, bulk paste of cement and a key zone as is the transition zone between the two elements mentioned before. With a width of few microns this zone defines, in part, the resistant characteristics of the concrete due to his high porosity.

3.2. Concrete composition

3.2.1. The cement

3.2.1.1. Production

When we refer to the cement we are going to do in reference to Portland type cement which is the most widely used around the world. For his production we will previously need to define their raw materials. Normally they are the following shown at Tab.3.

Table 3: Examples of raw materials for Portland cement manufacture [18]

Calcium	Silicon	Aluminum	Iron
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore
Calcite	Sand	Flyash	Millscale
Aragonite	Shale	Aluminum ore refuse	Shale
Shale	Flyash		Blastfurnacedust
Sea shells	Rice hullash		
Cementkilndust	Slag		

Although some of them, especially metals, must be accurately analyzed due to his harmful effects on concrete's rheology. The essential oxides to form what in Spanish is called "crudo" (a mix of crushed silicates, aluminates and calcium alumina-ferrite) will convert into "clinker" after they pass through the furnace.Tab.4.

Table 4: Raw materials composition and formula

Name	Composition	Molecular weight	Formula
Lime	CaO	56	C
Silica	SiO_2	60	S
Aluminium	Al_2O_3	102	A
Iron	Fe_2O_3	160	F
Water	H_2O	18	H
Sulfuric Anhydride	SO_3	80	S
Magnesia	MgO	40	M
Sodium	Na_2O	62	N
Potassium	K_2O	94	K

It should be point out that the most common elements are, by definition, lime (60 – 67%), silica (17 – 25%), aluminium (3 – 8%) and iron (0,5 – 6%) [18]

The mix of these components can be done with an accurate composition thanks to Bogue developed methods.

By passing the mix through the oven we will obtain an oxide combination that will form clinker and, after hydration, will form the principal resistant actors of concrete.
The oven is a huge cylindrical tube equipped with refractory material on the indoor walls that has 150 meters long and a diameter of approximately 5 meters. The whole cylinder spins around a sloped axis with around 2 or 5 percent inclination at 3 revolutions per minute.

At the lowest part of the oven there is the fuel burner and the discharge outlet while at the opposed extreme is being introduced the raw that, normally, has previously passed for a serial of heat exchangers. Exchangers whose mission is to gradually heat up the raw in order to get the transformation reactions start and obtain the initial compounds. Fig.4.
The rotation allows the raw to travel back current through the fuel burner (and against gas) and to follow the heating process until reach temperatures higher than 1300 ºC. This process is called: calcination.

Calcination is a process by which the raw loses the CO_2 from the calcareous phase, the remaining water in the mix evaporates and the siliceous and alumina-silicates are decomposed. At the same time the process creates sulphate.

The released CO_2 reacts with the others compounds and creates, at the beginning, Belite. By increasing the temperature (until 1300 ºC) through the Belite (C2S), o directly through the lime and silica, another compound is created: Alite (C3S). Finally these are the main compounds of the clinker which after discharge them from the oven they take shape of spherical nodules.

Figure 4: Clinker oven with heat exchangers

The clinker obtained is passed through a cooler. This process must be fast in order to avoid the formation of periclase (MgO that leads into a volumetric instability of concrete).

Finally, clinker is mixed and milled with gypsum (setting regulator) and other elements depending on the demands or properties that we want to infer to the final concrete. Hence, is habitual to add additions like pozzolans, flying ashes, silica fume or slag from the ironindustry. It is also common to add some additives that help in the bulk paste or concrete production as, for example, air entraining. The resulting milled is what we call Portland cement.

3.2.1.2. Potential composition

After visiting the oven, the resulting Portland cement is formed by an aluminate and silicate mix. Its principal actors (Tab.5) have many direct responsibilities on the concrete's behaviour and characteristics.

Table 5: Potential composition

Name	Composition	Molecular Weight	Formula	Mineral name
Tricalcic silicate	$3CaO,SiO_2$	228	C_3S	Alite
Bicalcic silicate	$2CaO,SiO_2$	172	C_2S	Belite
Tricalcic aluminate	$3CaO,Al_2O_3$	270	C_3A	
Ferrite-Aluminate tetracalcium	$4CaO,Al_2O_3,Fe_2O_3$	486	C_4AF	Celite
Bicalcic ferrite	$2CaO, Fe_2O_3$	272	C_2F	

Tricalcium Silicate (Alite): It is the most common and generous element of the cement, occupying approximately the 40% - 70% of the total volume [18], and the most important. It is responsible to confer the high initial strength of the concrete. (502J/g)

Dicalcium Silicate (Belite): It gives low initial strength in the first hydration days and has a higher level of impurities than the Alite. However, it slowly develops its strength until reach (in a long-term) medium values very similar to the Alite ones. (251J/g)

Tricalcium Aluminate: It has an enormous hydration Speedy capacity that can be managed by adding gypsum (setting retarder). Without being clear which role has it is believed that it acts as a catalyst in the silicate's reaction. (866J/g)

Ferrite Aluminate Tetracalcium (Celite): It has not a relevant contribution into the concrete strenght. Its iron content is responsible of the greenish-grey colour of the Portland cement. (418J/g)

Other potential compounds of cement, that play an important role and that have to be carefully monitored, although their small quantity, can be the free lime, the magnesium oxide and the alkali.

The first one owes his presence to a fabrication failure. Its hydration provokes an expansion that can lead to concrete cracks or, worst, its collapse. The second one is an expansive product in the long-term. The biggest risk of the MgO is that it can crystallize into Periclase. In consequence that's why the producers put a lot of emphasis on clinker's cooling period.

The last, but not the least, are the alkalis. They come from the raw materials (as clays) or from the fuel of the oven. They affect the concrete durability by reacting with certain aggregates (opals, andesites) and deriving into expansive compounds. For these reasons the present regulatory restrict the maximum content of all these elements on mass percentage[30]:

$$MgO < 5\%$$

$$Na_2O, K_2O < 2$$

$$SO_3 < 3$$

3.2.1.3. Hydration and hydration compounds

When the water and the cement go together, a reaction between the silicates and the aluminates starts and transform these dusty mass into a rigid product with a marked petreous character.

The hydration process can be seen from three slightly different perspectives depending on the theory that we prefer. Therefore, the French chemical Le Chatelier put forward the Crystalloid theory which explains that cementitious anhydrous grains when hydrate start to crystallize successively.

On the other hand, german Michaelis set the Colloidal Theory. As he postulated the hydrated silicates precipitates in gel form that fills the existing holes between the C_3A and CaO crystals.

Nowadays the most commonly accepted theory is based on a hybrid from the two previously mentioned theories. The hydration is a process where the compounds react with the water, they diffuse (also through pores), and then precipitate when the hydration is complete.

When the bulk paste gets hydrated it starts to vary the volume. The aggregates also start to increase the volume and allow the body to take lower porosity and, by the way, higher mechanical resistances. That is the main reason why water can be the limiting factor because, otherwise, the reaction would stop and the designed resistances wouldn't be reached. The process of maintaining the concrete with enough water is called "curado" in spanish.

3.2.1.3.1. Silicates Hydration

As was commented previously the first compound to react (and in a fast way) is the tricalcium silicate. In contact with water it reacts and forms tobermorite and portlandite in gel shape [18].

$$2\ C_3S + 6\ H = \underbrace{C_3S_2H_3}_{\boxed{\text{tobermorite}}} + \underbrace{3\ CH}_{\boxed{\text{portlandite}}}$$

The dicalcium silicate hydration is very similar although it gets developed slower than the tricalcium silicate.

$$2\ C_2S + 4\ H = C_3S_2H_3 + CH$$

Precisely, CSH (tobermorite) is the main responsible of the paste cement consistency and the mechanic resistance [18]. Contrary, portlandite is in charge to protect the concrete due to his basic properties (ph>12) although it is soluble and can be chemically attacked. In that way, a cement with higher contents of C_3S than C_2S is much more vulnerable under chemical attacks because it produces more portlandite when hydrates [18].

During the formation of these hydrated compounds the concrete starts to gain certain strength. Moreover, it is important to point out that the creation of this gel in conjunction with sulphates leads the ettringite appearance ($C_3A\ 3CaSO_4.32H_2O$).

3.2.1.3.2 Aluminates hydration

Even though the tricalcium aluminate is a small part of the whole clinker composition it is the responsible of the fast curing when hydrates [5]. It is what we know as the "lightning setting". A problem that must be considered if we have important quantities of C_3A and that is commonly accepted to solve by adding regulators as, for example, gypsum.

Its primal reaction with water gives as a result one crystallized structure with hexagonal shape.

$$C_3A + H = C_3AH_6$$

When gypsum is present the reaction with C_3A leads into an oversaturated solution. This allows the formation of primary ettringite as a result. Primary ettringite is responsible of the initial resistances and the paste solidification. This phase will turn into monosulphate with time when the solution comes subsaturated and the ettringite goes unstable.[5]

$$C_3A + 26H + 3CSH_2 = C_3A3CSH_{32}$$
$$C_3A3CSH_{32} = C_3ACS18H$$

Similar reaction to the one that takes place with the tetracalcium ferrite-aluminate.

$$C_4AF + H = C_4FH_{13} + AFH_3$$
$$C_4AF + 40H + 4CSH_2 = C_3A3CSH_{32} + CFCSH_{16}$$

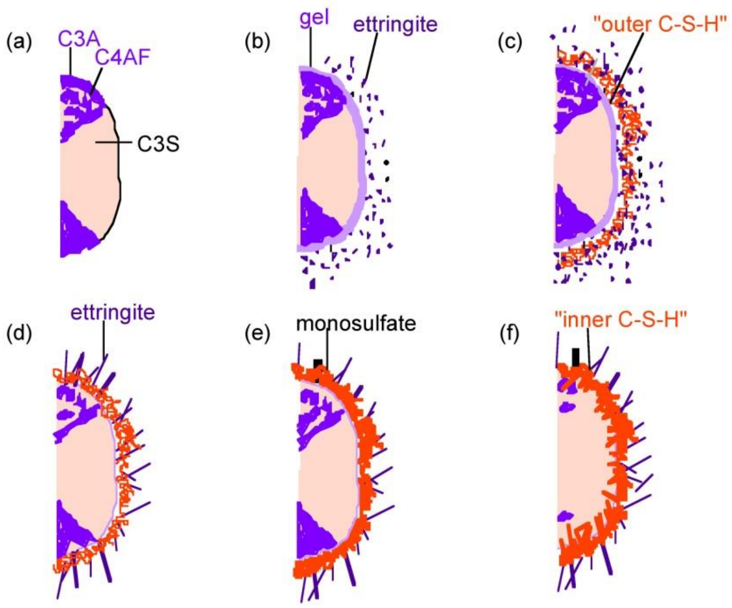


Figure 5: a)Initial state b)10min c)10h d)18h e)1-3d f)2 weeks [29]

At Fig.5we can see an accepted scheme of the cement grain hydration process. Cement grains contain different compounds that hydrate in different moments. In the first minutes after adding the water the C_3S particles start to turn into little particles of CSH and the C_3A reacts with gypsum and allows the ettringite formation that covers the C_3A.

After 3-4 hours of hydration the paste starts to gain consistency as long as the C_3S keeps reacting. After approximately 24 hours the gypsum runs out and the solution turns sub saturated of sulphate and calcium ions. Then, the ettringite dissolves with C_3A to turn into monosulphate.

Two days later the water occupied place is now plenty of hydrated products. During this process the CSH keeps advancing into the inner part of the cement grains. The reaction dynamic can be seen on Fig.6.

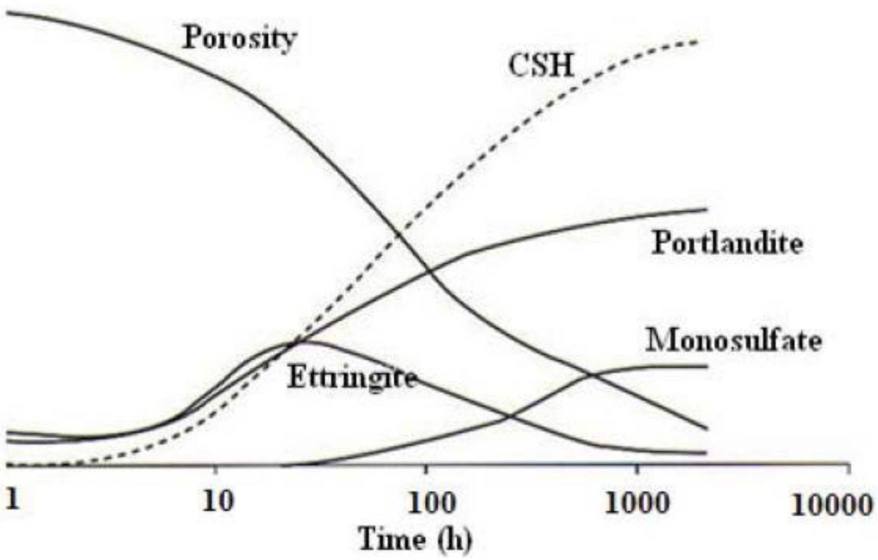


Figure 6: Hydration compounds evolution and relation with porosity[27]

3.2.1.4. Properties of the bulk hardened paste

Once the hydration process has taken place and the settling process has conferred enough hardness to the cement, the hardened paste keeps the concrete and their aggregates working together as one single object.

Then, the hydrated paste is the main concrete properties' contributor that defines his behaviour much beyond than the elastic modulus (which is dominated by the aggregates).

The most characteristic property of the hardened paste is the porosity. Pores apparition in the cement paste due to the existing w/c relation is of the capital importance in terms of strength, creep and shrinkage [5].

On the one hand the pores (resulting from the lack of homogeneity of the cement paste) may be macroscopic (>50nm) or microscopic having different responsibilities on the concrete behaviour depending on the typology. Hence, the macro-pores influence can lead into strength problems by cracking under loads or permeability problems that can allow the entry of external agents.

At that point the micro-pores start to play their role and more specifically the concept of capillarity (interconnection between pores) that not only allows the polluted water to flow but also enhance the concrete shrinkage and creep.

Hardened paste also has a strong inverse relation between porosity and strength capacity. A less porous paste admits higher loads and inversely. A strength that mainly comes from the attraction forces, the CSH and the CH. That is why the composition of cement is extremely important.

Finally, it is important to point out that the saturated paste has not a volumetric stability when the environment's relative humidity starts to decrease. When this phenomenon happens the paste starts to loss water and shrinkage appears.

3.2.2. Natural aggregates

The aggregates that form concrete are granular inert materials with no reactivity versus cement compounds that represents about 60% - 80% [4] of the whole concrete volume. They contribute decisively on its strength, volumetric stability and the economic savings of the manufacturing process.

Aggregates are classified as naturals if they are obtained directly from rock disintegration either by artificial or natural methods. At the same time and because aggregates can have different origins it is currently established an additional classification depending on their shape: Shooted aggregates and crushed aggregates.

The first ones, as their name indicates, take a rounded shape with smooth surface and without edges. They currently come from natural disintegration and rocks degradation. Oppositely the second ones are obtained by artificial crushing and have rough surface with sharp edges.

The latter are obtained from rocks that due to his excessive size must be crushed through explosives and reduced by crushing. Then, as the natural aggregates, they must pass through a screening process in order to classify sizes: graves or sands for example.

For practical purposes and properties (depending on their use) the rounded shape aggregates have highly variable qualities and irregular gradations which traduce in workable and tractable concretes. Oppositely, the crushed aggregates, provide a more physical and chemical resistant concrete.

In respect of what type of rocks can we use for concrete we must pay attention to their reactivity with the cement compounds. Hence, it is necessary to carry on tests as for example chemical and petrographic exams and even electronic microscopy in order to know exactly if the rock we want to use has some incompatibilities with cement.

It must be prioritized the use of silica aggregates and volcanic origin's rocks or high density limestone. On sedimentary rocks it is recommended to do the previously commented tests to decide if they are useful or not.

3.2.3. Recycled Aggregates

It is known as recycled all these aggregates which are reused (what we call valorisation) for many different purposes after being carefully selected and treated due to a previous demolition of civil works, constructions, roads, etc.
Their several origins make that classification and characterization take special importance to define correctly in what conditions can be used afterwards.

Hence, recycled aggregates (RA) have multiple elements in their composition that affect decisively their own properties; either in a positive or negative way through non-desirable reactions or behaviour.
As an example is current to find impurities (contaminants) in RA that come from dumping or other elements like glass, asphalt or wood which depending on their concentration can be dangerous. Glass, for example, produces a general descent in the concrete strength because of not only its fragility but also its texture. Oppositely if it is used with a fine gradation it can act as filler and increase the durability of concrete in front of chloride penetration.

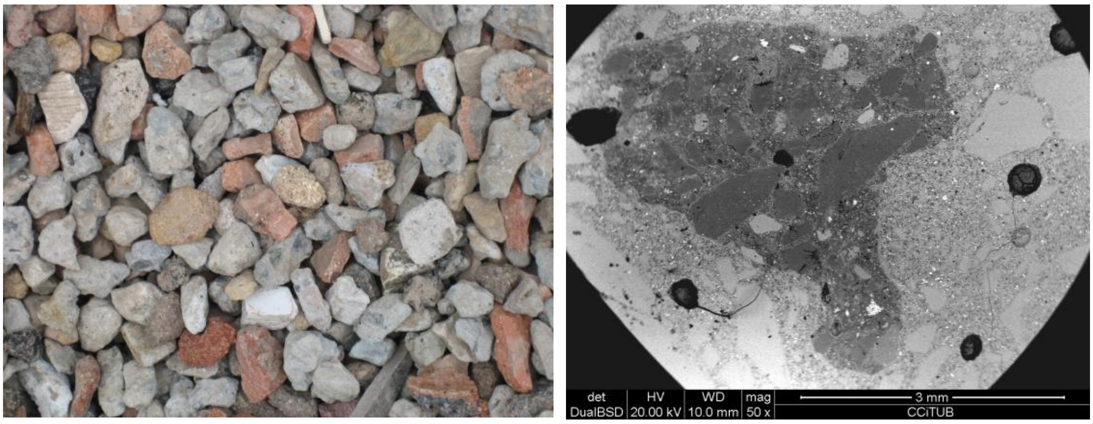


Figure 7: RA macroscopic and microscopic view by SEM

The RA coming from demolition is normally constituted by natural aggregate (NA) with adhered mortar but also by different kind of materials as ceramics or masonry. Fig.7 shows the heterogeneity of the RA compounds by representing them with different colours intensity and the two different mortars coexisting in a concrete with certain natural aggregate replacement. Depending on the material RA will have better or worst qualities for structural purposes and that is a key point related to final concrete properties.

In addition, as far as we don't know the previous history of the RA is convenient to carry out an analysis and classification of them in a variety of important aspects like sulphate, chloride or alkalis content. Its presence can lead into expansion problems in concrete and corrosion in steel reinforced bars [15]

The sulphate content is, in general, higher in RA than in NA. That is because the existent mortar in RA and the gypsum and clay adhered to it. Therefore sulphate content must be limited in order to avoid expansive reactions.
Contrary, the chloride content depends on the environment in where RA had been living previously (i.e. marine). In relation to alkalis its content usually comes from the original cement.

Another important aspect of RA is their shape and size. In general due to its demolition origin, they usually have sharp shapes with rough textures and heterogeneous sizes. These shapes can be a problem or difficulty in what concerns to concrete workability. That's why RA are put under crushing and gradation processes to be like NA.
Some authors [26]have shown that the less size the RA have the greater percentage of mortar adhered for aggregate unit there are and, therefore, worst behaviors can be expected.

That's mainly because the role played by density. Lower mortar density (always depending on the original cement quality) infers to RA lower densities compared with NA. The difference gets bigger if RA don't content NA but ceramic or masonry materials.

The density depends then on the existent porosity in RA. Greater porosity is related unequivocally with the water absorption capacity. As an example NA currently have water absorption ratios about 1 – 2 % while RA can reach intervals in-between 5 – 10 % or even greater..

Porosity also depends (as density) on the cement quality used in the RA mortar.

3.3. The Interfacial Transition Zone (ITZ)

As it was commented before, concrete is a mixed element with two principle phases: The aggregates and the bulk paste of cement (matrix). In fact, at macroscopic level, that is right. But research reports presented on last decades based on microscopic properties of concrete revealed that could exist another phase: the so-called interfacial transition zone (or ITZ in its acronym).
Nowadays the existence of it is widely extended. The ITZ is located enveloping the aggregate and, as it name indicates, it enables the transition between the aggregate grain and the cement paste (Fig.8)
The ITZ becomes a crucial zone in the mechanic behaviour of concrete and it presents slightly different characteristics in comparison with the whole bulk paste.

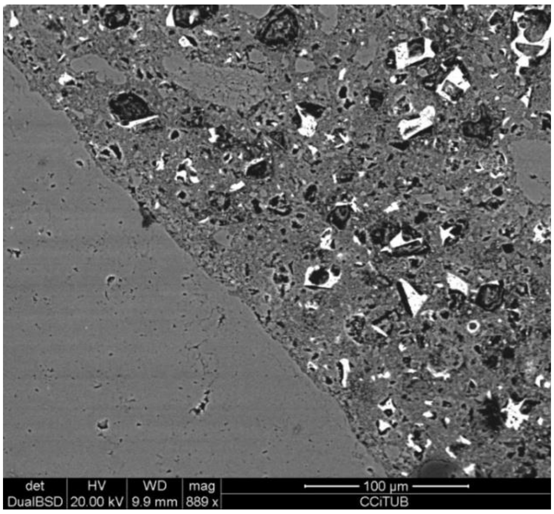


Figure 8: ITZ between natural aggregate and bulk cement paste

The ITZ is a zone which extension is very limited, focused and variable. Studies have determined that the thick length of ITZ can vary between 40 – 50 µm [32] although in some cases it can reach the 60 µm under certain conditions (aggregate, mix, etc.).

The variability of the ITZ can be caused by an enormous amount of parameters (mainly those that can affect the mixing or composition of concrete) but it seems to be an agreement about the importance of some of them such as water-cement relation or the anhydrous concentration. Those parameters are the principals who can affect the mechanical behaviour and strength's transmission between the bulk paste and the aggregates through their capacity of build up a more or less porous zone.

Formation

During the hydration process many phenomena are taking place on the bulk paste and the vicinity of an aggregate. They are similar but, at the same time, different. These differences can be explained through the 'wall effect' barrier theory which affects the hydration process not allowing the correct formation and distribution of CSH around the aggregates.

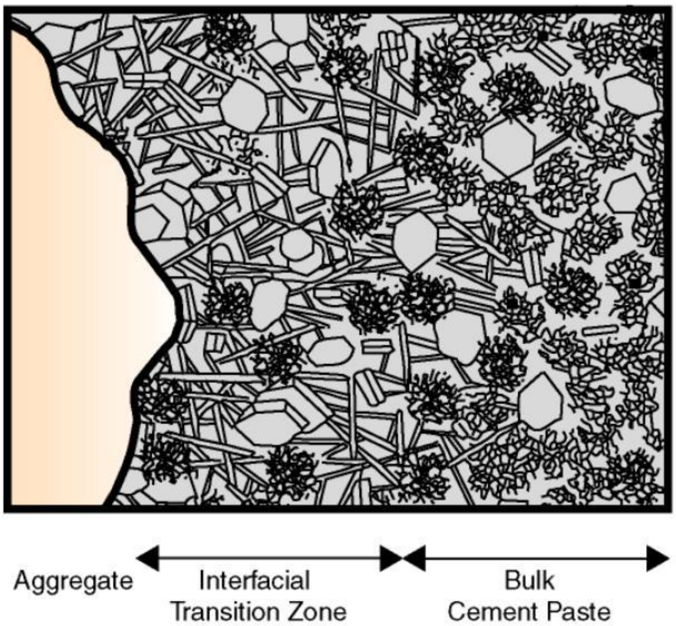


Figure 9: ITZ composition scheme

Therefore, it is a process of packing where the anhydrous compounds and the portlandite coming from ionic diffusion are concentrated. Those compounds build up a barrier around the aggregate that not let the CSH gel pass (Fig.9). As a consequence CSH cannot fill the microscopic zone and induces a high gradient of C3S and CH [13] between aggregate and bulk paste as well as a high porosity due to the lower density.

During the mixing, the concrete particles suspended on water are segregated by the greater particles (like aggregates) interaction. That causes a water deficit at the vicinity of the aggregate that reflects on a lack of hydration process.

Another explanation for the ITZ formation appeals for the non-symmetric hydration behaviour. This theory calls that hydration starts on the cement grains, not on the aggregate surface, resulting in different degrees of hydration compounds filling.

Most of the studies have shown that ITZ properties vary with the w/c relation, aggregate size, cement particle size or additions. For example, is known that adding silica fume (or using Portland cement with stronger crushed particles) the ITZ becomes stronger and less porous. Therefore, the composition of the concrete is a critical decision which has to be made taking into account different behaviours like the followings carried out by different researches.

Elsharief et Al; [14] showed that the size of aggregate grains affects slightly the porosity of ITZ. They saw that larger aggregates have a thickest transition zone than those which are smaller. In addition they found that larger aggregates tend to have more porosity than the smaller ones whereas the anhydrous concentration does not seem to vary significantly.
One possible explanation for that phenomenon is that greater aggregates tend to accumulate more water in their surface leading the ITZ to be more porous.

At the same time, Ollivier et Al;[32] verified that the porosity reduces all along the ITZ with time because of the continued hydration of concrete. A result that seems to confirm the existence of the diffusion theory. The same study concluded that loads and shrinkage affects somewhat the ITZ's natural state.

Another important information for our research is to know what the implications of changing natural aggregate by recycled aggregate are. Few studies have been carried out but as far as we can see there are marked differences on behaviour facing mechanical demands.
Firstly, is strongly believed that in recycled aggregates ITZ is thicker and has weaker strength due to different phases coexisting in the same place: the ITZ of older concrete and the ITZ of new concrete, for example.

Secondly, a study of [32] has revealed a decrease of resistance at compression test between different specimens of recycled concrete and normally used concrete. That decrease is not negligible: more than 10%. In addition, the study revealed that recycled concrete and natural concrete have different failure mechanisms.
While natural aggregate concrete fails through the ITZ, the recycled aggregate concrete fails through the ITZ and through the main aggregate. One plausible explanation is the weakness of old aggregates which contains fractures produced on their past use.

In conclusion, those results reinforce the importance of such a microscopic zone as the ITZ is. It is important to describe its behaviour in order to improve the mechanic properties of concrete and to clarify its usage.

3.4. ITZ common Tests

3.4.1. The Micro-hardness Test

The micro-hardness test is a very used and extended method in the mechanical properties characterization at microscopic level of materials, whatever the origin or condition. Its basis is very simple. It allows us to obtain the hardness value of materials by introducing one indenter to their surface under a certain load and period of time and to measure the corresponding descent of that surface in depth.

There are a lot of different hardness or micro-hardness tests around. A bunch of them are the Knoop, Brinell and Rockwell test, for example. Every one has its own different properties and capacities. Slight differences that make them better for one purpose or another.

On the one hand the Brinell hardness test is the older method (carried out in 1900) and is mostly used for soft and thin specimens of material. Its indenter takes sphere's shape and uses huge loads. The functional principle is the same as it has been described before.

On the other hand the Rockwell test uses the same type of indenter as Brinell test but, in addition, this one is indicated for measuring the hardness of harder materials like, for example, steel.

The last one, the Knoop test is indicated for studying the micro-hardness due to its capacities on low loads. Its indenter takes a different shape than the others tests described above. The indenter has an inverted pyramidal shape whose internal angles are 130º and 172º respectively.

All of them allow a good characterization of the materials (metallic, plastic, rocks or concrete materials). On this thesis has been elegied the micro-hardness tests of Vickers as the one to be used. Vickers test is a primal derivated method from the Brinell test but it allows us to use a wide range of loads. Its indenter has form of inverted pyramid too, as Knoop test, but it has a different internal angle: 136º. (Fig.10)

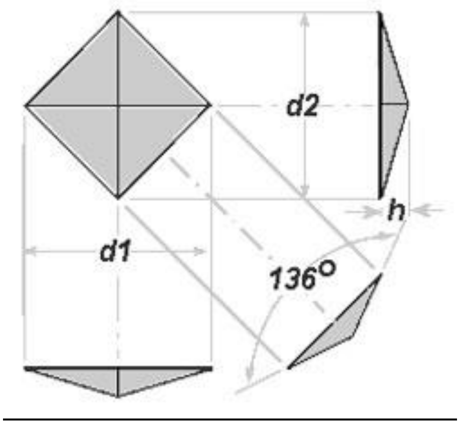


Figure 10: Geometry of the Vickers test indentation [34]

As it was commented before this test is based on the introduction of a metallic indenter with a diamond tip on the material's surface (in this specific case concrete) under the effect of predetermined load. The range of loads can be very different. In fact it will depend on our final purposes. For example, the Vickers test has a wide range from the $9{,}807.10^{-3}$ N to 9,807 N.

That penetration produces an indent on the specimen surface with the appearance showed onFig.10. That rectangular form with two diagonals is fundamental. By measuring their lengths it is possible to know the hardness value and indent depth on the material.
In order to determine the length of the diagonals it is necessary to use optical microscopy because we are working in a very little scale, remember, micro-scale.

When the two diagonals are measured and their media is calculated one can proceed to know which is the value of Vickers micro-hardness (HV) by the presented formula:

$$Hv = 1000 * 10^3 * \frac{P}{A} = \frac{2000 * 10^3 * P * \sin\frac{\alpha}{2}}{d^2}$$

$$Hv = 1854{,}4 * \frac{P}{d^2}$$

Where P represents force (expressed in gramforce 1gf= $9{,}807.10^{-3}$
A = superficial indentation area
d = diagonal length
α = inner angle (136º)

The indentation as well, has to be carried with a certain period of time, in fact standardized time: of 10 or 15 seconds. Whatever other period of time used has to be specified.

On the realization of the Vickers test one has to take into account some particularities and problems that can emerge during the process and studying the results. To obtain good and confident results the previous specimen preparation is a vital process. Due to its microscopic scale the Vickers test requires an optimal surface texture of the material, free of impurities and without abrupt topography.

If not, the specimen can guides us to incorrect hardness values (by excess or defect) or to an irregular indentation. The texture is, then, one of the most important aspects of the test and we have to pay attention to it.

Another fact to take into account during the test is the correct subjection of the specimen and also its perpendicularity to the indenter axis. At this scale every single slope can mean anormal results.

There are several problematic associated to the test. The most common it to collect wrong HV values due to impurities on the surface or to the presence of obstacles behind the surface which affects the deformation bell that causes the indenter.
Another problem, mainly on low loads, is that for the same material the value of HV can be different. That effect is what the scientific community calls the Indentation Size Effect (ISE). The ISE means that the load value affects the HV module as follow: The hardness value rises up when the penetration depth decreases.

The basis of this phenomenon is that when the indenter penetrates into the material two deformations are happening with that low loads: elastic and plastic. When the indenter is retiring from the material surface the elastic deformation allows the material to recover the initial shape. That traduces to a smaller indent and diagonal length, and at the same time to a greater HV value.

Chapter 4

USED MATERIALS AND METHODOLOGY

4. Generalities

After setting the theoretical basis of this thesis in previous chapters it is convenient to point out the importance and the need of having an empirical support behind. The experience becomes fundamental in order to investigate the material's behaviour and, therefore, to know which role develops the previously presented ITZ on concrete resistance.

This chapter will provide and describe the materials used on the empirical research and the methodology we followed to obtain the results that can be seen on chapter 5.

4.1. Material Properties

4.1.1. Properties of aggregates

It is important to specify that all concrete specimens used in this thesis come from an experimental campaign carried out by a doctoral student. We believed they perfectly fit with our purposes.

These concretes, whose properties will be shown in detail later, have natural aggregates in their composition which come from the Foj quarry, placed in Vallirana, and whose medium gradations (sand and gravel) are shown on the following table (Tab.6).

Table 6: Sand, gravel and recycled gravel gradation

	Sample Medium Data					
	Sand		Gravel		RecycledGravel	
sieve	%Retacc	%Pass acc	%Retacc	%Pass acc	%Retacc	%Pass acc
16	0	100	0	100	0	100
14	0	100	0	100	0,2	100
12,5	0	100	1	99	2,4	98
10	0	100	25	75	16,7	84
8	0	100	62	38	36	65
6,3	0	100	91	9	58	44
4	0,3	100	98	2	89	12
2	23,0	77	99	2	95,5	5
1	55,4	45	99	1	96,9	3
0,5	72,3	28	99	1	97,8	2
0,25	81,3	19	99	1	98,3	2
0,125	86,5	14	99	1	98,7	1
0,063	89,5	11	99	1	99,2	1
% fines	11,7		0,8		0,9	
MF	3,2		6,5		6,1	

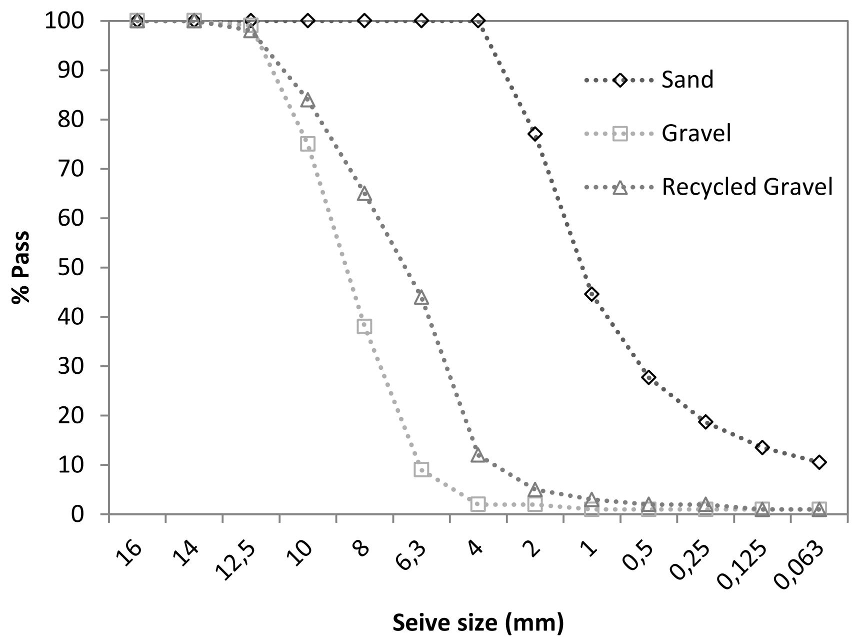


Figure 11: Gradation of sand, gravel and recycled gravel

As we can see in the graph (Fig.11) recycled aggregates have a slightly greater fraction of fines than the natural gravel but, at least, they are very similar.

It is also useful to point out the density and absorption data (Tab.7) carried by the laboratory tests. In there we could realize what it seemed to be obvious at first sight: recycled aggregates have higher absorption and lower densities than natural ones. The main reason that explains this behavior is due to the mortar added to the natural particles which has pores.

Table 7: Density properties of sand, gravel and recycled gravel

	Sand	Gravel	Rec.Gravel
Da (t/m3)	2,763	2,720	2,676
Ddry (t/m3)	2,677	2,682	2,292
Dsurf.dry (t/m3)	2,708	2,696	2,436
Wabs	1,166	0,514	6,529

That behavior becomes clearer when we do a tamper test. In there the results show the lower existence density in recycled aggregates, around 1,3 t/m^3 in front of the 1,5 t/m^3 of the natural aggregates from the quarry (Tab.8)

Table 8: Gravel and recycled gravel medium density

Gravel				Recycled Gravel			
#1	kg	#2	kg	#1	kg	#2	kg
Bin	3,8	Bin	3,8	Bin	3,8	Bin	3,8
Volume (cm³)	4,932	Volume (cm³)	4,932	Volume (cm³)	4,932	Volume (cm³)	4,932
Aggregate (kg)	7,374	Aggregate (kg)	7,436	Aggregate (kg)	6,296	Aggregate (kg)	6,412
Density	**1,495**	**Density**	**1,508**	**Density**	**1,277**	**Density**	**1,300**
Medium Density(t/m3)	**1,501**			**Medium Density(t/m3)**	**1,288**		

4.1.2. Properties of concretes

The study of concrete characterization to find out the ITZ behavior in different dosages and replacements is essential. ITZ may respond different depending on the concrete composition, and to make sure how this little borderline in-between aggregates and paste responds we have to carry with large sample variety.

This thesis has decided to use a vast amount of typologies in conventional concretes (without recycled aggregates) as well as recycled ones with different characteristics. The list of samples used is resumed in Tab.9.

Table 9: Samples properties and strength at 28 days

			%Subst	W/C	density	Absorption	Comp.Resist (Mpa)	E Module (Mpa)
Conventionals								
HC	0,5	SP 1,2%		0,5	2,25	3,26	50,4	38528
HC	0,5	SP 1%		0,5	2,33	3,14	51,4	34597
HC	0,4	SP 1%		0,4	2,35	2,46	62,1	40422
Recycleds								
HR 20	0,4	SP 1,2%	20	0,4	2,33	2,19	58,9	38465
HR 20	0,4	SP 1%	20	0,4	2,34	2,24	59,8	38032
HR 20	0,5	SP 1,2%	20	0,5	2,36	2,45	44,8	35778
HR 20	0,5	SP 1%	20	0,5	2,33	2,69	37,9	36121
HR 35	0,4	SP 1,2%	35	0,4	2,28	3,58	59,1	33762
HR 35	0,5	SP 1,2%	35	0,5	2,25	3,92	49	31275
HR 35	0,5	SP 1%	35	0,5	2,29	3,56	59,9	36869
EMV 20	0,4	SP 1,5%	20	0,4	2,36	2,46	64,1	36156
EMV 20	0,5	SP 1,2%	20	0,5	2,27	3,44	48,8	34079

As can be observed on the table we have concretes with high strength resistances and concretes with different percentage of recycled aggregates in their composition. At the same time, the recycled samples have two different typologies of composition making process: The conventional process following Bolomey method and, newer one, the EMV method (Equivalent Mortar Volume).

EMV is a composition making method that takes into account the biphasic natural state of recycled aggregate (mortar and natural aggregate) in order to quantify the total existing mortar on the recycled aggregate and, therefore, save cement on the final concrete composition. On our samples the percentage of mortar adhered to the aggregates is around 36%. Following this method we obtain a new composition with the same mortar volume as the traditional methods but without a loss of cement which traduces into a less CO_2 emission concrete. Since now what has been doing is to add extra cement in the mix to reach similar strengths as conventional concretes.

A recent research from the UPC [26] has shown that following the EMV method it is possible to have potentially useful concretes with less cement than current methods without a loss in structural properties and uses.

All concretes have been made with CEM I 42,5Mpa cement and with a super plasticizer from the BASF company.

4.2. Sampling process

The sampling process to carry our tests began from cylindrical concrete specimens of 10x20 (15x30) centimeters dimension.

The first step followed was to cut the cylindrical specimens by a saw machine in order to obtain slices with little thickness that allows carrying out the polishing process without problems.

Once we have the slices the next step to follow was to start with the first polishing phase so as to eliminate the existing impurities on the sample surface and to level it. This process was done through the use of sandpaper of different grain gradation (From P80 to P1000) applied in a successive manner until we reached a satisfactory texture (Fig.12)

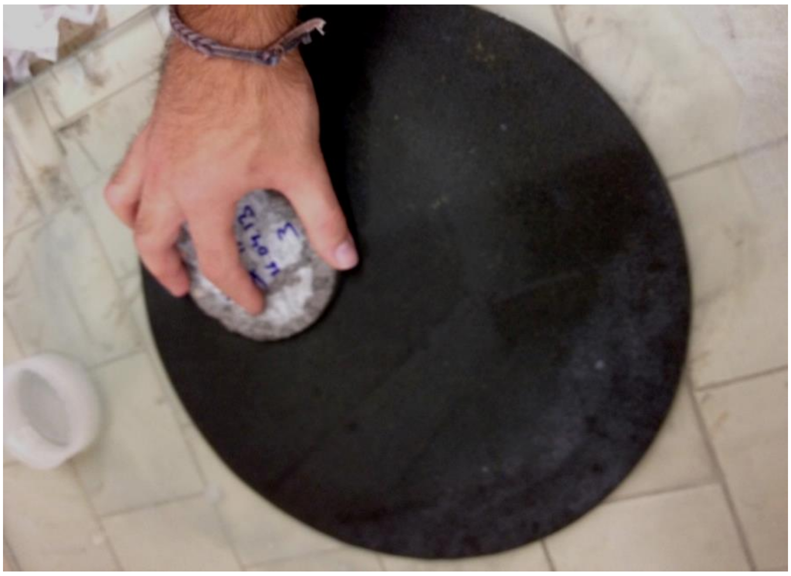


Figure 12: Polishing process with sandpaper

It is important to mention that this process is fundamental and requires a lot of attention because in that point lies the success of the up-coming tests. The surface imperfections could lead into bad measurements in the Vickers hardness test. In a similar way a flat surface is necessary to obtain clean interfacial transition zones between aggregates and bulk paste.

Having the slices well-polished the next step of the process is to adapt our samples to a more useful size (machine tests do not accept big samples). We selected a standard rectangular size of few centimeters and marked it into the slices (Fig.13). Then the saw machine cut them in a proper way. (Fig.14)

When we have all our samples with the correct size the following step was carried by the level machine which has a diamonded disk that works by abrasion. This step made sure that our samples had parallel faces and correct rectangular shapes to be held properly by the tests machines.

Figure 13: Cut slices of concrete

Figure14: Saw machine with a sample ready to cut

The last step, and the most important, consisted in a second polishing phase that allows the samples to be ready for testing. The polishing was carried by using liquid suspensions of 15, 6 and 1 grain micron. To give an optimum finished touch we used an alumina suspension of 0,01 microns. Finally, to eliminate the existing alumina in pores and cracks of concrete was used a special soap called Triton.

This was definitely the best option among others. Using an ultrasonic cleaner we realized that could lead into more cracks in the concrete specimens and therefore do not allow our post-analysis mainly because it affected the ITZ zone. Triton soap was much better to clean the specimens.

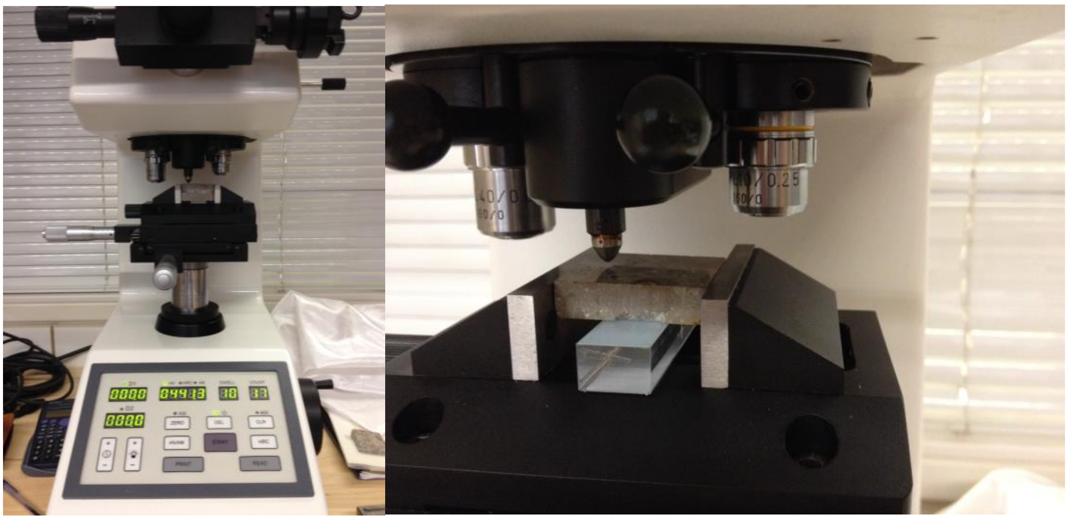


Figure 15: Vickers Hardness test machine

Once we have the whole bunch of samples ready to test we started to plan our program.

We decided to start with the Vickers Hardness test (Fig.15) in order to characterize the medium hardness module of three different phases: natural aggregate, recycled aggregate and bulk paste with different w/c relations. Hence, this would help us to know in which phase we are when we study the ITZ carefully.

Our test program consisted on making a two different matrix of 4x4 (16 indentations) for two different loads. Because our purpose was to study at micron level we opted to apply 10and 50 gf (gram force; 1gf = $9{,}8.10^{-3}$ N). We indented conventional and non-conventional concrete samples with different w/c relations and different percentages of natural aggregate substitution.

The next step in the hardness test was to evaluate the ITZ. We opted for making 4 rows of indentations for all three loads going from the aggregate to the bulk paste considering a safety distance between each one in order to prevent affections due to the bell deformation that appears when we indent the material. This path structure can be seen on Fig.16.

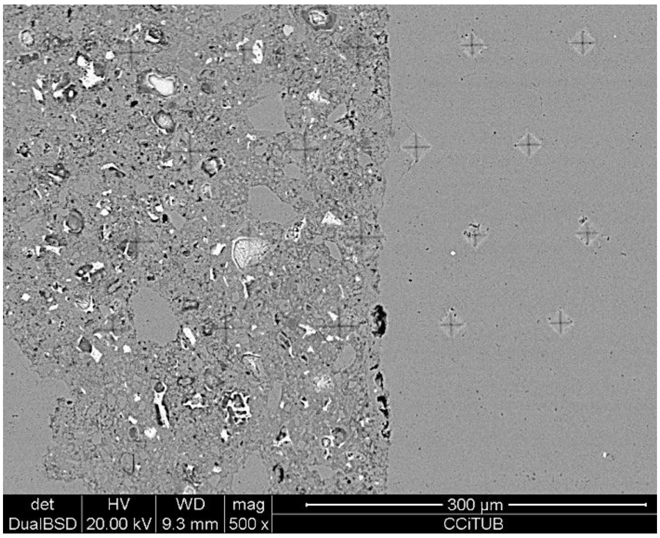


Figure 16: Indentation structure from the cement paste to the aggregate (SEM)

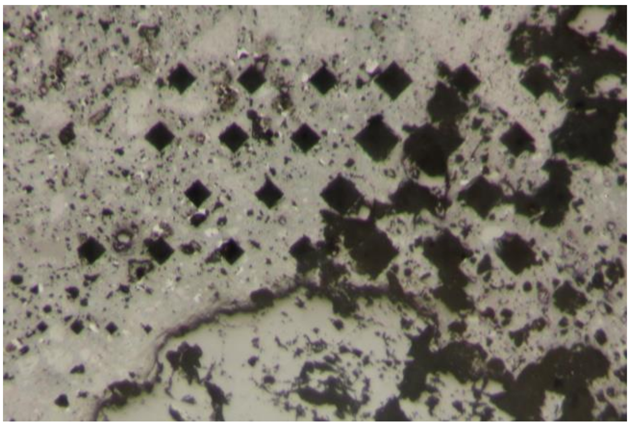


Figure 17: Optical microscopy of an indentation from aggregate to the cement paste

Once we collected all data information of these tests we started to analyze the results. This can be found on chapter nº5 of this thesis. Before doing that we considered to carry a micro-structural study by microscope (Fig.17). For this purpose we used an optical microscope in first instance as an approximation to what we have done; and finally we used a typical SEM microscope (Fig.18) to take pictures in detail associated to a chemical analysis of the samples.

Figure 18: SEM microscope

A SEM (whose name means Scanning Electron Microscope) is a type of microscope which does not work through lights as the optical microscopes do. It works by focusing a beam of electrons on the specimen and then collecting all the different signals emitted by the interaction between the specimen's atoms and the electrons. The most common method of signal detection is by secondary electrons. These secondary electrons captured by different sensors allow us to know the topography of the specimen and its composition.

Chapter 5

RESULTS AND DISCUSSION

5. Hardness test results

To undertake the analysis of the Vickers hardness tests and to identify the main properties of the concretes, and consequently the ITZ properties, we have been fixed several force values of 10, 25 and 50 gf (gramforce). Properties have been characterized in each different existent phase of concrete (natural and recycled aggregates, cement paste and interfacial transition zone). Obtained properties are detailed and discussed on the following lines.

5.1. Aggregate characterization

Both the conventional concretes and the recycled ones present aggregates with limestone origin, so we carried indentations test in both concrete types and, finally, we found the existence of two different ranks of hardness for aggregates. The first group of specimens showed a medium hardness value of 187 HV with a variance coefficient of 14%. The second group showed, in contrast, a medium hardness value of 261 HV with a variance coefficient of 15%. Both results for a 10gf force applied load.

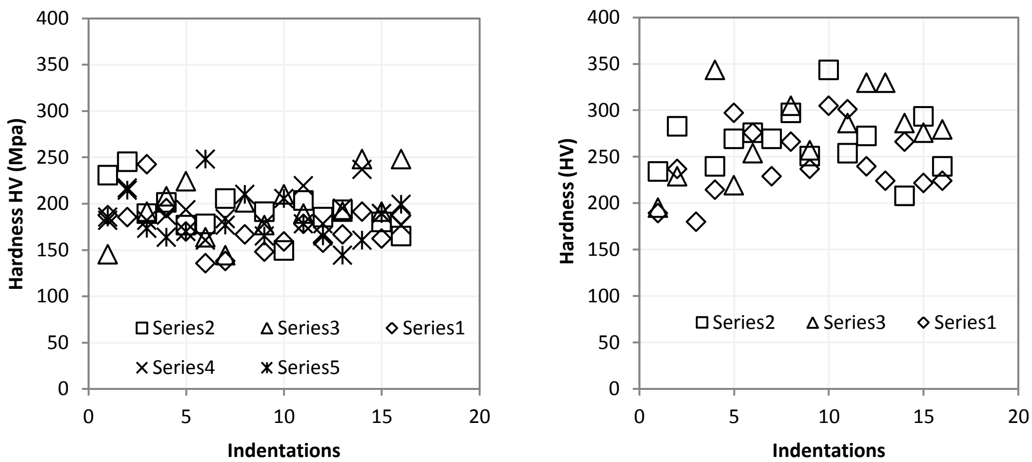


Figure 19: 10gf micro-hardness analysis of natural aggregate specimens (Type 1 and Type 2)

Fig.19(Left) shows the hardness value results of each indentation in five different specimens that contains natural aggregates of the same rank level. As has been said before,Fig.19 (Right) shows the other typology of natural aggregate that coexists on our concretes that have higher Vickers hardness levels.

This patron repeats for the other analyzed force, 50gf (Fig.20). However, for the 50gf the difference between the hardness values of the different indentations on the aggregates reduces. The first group of aggregates obtains a medium hardness value of 208 HV with an 11% variance coefficient, while the second group obtains a medium hardness value of 230 HV and 14% variance coefficient.
One possible explanation to this phenomenon can be found in the mechanical behavior of the crystalline structure under several kinds of loads. While the affected area of the indentation in the 50gf load implies lower dislocations than the 10gf load, the 10gf dislocation produces bigger dislocations over the crystalline structure. Finally, this effect is closely related to what is known as the ISE (Indentation Size Effect) effect that is going to be commented later in this document.

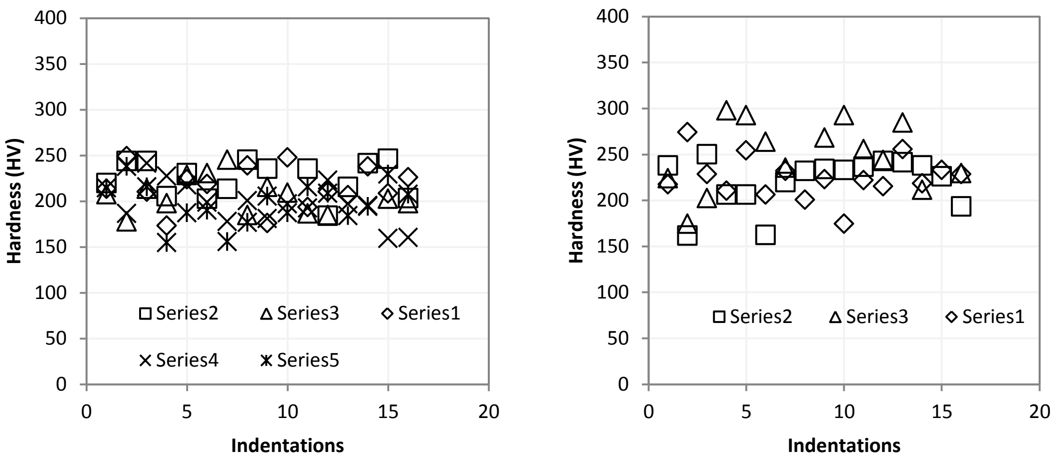


Figure 20: 50gf micro-hardness analysis of natural aggregate specimens (Type 1 and Type 2)

The existing difference between the limestone aggregates hardness may be due to the geological history they have. Therefore, the higher hardness aggregates may be submitted to higher pressures in their litological location during their formation leading to a stronger crystallization process than these lower hardness aggregates. Then, when a very concentrate force (10gf) hits the structure the crystals can deal with more or less pressure and give several hardness values for an aggregate equal in appearance.

5.2. Cement paste characterization

To characterize the cement paste we proceeded in a similar way than we have done before. But, this time we have analyzed several specimens with the different water/cement ratio we have. Because our dosages have been done with the same type of cement, it was important to know which hardness corresponded to each water/cement relation either 0,4 or 0,5.

The tests results have shown for the 10gf a very regular behavior in which the medium hardness value for cement paste with w/c=0,5 relation was 70 HV Mpa(Fig.21 Left) while the cement paste with w/c=0,4 relation was 86 HV Mpa (Fig.22 Left) with a variance coefficient around 15% in both cases.

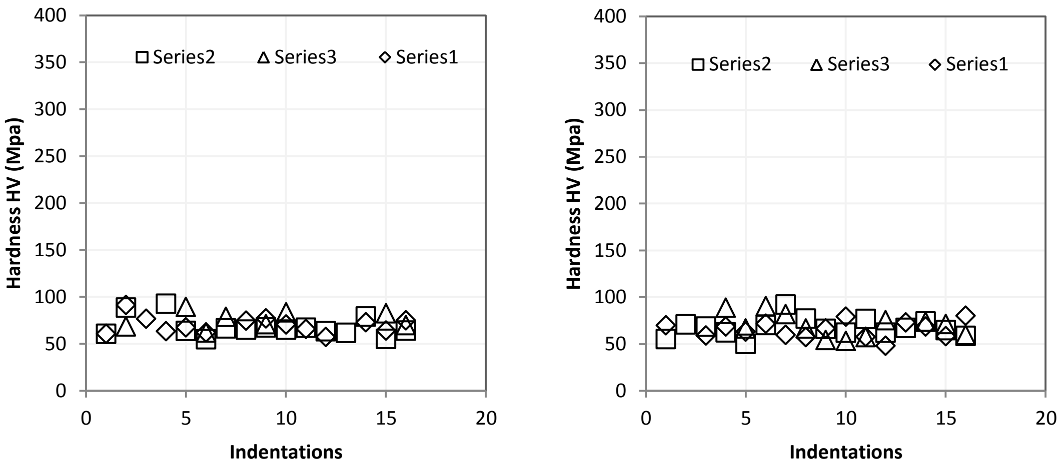


Figure 21: Hardness values for cement paste (w/c = 0,5) 10gf and 50gf

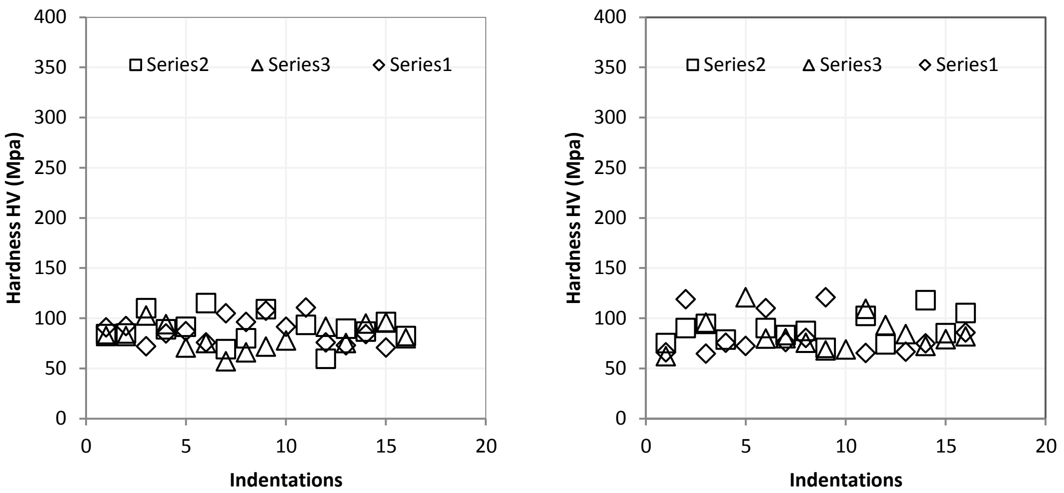


Figure 22: Hardness values for cement paste (w/c = 0,4) 10gf and 50gf

At the same time, for the 50gf load indentations the results have shown a medium hardness value of 67 HV Mpa for the w/c=0,5 relation(Fig.21 Right) and a medium value of 85 HV Mpa for the w/c=0,4 (Fig.22 Right).

Just the results we expected initially. The differences between both w/c ratios are mainly due to the water content. Water makes the paste to become more porous and to show lower hardness under the tip indenter. The pores, with a major presence in the w/c=0,5 ratio, drive into a decrease in the cement paste hardness. Then, depending on the concrete sample we examine we will have ones or others values as a reference to identify the paste in the ITZ.

Table 10: Hardness variation with w/c ratio

	w/c = 0,4	w/c = 0,5	% Hardness Variation
10gf Hardness	86	70	23%
50gf Hardness	85	67	27%

When we compare the medium hardness results between the two water/cement ratios (Tab.10) we have in our study, we can find a significant difference in favor of the lower ratio in both loads. Specifically, a 23% hardness variation, for the lower load, and a 27% hardness variation for the higher load. As a result the water/cement relation becomes fundamental and must be taken into account later.

However, the slightly differences between the 10gf and the 50gf results (where the latter have lower hardness values) may be explained by the ISE effect. A current failure at the micro scale level.

It is important to note that all the collected and presented data shown in this chapter are obtained from different concretes with the same w/c ratio and, in addition, the same cement. They have been subjected to an analysis of variance to confirm that there are no differences between them in hardness terms. The analysis showed that we were treating with the same kind of cement paste.

5.3. Recycled aggregate characterization

The characterization analysis of the recycled aggregate has been a difficult task because the recycled aggregate is a mix of limestone aggregates and old mortar. This fact drives into very variable results, and even knowing the value ranks of the limestone aggregates, the study of the old mortar (which is the purpose of this thesis) leads into a huge variability in the hardness results.

The great heterogeneity of the recycled aggregate, whose mortar has, in general, higher porosity, also depends on the used cement in its original manufacturing. Precisely, these two factors in combination with the presence of sand incrustations with huge hardness cause a complex identification of the standard rank values for the old mortar.
Vickers hardness tests results by indentation on the old mortar have given, as it was expected, lower values than these obtained on the cement paste before. Hence, for a 10gf force we have obtained medium hardness values around 62 HV Mpa(Fig.23 Left) while for 50gf force we have obtained 72 HV Mpa approximately (Fig.23 Right).
Both medium results have a really high variation coefficient between 26% and 36% which reflects the intrinsic heterogeneity of the material. In fact, under an ANOVA analysis the p-value obtained confirms this propriety.

In comparison with the cement paste results, we note a descent of 12%, respect to the w/c = 0,5 paste, and a descent of a 28%, respect to the w/c = 0,4 paste, for a 10gf load. We have also found these phenomenon for the 50gf load but, in this case, for the lower w/c = 0,5 relation there is an increase of 7%. In respect to the w/c = 0,4 relation the old mortar continues to reflect a decrease of 15% (Tab.11)

Table 11: Comparison between old mortar and cement paste hardness

Load applied	Old MortarHV	Cement paste HV	% Variation	w/c relation
10gf	62	70	-12%	0,5
10gf	62	86	-28%	0,4
50gf	72	67	7%	0,5
50gf	72	85	-15%	0,4

As far as the water has a great effect in the cement paste properties we can assume that the porosity also has a predominant role in the old mortar adhered to the recycled aggregates.

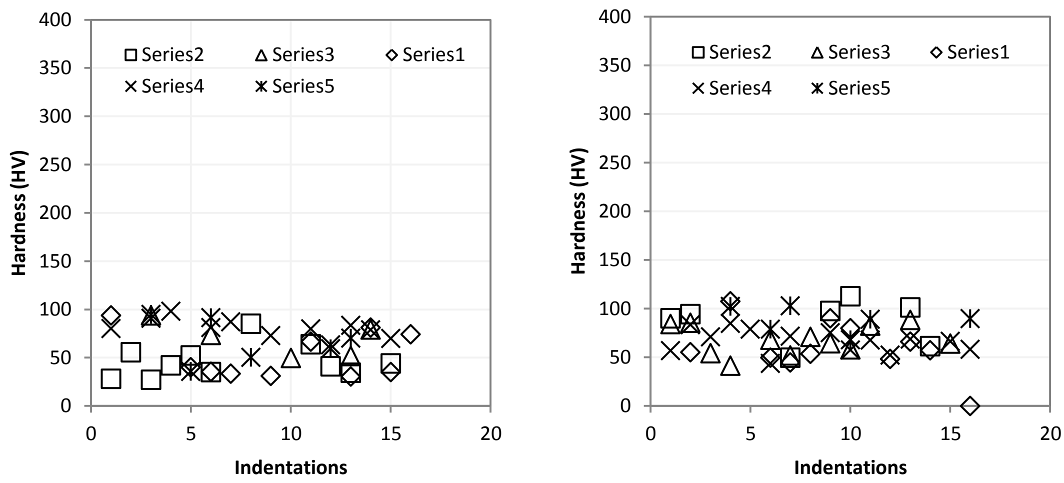


Figure 23: Hardness values for recycled aggregate (10gf and 50gf)

This variability will difficult the identification of the ITZ and this will have to be done combining visual support as SEM or optic microscopy.

5.4. The ISE effect

One of the main problematic during the experimentations has been the non-constant behavior of hardness (in medium values) depending on the load applied. The differences previously appreciated between the 10gf and the 50gf are probably due to micro-scale effects and, more precisely, to what is call indentation size effect (ISE).

When we indent our samples with a low-load range, and at microscopic size, we not only affect the surface that we indent on. Beyond letting a residual plastic trace on it, and measuring it, we generate a deformation mechanism behind the surface that contributes on dislocating the structure grains that compose the material. In addition, the grains under load tend to organize in preferred orientations around the boundaries of the tip indenter. This deformation is close related to the density of packing grains in the material's structure and, therefore, the w/c ratio.

When the indentation size is to the same order that the grain size a different deformation is done than when several grains interact. This is the fact that allows that we can obtain higher hardness values (normally higher when indentation is less). Supposing, of course, that other principal factors do not take place in the hardness value, such as the bad quality of the polishing process, the excess of polishing (that makes the surface stronger to the indenter) or the presence of third materials incrustations.

The relation between the applied load and the indentation diagonal of the residual trace shows a linear relation (under logarithmic scale) but, if we look at the hardness value results we note slightly differences between each load. This linear relation emphasizes the existing anomaly behavior of material at micro-scale. (Fig.24)

At the same time the low water/cement ratio also traduces into greater hardness levels in the poorest water mixes. (Fig.25).

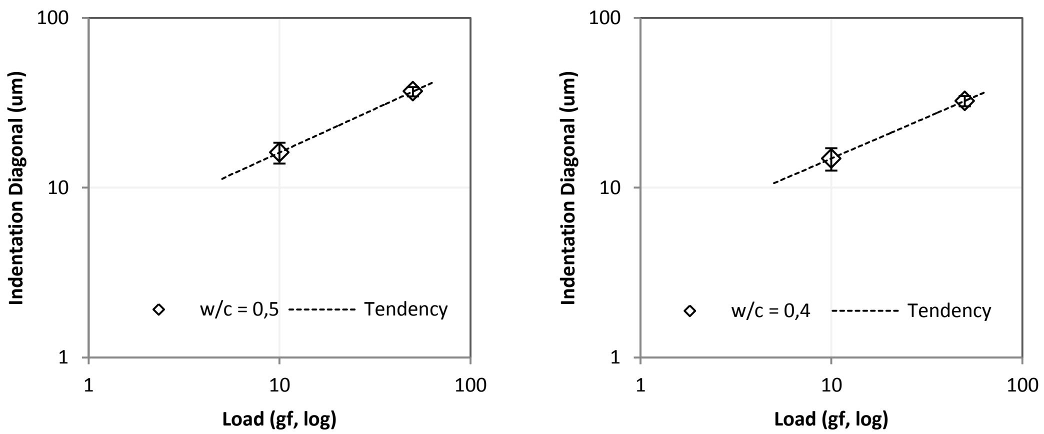


Figure 24: Indentation Diagonal – Load relation on cement pastes

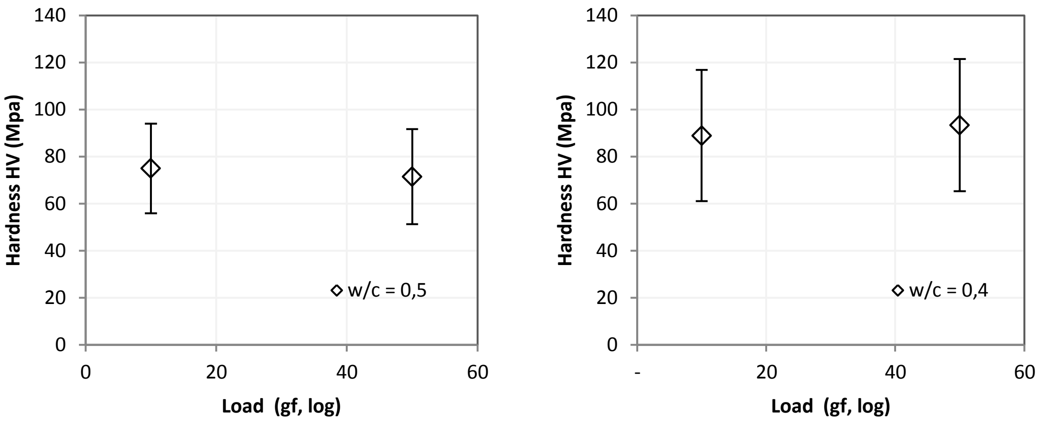


Figure 25: Hardness – Loadbehavior on cement pastes

Intrinsically related to the diagonal indentation size, in the Vickers Hardness test, there is the depth of indentation. In a perfect plastic material the depth of the surface, after applying the indenter, will be independent of the hardness value; remaining constant the relation between the two parameters. [33]

But under low-loads (microscopic range of action) the hardness begins to vary with the depth of the indentations. This process, which is the ISE, leads to higher hardness values for small traces than those should be.

As an example, we proved that our samples are affected by this micro-scale phenomenon. No matter which part of the concrete we test, the hardness value rises when the depth decreases.

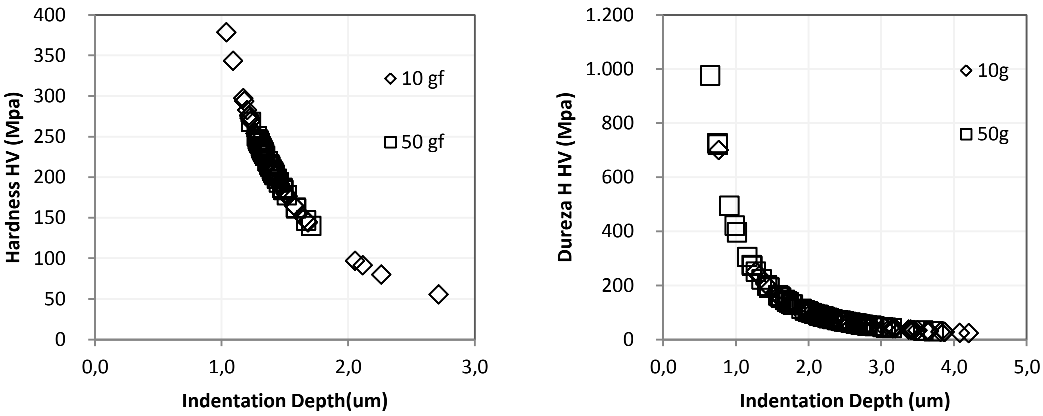


Figure 26: Hardness-Depth relation for natural aggregates (Left) and recycled aggregates (Right)

On Fig.26we can see the depending relation between hardness and depth regardless of the load, which are from the low-range. Note that both, the natural aggregates and the recycled ones, are affected by the ISE phenomena. Although the recycled aggregates have higher hardness values due to the different petrous origin of their compounds.

The same patron is followed by the cement pastes on Fig.27 but noticing that the lower w/c relation paste has a steeper slope and lesser depths indentions than the w/c = 0,5 relation. Therefore, the medium hardness values are different too.

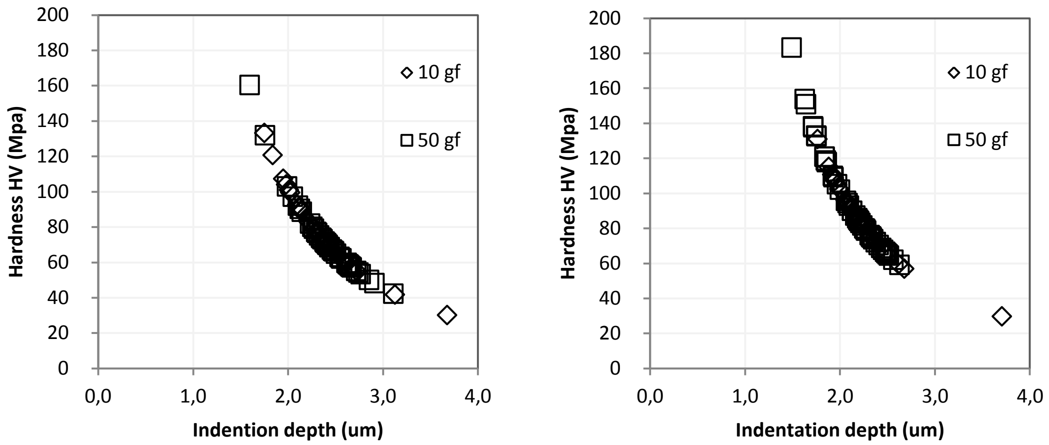


Figure 27: (LEFT) Hardness – Depth relation for w/c = 0,5; (RIGHT) Hardness – Depth relation for w/c = 0,4.

At this point, it is interesting to stress that while the Hardness-Depth graphics for both water/cement relation remain with a known patron, if we have a look to the Hardness-Diagonal of indentation relation we will see a flat behavior (non-curved) for the w/c =0,5 samples as can be seen onFig.28.

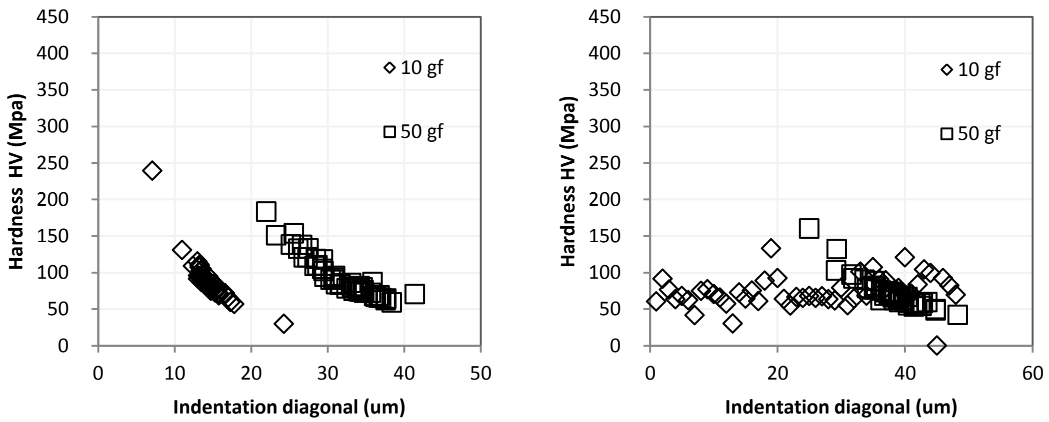


Figure 28: (LEFT) Hardness – Diagonal relation for w/c=0,4; (RIGHT) Hardness – Diagonal relation for w/c = 0,5.

This quiet behavior is, possibly, due to the high porosity of the w/c = 0,5. The existing pores of the cement paste lead into a weaker surface. Then, when the indenter penetrates, it makes larger residual marks than when we are dealing with the w/c = 0,4 relation paste.

5.5. Analysis of the ITZ

As it was explained in Chapter 4, we used a special scheme of indentation of 4 rows going from aggregate to cement paste following a zig-zag path that provide the maximum profit of data in reduced spaces.

We have done it firstly, with the conventional concrete samples, those which doesn't have recycled aggregates, and later with the recycled ones. Finally we compare the results and discuss the existence of the ITZ in both cases.

5.5.1. Conventional concrete

For our analysis we have used our two different samples of conventional concrete that only differ in the w/c relation. The first one have w/c = 0,5 and the second one have w/c = 0,4 as it was explained before. We start with the greater w/c sample.

As we can see in Fig.29 (which corresponds to a 10gf test) the behavior in hardness terms fits perfectly in what was exposed before. In other words, coming from the limestone aggregate to the cement paste it is possible to classify the different phases on the several groups of hardness mentioned in the previous exposition.

For a better understanding of Fig.29 we opted to show the test information in two different series. In that way Series1 corresponds to the first two rows (upper rows) of the zig-zag scheme while Series2 corresponds to the last two rows. Following this presentation of the results we can avoid errors caused by extrapolating large space data into one single graph made of approximation values.

Both Series describe the same performance as far as we can see the two main phases, but note that exist one little space between the aggregate and the cement paste which has lower hardness values than the other cement paste values. That is the ITZ, a little space of less than 50 microns which presents weakness.

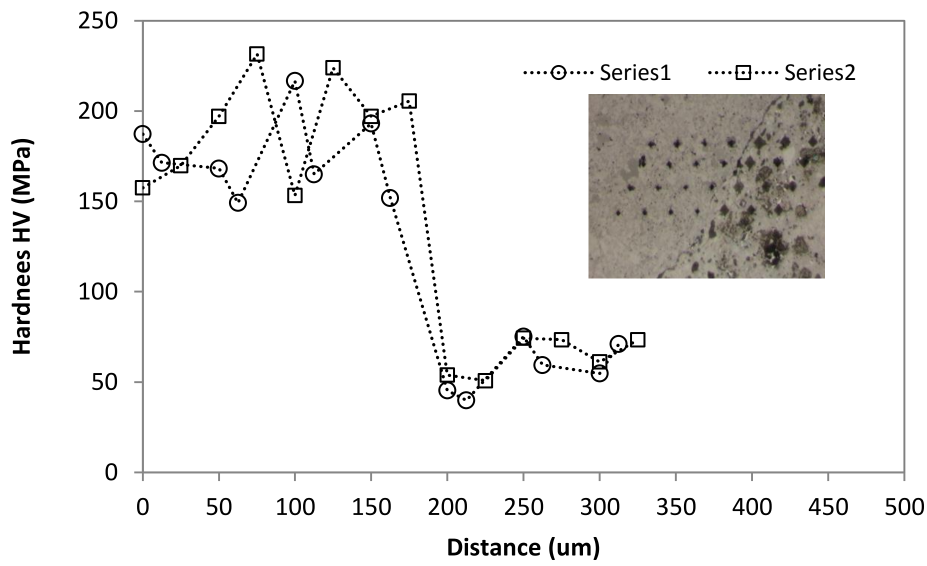


Figure 29: ITZ Analysis for 10gf load and conventional concrete (w/c=0,5)

The same happens when we show the results carried out by the 50gf test, although it becomes more difficult to see due to the higher spaces between one indentation and another with the heavier loads, which make unclear the specific place of ITZ.

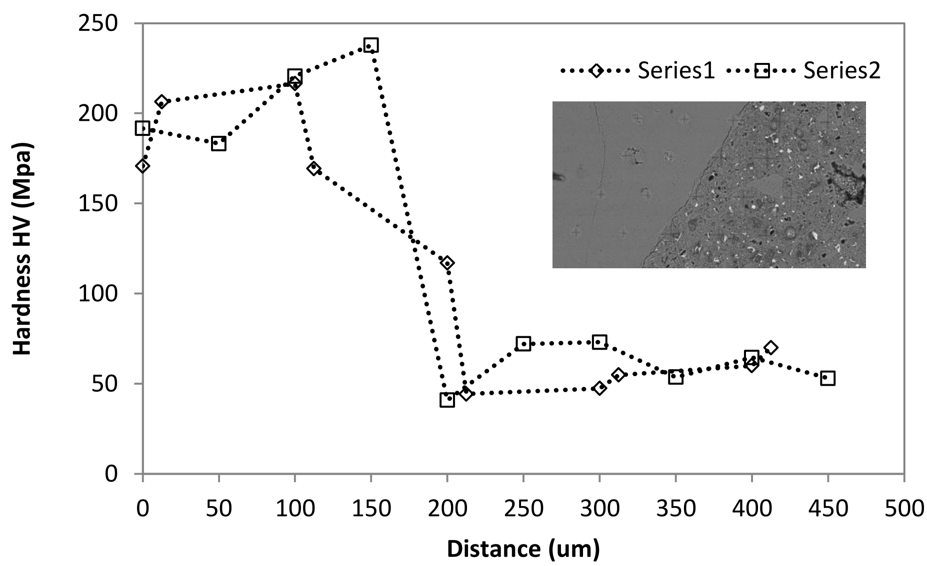


Figure 30: ITZ Analysis for 50gf load and conventional concrete (w/c=0,5)

Changing from the 0,5 w/c ratio (Fig.30) to the 0,4 w/c ratio sample (Fig.31) we can analyze a very similar response under the Vickers Hardness test results. Our sample shows a marked descent in hardness on the ITZ. Hence, the behavior remains. This patron repeats in all micro-loading conditions.

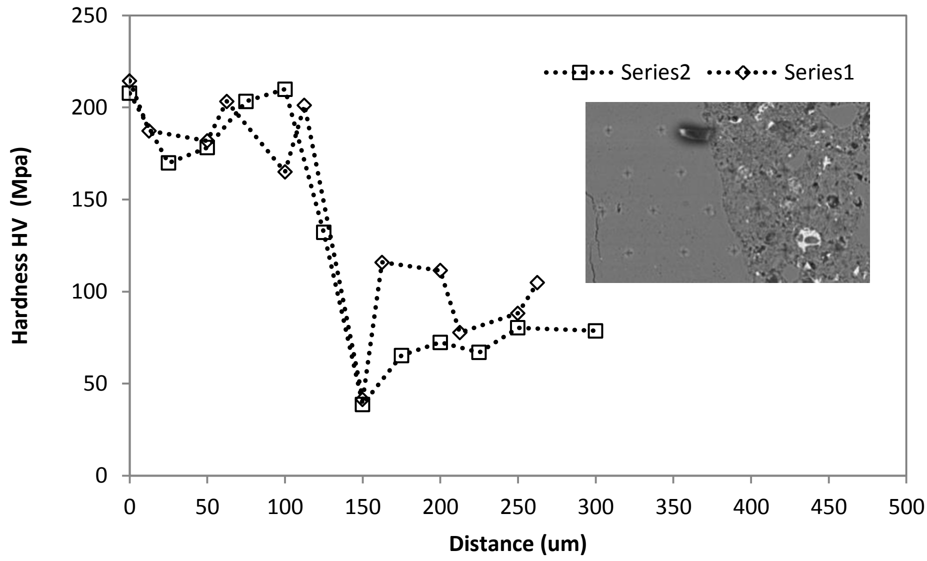


Figure 31: ITZ Analysis for 10gf load and conventional concrete (w/c=0,4)

As it was expected the 0,4 w/c relation sample has a harder cement paste in comparison to the 0,5 w/c relation sample due to its lower porosity and higher density.

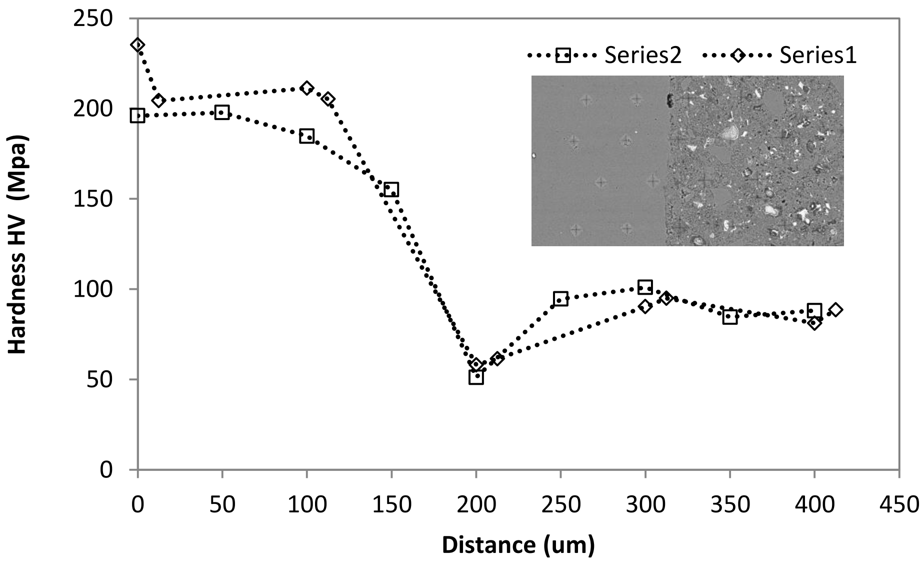


Figure 32: ITZ Analysis for 50gf load and conventional concrete (w/c=0,4)

5.5.2. Recycled concrete

To study the recycled concrete's ITZ we selected a cluster of different samples from the original group with different w/c ratios, different percentage of natural aggregate substitution and even different dosage proceeds. During the Vickers Hardness test we opted to follow a pre-designed path from the old mortar from the recycled aggregate to the new cement paste. It was expected to be difficult to characterize the behavior on the transition zone between recycled aggregates and paste because, for example, recycled aggregates contain both limestone aggregates and old mortar.

Fig.33 shows the Vickers Hardness test results of a 20% natural aggregate substitution, by recycled aggregates, with a w/c of 0,5 under a 10gf load. As we can see it presents larger differences in comparison to the results obtained in conventional concrete. For example, recycled aggregate contain fractured and porous aggregates which can lead into these results: Extremely high variance in hardness.

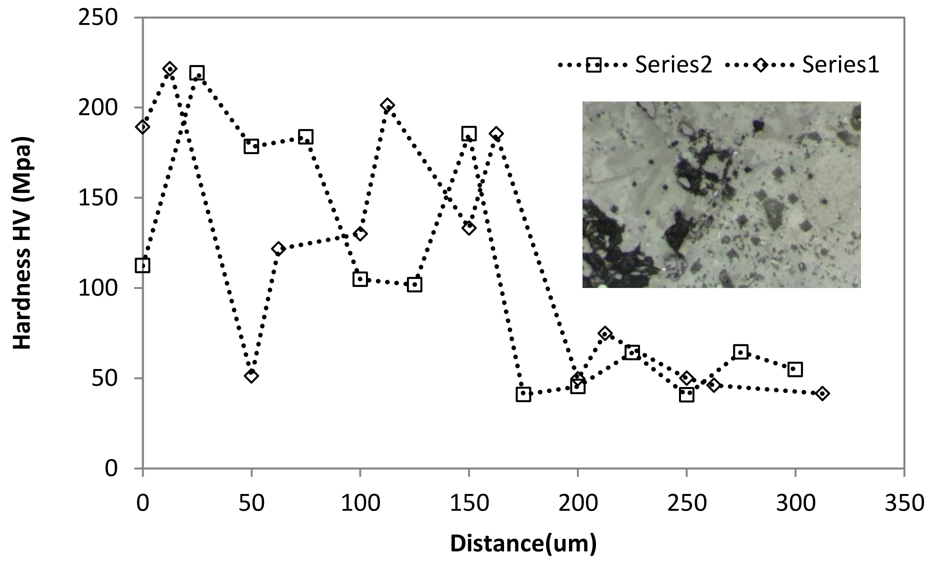


Figure 33: ITZ Analysis for 10gf load and recycled concrete (20% substitution w/c=0,5)

In this specific case the test goes from an aggregate to cement paste. But the test can also be done between the old and the new mortar (Fig.36) because exists an ITZ which also has a slightly decrease in hardness values. Fig.34shows this fact and reinforces the hardness differences between cement pastes.

When we analyze and make the comparison with Fig.35 which also has a 20% replacement percentage of natural aggregate, but a 0,4 w/c relation, it becomes more difficult to see the ITZ clearly. It also becomes difficult to sight the higher hardness in the cement paste with 0,4 w/c relation than it was in the conventional concrete but, in the end, the test reflects the different hardness between the different dosage samples. We also can note the high variability in a few microns between the first Series and the second ones on the graph.

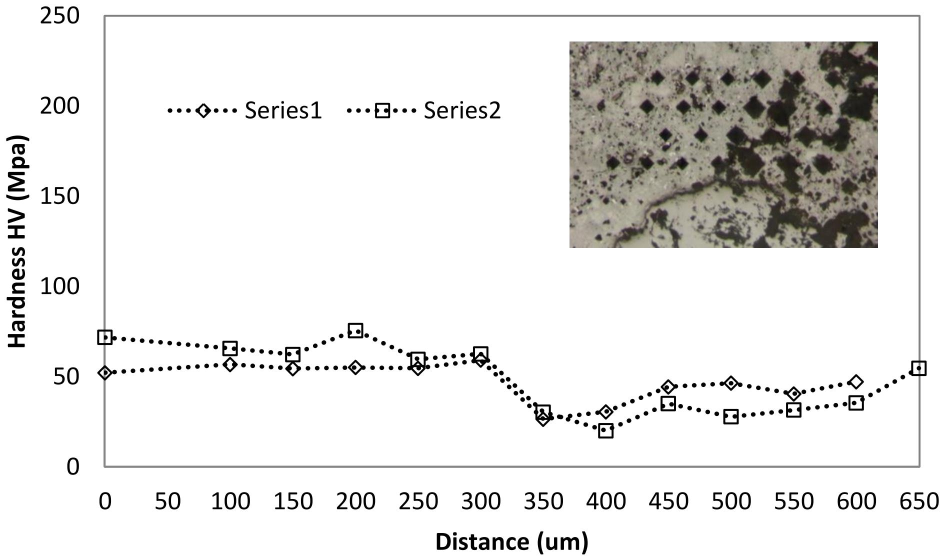


Figure 34: ITZ Analysis for 50gf load and recycled concrete (20% substitution w/c=0,5)

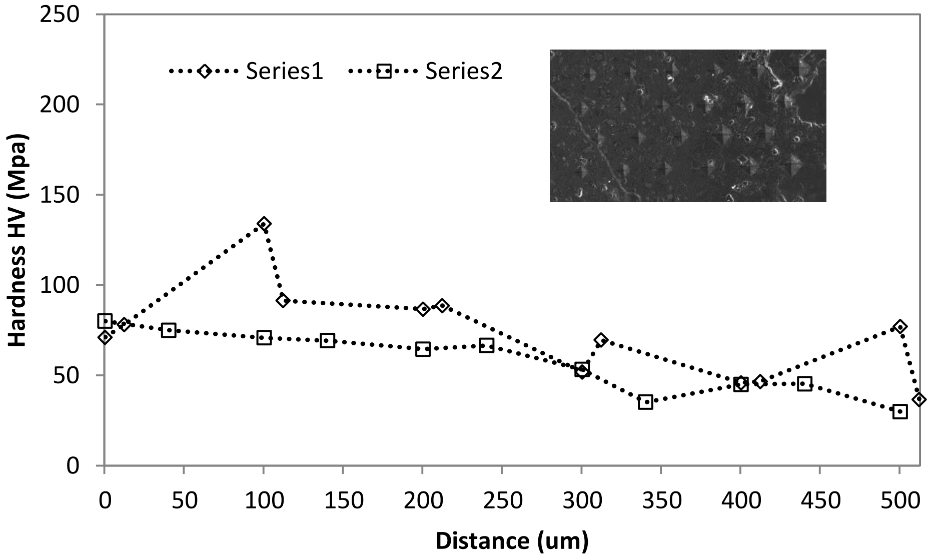


Figure 35: ITZ Analysis for 50gf load and recycled concrete (20% substitution w/c=0,4)

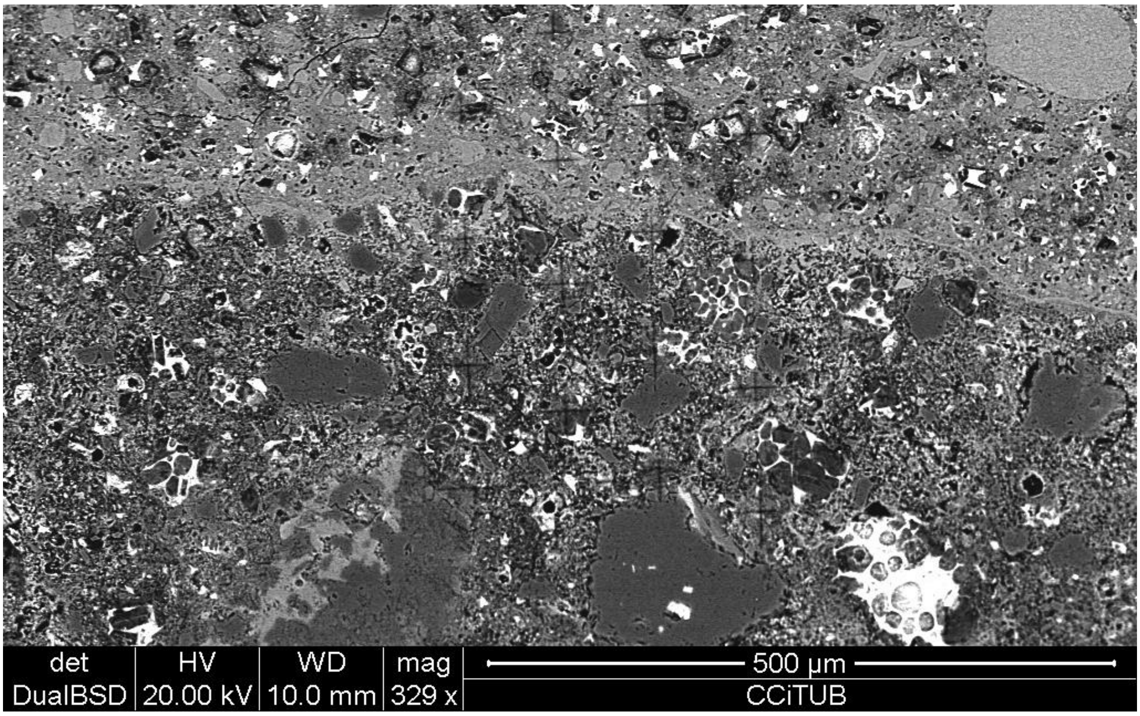


Figure 36: SEM Image of the ITZ between old mortar (below) and cement paste (above)

In the same comparison between different w/c relations but with samples that own a 35% percentage of replacement the analysis turns difficult. (Fig.37 and Fig.38).

Firstly, with the numbers of the hardness test in front, we can see that the sample with the higher w/c relation shows slightly high hardness levels but, when we do the medium value we cannot see the difference even though the variance value of 0,4 w/c relation sample is lower (15% in front of 12%).

In both graphic representations we can see once again the variability present in the recycled aggregate with two peaks in hardness that represents the presence of little aggregates. That problem is a constant in recycled aggregates. But more important is to see that the borderline between old and new mortar, the ITZ, is not clear and, in fact, it is almost impossible to differentiate.

That can be the consequence of multiple reasons, from insufficient polishing process to bad test location or even the great heterogeneity of the sample.

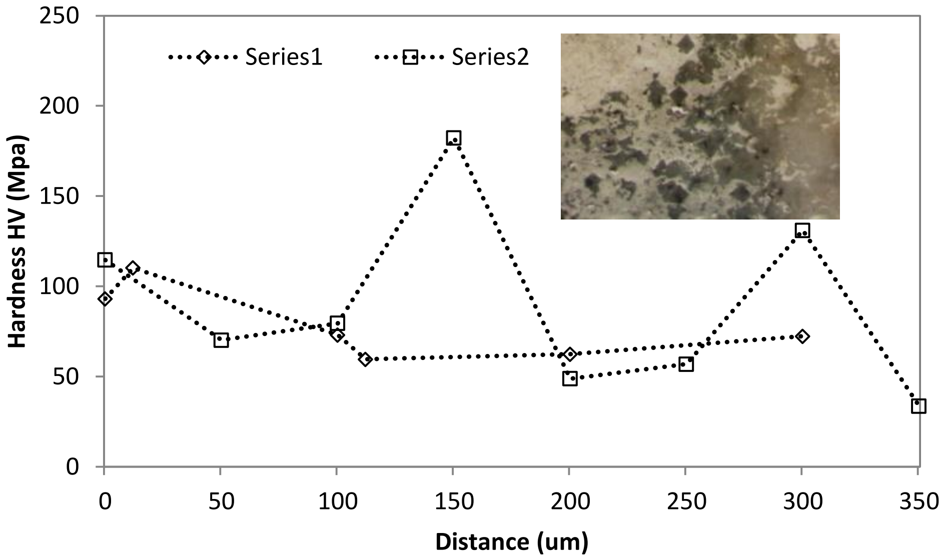


Figure 37: ITZ Analysis for 50gf and recycled concrete (35% substitution w/c=0,4)

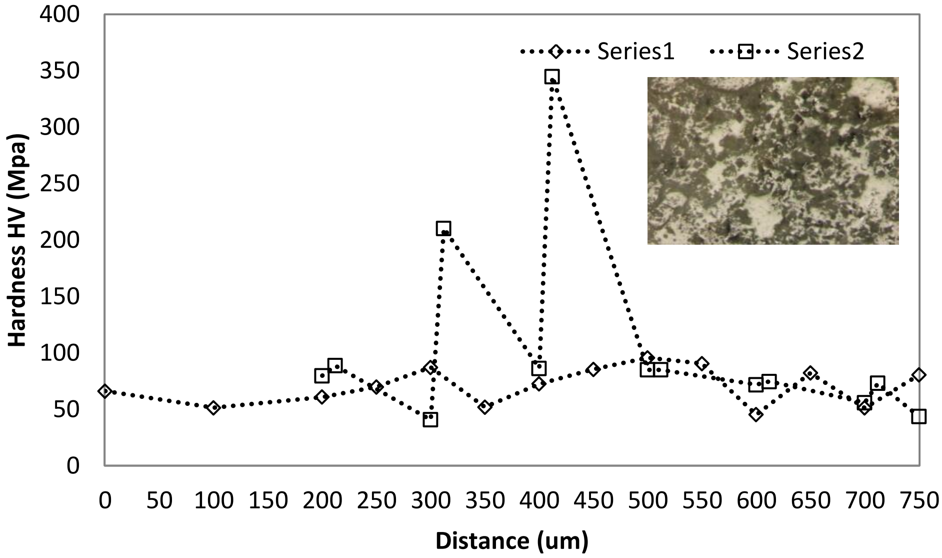


Figure 38: ITZ Analysis for 50gf and recycled concrete (35% substitution w/c=0,5)

Finally the results on the sample made with the equivalent mortar volume method (EMV) with a w/c ratio of 0,5 and a natural aggregate replacement of 20% shows the existence of the ITZ. In Fig.39it is easy to see the slightly hardness decreasing in the inter-phase. We also see two high peaks in the new cement paste that can be produced by an aggregate which may be behind the surface, which is a common problem.

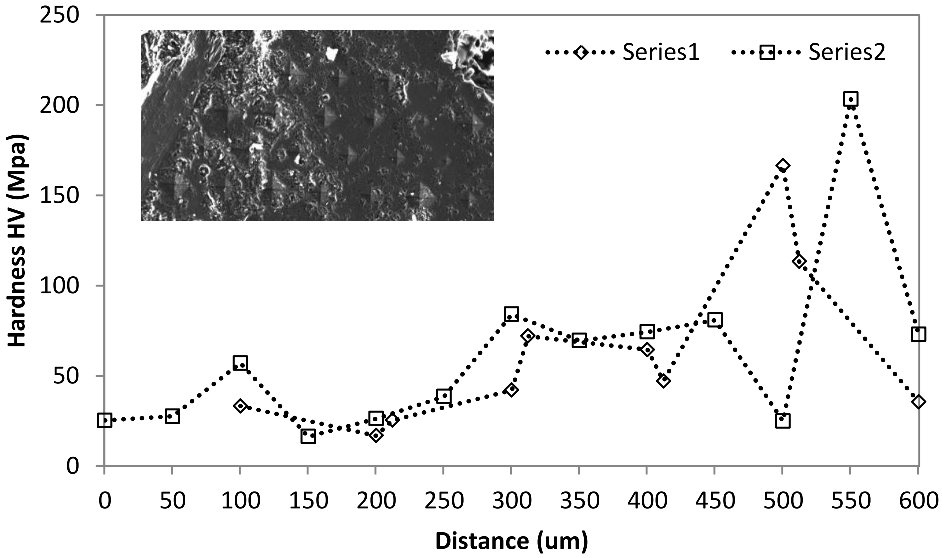


Figure 39: ITZ Analysis for 50gf and recycled concrete (EMV dosage, 20% substitution w/c=0,5)

That happens for the 50gf test but it is not easy to find the same behavior on the 10gf test which only presents a decrease tendency on the hardness value from the old mortar to the new one.

In comparison with the same concrete typology (w/c relation of 0,5) but with different dosage method the values obtained are very similar even though the EMV sample presents slightly lower values in recycled aggregate. But in the previous chapter the analysis carried out that the hardness value ranks are almost the same.

5.5.3. Comparing ITZ in different concretes

Once we have examined the different results for the several concrete specimens may be interesting to compare the behaviour, between them, in the interfacial transition zone. The main reason is that in the conventional concretes the changes in hardness are so marked that is easy to delimitate the ITZ.
In contrast, in the recycled concretes those decrease in the hardness values remain difficult to differentiate. That is because the normal hardness rank of the old mortar from the recycled aggregates is similar to the rank that cement paste shows.

Another key point of the topic is the morphology of the recycled aggregate. It is important because defines a more rough texture and a more intrusive behaviour in the borderline between the aggregate and the cement paste.

That is due to the great amount of pores and micro-holes in the recycled aggregate surface. They allow the cement paste to fill them and to define a diffuse transition as can be seen on Fig.40.

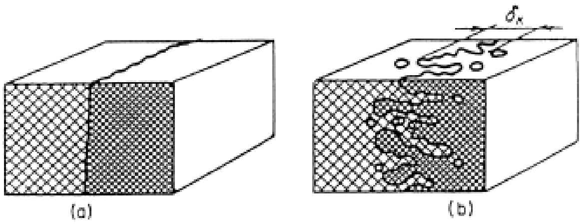


Figure 40:Recycled aggregate effect on the contact between it and the cement paste. [22]

To compare the different behaviour on the ITZ we opted to draw several graphics from our specimens. In order to understand better the graphics we let a conventional concrete as a reference.

Fig.40.traduces in a great difference between the conventional concretes and the recycled ones. On Fig.41. we can see that the conventional concrete behave well with a visible transition zone which has a slightly decrease in the hardness value. Oppositely, the recycled concretes has an intrusion on the old mortar that allows the hardness to rise and to hind the transition zone. In that way, the old mortar shows a low hardness range in comparison to the natural aggregate.

On Fig.42. we can see two extremely different transition zones. On the one hand, we have a mineral inclusion that makes the hardness to rise up before decreasing, in the 35% natural aggregate substitution concrete. On the other hand, we have an HR 20% concrete going from the old mortar to the cement paste. As can be seen on the figure, the ITZ's hardness decrease is almost unappreciable because of the flat behaviour.

Finally, on the Fig.41. we can see how the HR 35% behaves in a quite irregular way, making the fact of discerning the ITZ difficult.

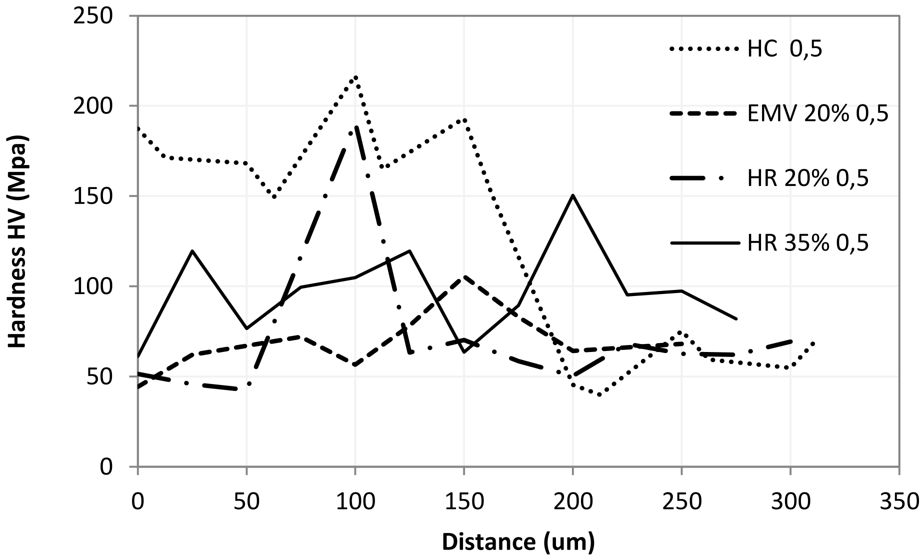


Figure 41: Comparison between conventional concrete and a recycled concretes

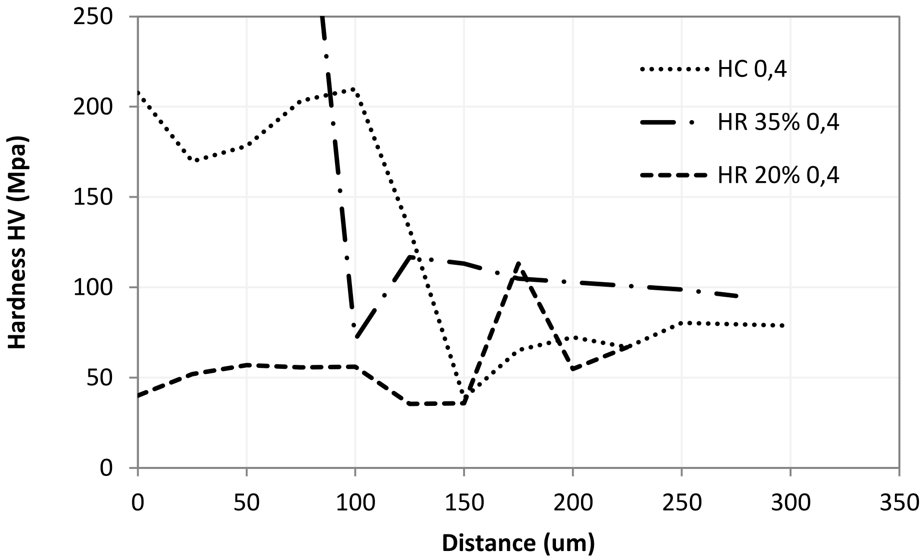


Figure 42: Comparison between conventional concrete and recycled concretes

5.6. Mechanical properties: compressive strength, elastic modulus and hardness.

5.6.1. Compressive strength and hardness on cement paste

One of the main purposes of this thesis was to determine the existing relation between the measured micro-hardness in concrete and its compressive strength. Some researches [37] have shown that these two parameters are close related and, in the analysis that we carried out on this thesis, we have found it too.

Firstly, we have taken the same indentation data that we used before, in the characterization of the cement pastes' micro-hardness, to represent that data associated to its compressive strength results.

We start from several concrete samples, few of them with a w/c = 0,5 and the remaining ones with a w/c=0,4. As we can see at the Fig.43, the previously shown differences in the hardness values translate into differences on the compressive strength.

And, in the end, the most important factor, which dominates the material response, is the water/cement relation or, more specifically, the porosity. The difference between the higher relation and the poorer is significant. What is also significant is the tendency (linear regression) between the two parameters. This tendency shows a good level of goodness of fit for the 10gf analysis. As can be seen in Fig.43 (Left) the goodness of fit reaches a non-depreciable 0,71, which confirms the certain relation between both factors.

When we work with the medium hardness values for each w/c ratio (Fig.43 Right) we obtain a better goodness of fit, until reach the 0,87 coefficient that leads into believe in the relation between compressive strength and hardness on cement paste.

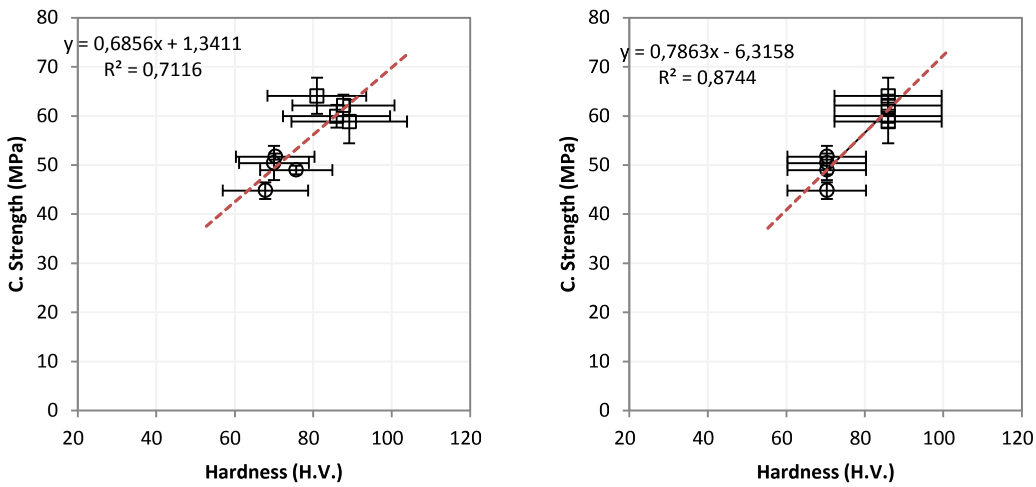


Figure 43: Compressive Strength – Hardness for cement pastes (10gf)

If we take a look on the 50gf results for the same relation we can see that the linear regression fits even better than in the 10gf results. This may be the consequence of larger indentations and lesser micro-structural phenomena as has been described before.

As can be seen on Fig.44 the goodness of fit for the several concretes (Left) reaches the 0,76 coefficient, while the medium packed values for each w/c ratio reaches a 0,87 coefficient. Enough to consider the strong relation between the strength and the hardness of the cement pastes.

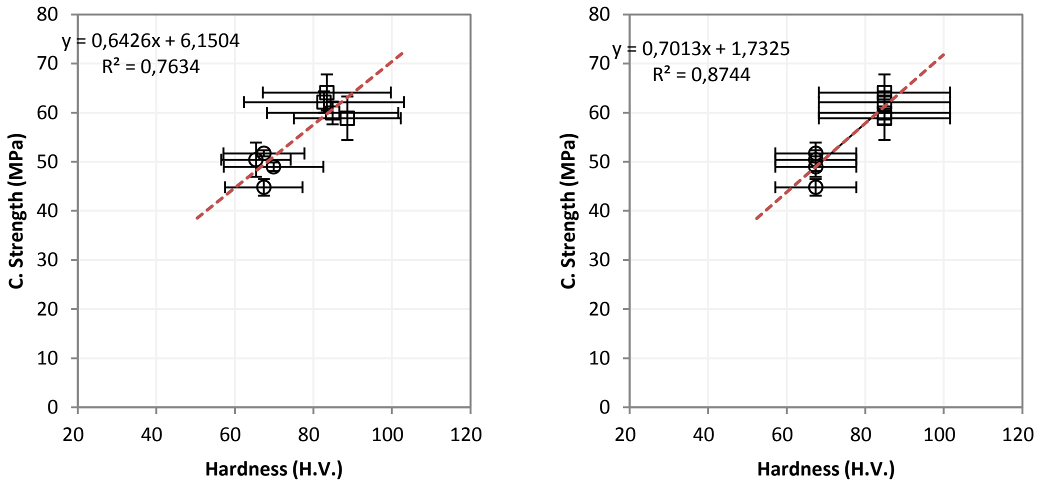


Figure 44: Compressive Strength – Hardness for cement pastes (50gf)

In order to enhance this goodness will be interesting to have a better and large number of data. Not only to adjust better the straight line, but to ensure the fair behaviour of the material.

5.6.2. Compressive Strength and Hardness on the ITZ

Once we have realized that the cement pastes accomplish the resistance-micro-hardness relation is time to relate, in the same way, if the ITZ medium values obtained in our experiments fit right with the compressive strength shown under the testing machine.

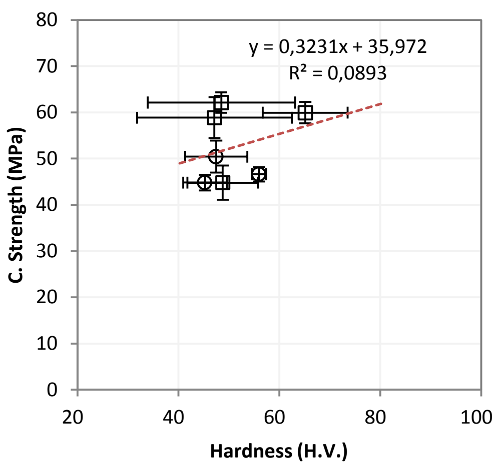
The analysis in the ITZ is dependent of multiple factors: the well polishing process, the porosity or the heterogenic composition as well as the specific properties of the place we make the indentations. Then, the medium micro-hardness values obtained can be pretty different from these one can expect in relation to the cement pastes experience.

The results for the 10gf analysis of the ITZ shown in Fig.45 reveal the high variability of our collected data. For example, it is surprising that some specimens with high resistance levels (up to 60Mpa) give us poor micro-hardness results (between 40HV and 50HV). Or that one specimen with high medium micro-hardness value gives us a really moderated compressive strength. All this variation leads into a very bad goodness of fit when we try to do a linear regression. Then, it seems to be no relation between the two parameters.

Oppositely, for the 50gf analysis the goodness of fit of the linear regression is right with a 0,81 coefficient.

One possible explanation for such a great variability between the 10gf analysis and the 50gf analysis results may be found in the previous chapters but, in addition, the place where the indentation takes place is fundamental. Micro-cracks, pores, little incrustations, etc; can be determinant in the final results. Even more when we treat with recycled aggregates where the ITZ is not clear at all.

If we take a look on Fig.45 (Left), the three major resistance values correspond to concretes with a w/c = 0,4 relation and, at the same time, all of them are recycled concretes. In addition, two of them show a really low micro-hardness range.



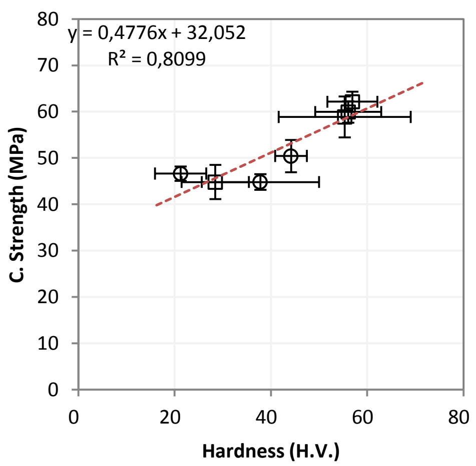


Figure 45: Compressive Strength – Hardness for ITZ (10gf Left and 50gf Right)

The higher existent porosity in the ITZ [28] can lead into lower hardness values that those which are expected following the cement paste patron. However, the fact that we are dealing with recycled concrete makes the ITZ even more heterogenic. The transition zone between the old mortar, from the recycled aggregate, to the cement paste can be unclear and highly porous depending on the origin of the recycled aggregate. This behavior is reflected on the SEM images of the next chapter.

Finally, we can accept that there is an important relation between the strength of the concrete and its micro-hardness. A larger number of samples will verify it better.

5.6.3. Elastic modulus and hardness

Once we have proved that there is a strong relation between the compressive strength and the micro-hardness in concrete, we tried to know if the elastic modulus of every specimen can be related to its hardness values. This purpose comes from the fact that the elastic modulus has relation with the deformation that can take place in concrete.
Therefore, through the hardness values that come from the residual deformation in every indentation, we made the direct relation.

But, as can be seen in Fig.46 and Fig.47 for both 10gf and 50gf load; there is no relation between the two parameters. Even when we tried to relate the parameters by the medium hardness values for each w/c ratio as we did in the compressive strength – hardness analysis.

The most probable explanation to this non-relation may be that, in concrete, the elastic modulus not only depends on the cement paste. It largely depends on the aggregates stiffness. Neville [31] proposes to treat the concrete as a composite between a matrix and free particles. This supposes that every part has their own elastic modulus and, depending on which part has de higher elastic modulus value, the final equation which describes the elastic modulus would be different. The stiffness of the aggregates is, by large, higher than that of the cement paste; then the elastic modulus takes the following form:

$$E = \left[\frac{1-g}{E_m} + \frac{g}{E_p}\right]^{-1}$$

Where Em is the elastic modulus of the matrix phase, and Ep is the aggregates' one.

Precisely, the higher stiffness of the aggregates produces that when we study if the elastic modulus has any relation with the micro-hardness on the cement paste we find any good relation between the parameters. The aggregates stiffness is, then, dominant.

Fig.46 and Fig.47 shows this poor relation with a goodness of fit values of 0,23 and 0,33. When we pack this results around the medium hardness value of each w/c the goodness of fit values rise until a 0,49 coefficient.

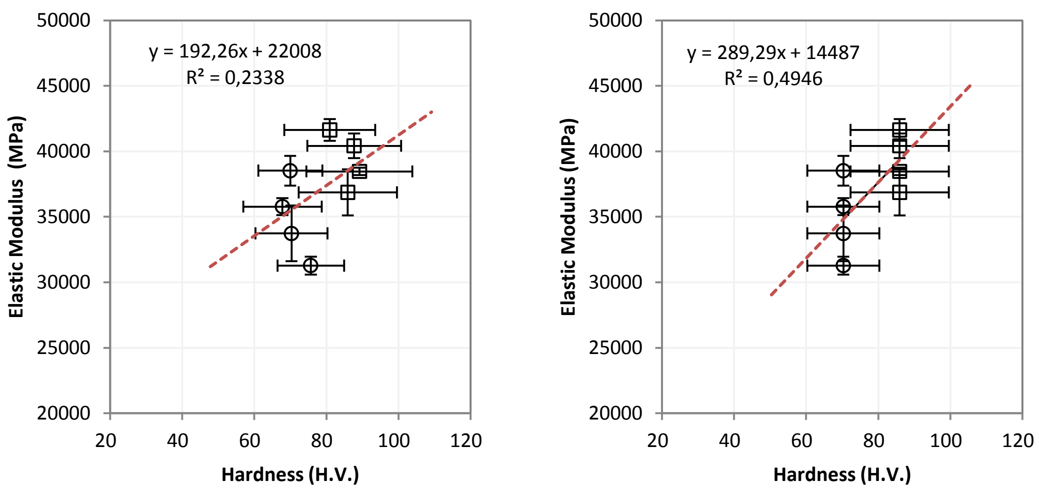


Figure 46: Elastic Modulus and Hardness relation for 10gf load (Left) and depending on the w/c ratio (Right)

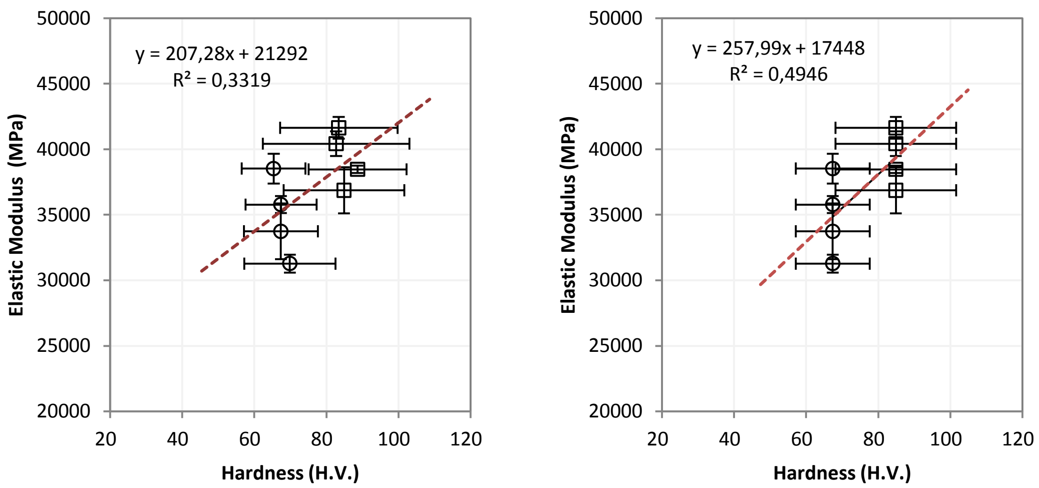


Figure 47: Elastic Modulus and Hardness relation for 50gf load (Left) and depending on the w/c ratio (Right)

It is important to point out that those concretes which have aggregates with higher stiffness modulus will also have greater stiffness modulus overall. This fact will make even more difficult to correlate the elastic modulus with the micro-hardness in the concretes that have a percentage of recycled aggregates in their mix.

The heterogeneity of the recycled aggregates, which can be compound of different origin aggregates, add an extra difficulty to the relation we treated to show.

When we try to relate the elastic modulus with the hardness values in the ITZ results the relation goes even worse than in the cement paste as can be seen in the Fig.48. We found extremely bad goodness of fit coefficients for both kinds of loads.

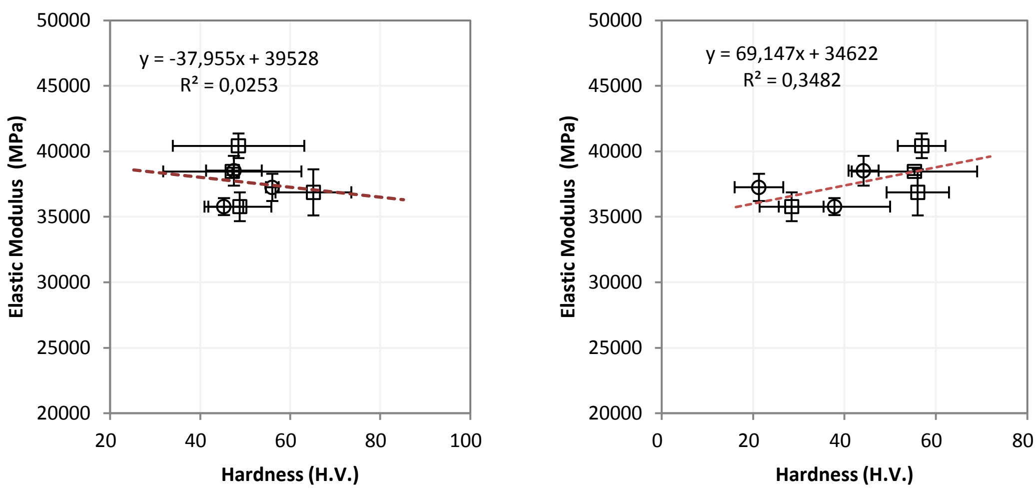


Figure 48: Elastic Modulus and Hardness relation for 10gf load (Left) and 50gf (Right)

5.7. SEM study of different concretes

After all the data analysis shown on the previous chapters, it is important to reflect the reasons of these behaviours by examining the visual part of them. To take the following images we used the Scanning electron microscope (SEM), which provides a good balance of quality images.

The purpose of this chapter is to show the main properties of the ITZ in the different types of concrete, conventional or recycled ones, and to emphasize the heterogeneity of the recycled aggregates.

On Fig.49(left) we can see the ITZ between a natural aggregate (right) and the cement paste (left) on a conventional concrete with a w/c ratio of 0,4. In there, we can see that the adherence in the ITZ between the two mediums is good, and the cement paste does not seem to have large pores. In addition, the figure shows the indentation path and the different size of the tip indenter.

But, the adherence is not always good. Fig.49 (right) shows other conventional concrete which has a long crack along the aggregate's surface. This can be produced for different factors, from the polishing process to the cutting process of the specimen.
Cracks reinforce the weakness of the ITZ and, therefore, of the concrete under great demanding load conditions.

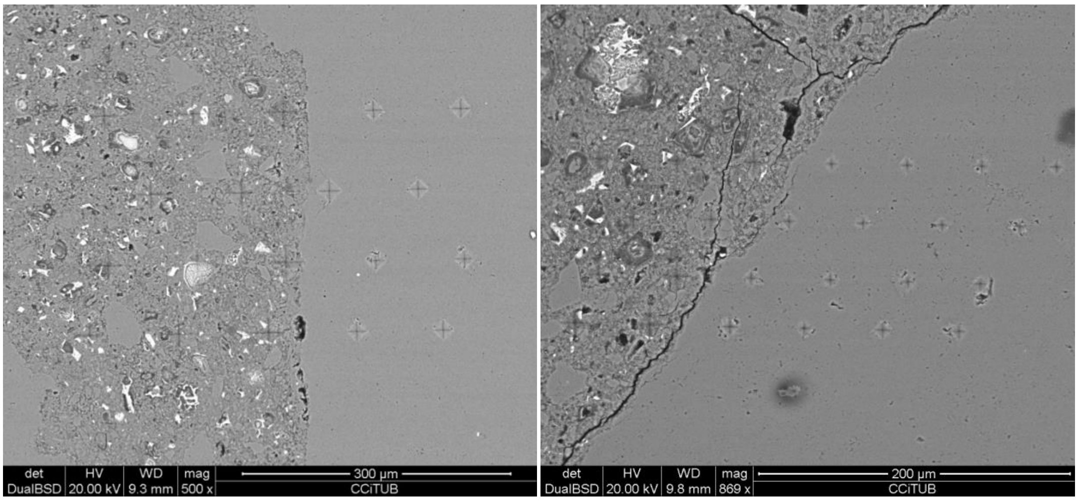


Figure 49: ITZ of a conventional concrete with w/c=0,4 (left) and ITZ of a conventional concrete with w/c=0,5 and cracks along the aggregate (right)

In both cases the ITZ is well-determined. In fact, the indentations in the first 50 microns of the ITZ show slightly greater marks than the media in the cement pastes.

If we make the comparison between the clear ITZ shown in Fig.49 and the ITZ in Fig.50 we will rapidly understand the difficulties associated in working on recycled aggregates. In the left image of Fig.50 we can hardly see where the ITZ is located. In contrast, in the right image we can easy detect where the transition zone between the old mortar and the cement paste is.
In both cases the recycled aggregate is located on the top of the images. On the first case we only detect its existence because the porosity rises up in comparison to the cement paste. On the second case we can easy draw the borderline and we can pay attention to the heterogeneity of the mix: little incrustations, aggregates, pores, etc.

In terms of adherence both concretes have a good transition zone without cracks but, as happens in the conventional concretes, they can also have fissures near the ITZ as can be seen on Fig.51. The specimen is the same of the Fig.50 (left).

Hence, working with recycled aggregates depends a lot of the place where we apply the tests and, in fact, depends on the original kind of concrete and cement used.

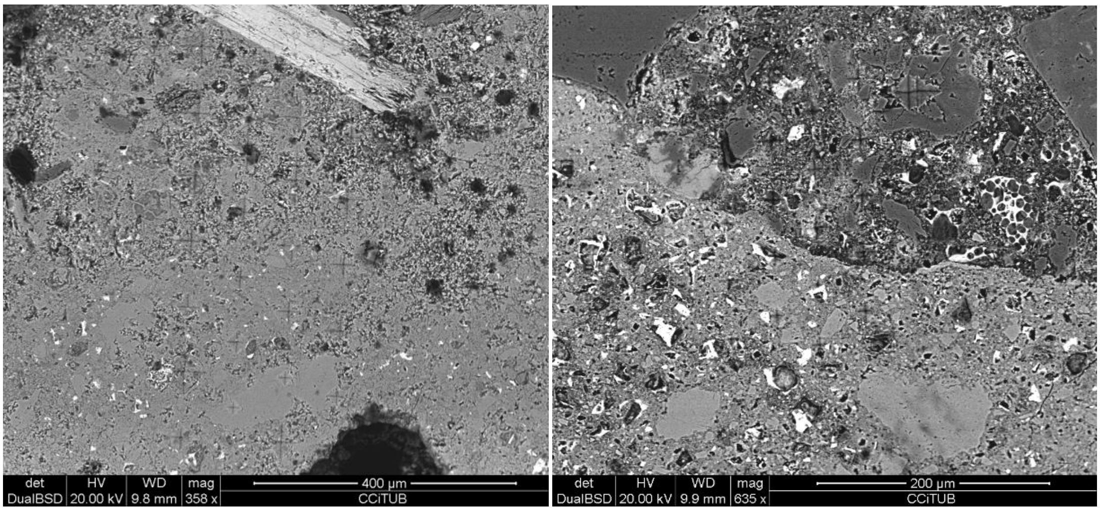


Figure 50: ITZ in recycled aggregate from old mortar to cement paste for EMV 20% w/c=0,5 subs. (left) and for HR 20% w/c=0,4 (right)

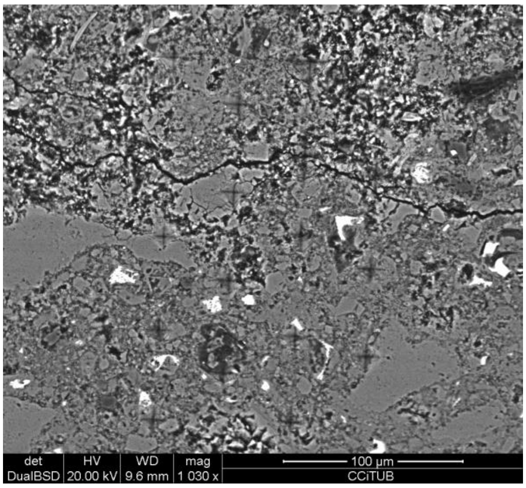


Figure 51: ITZ in recycled aggregate from old mortar to cement paste for EMV 20% w/c=0,5 subs with cracks.

Finally, in Fig.52 we can see the direct differences between an ITZ of conventional concrete and recycled concrete. The main differences are reduced to the indentation size marks (which traduce in different hardness values) and to the fair transition between phases.

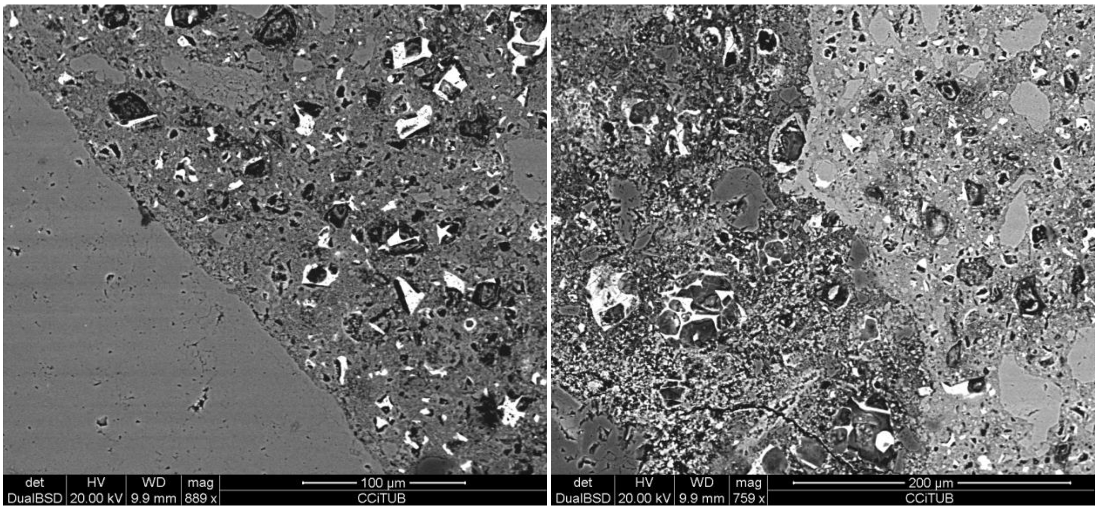


Figure 52: ITZ between natural aggregate to cement paste (left) and between old mortar to cement paste (right) for the same concrete.

Chapter 6

CONCLUSIONS

After testing a large variety and quantity of different concrete specimens, and an accurate analysis of each result, we can say that we reach our objectives even the difficulties we have found during the study.

The main conclusion is that we have studied the micro-structure and the ITZ, by micro-hardness testing, and we have observed their properties which have allowed us to determine the different phases of the concrete. We have also reach the purpose to determine the differences between one type of concrete or another one with recycled aggregates added.

We also reached the specific objectives:

- We have succeeded in the characterization of the natural and the cement pastes (we achieved to do so and to demonstrate the different characteristics depending on the w/c ratio).
- We also succeed to demonstrate that characterizing the recycled aggregates is possible although it needs great amount of data and a very special mix of factors.
- We have confirmed the weakness of the ITZ and the decreasing hardness values in there.
- We also differentiate the hardness behaviour between the conventional concretes and the recycled ones in their ITZ. The first ones have a more homogenous behaviour, with less variability in the hardness results.
- We have analyzed case by case the particularities of each ITZ and have realized the difficulties in the recycled aggregates behaviour definition.
- We verified the strong existent relation between the compression strength and the hardness values, in the cement pastes and, in a more moderate way, in the ITZ.
- We have also differentiated the compression strength – hardness relation depending of the w/c ratio of the cement paste.
- We proved the difficulties on defining a relation between the elastic modulus and the hardness values on cement paste due to the governing stiffness of the aggregates.
- We have learnt to use and understand the Vickers Hardness test and the SEM.

Finally, it is important to conclude and to point out a couple of things that can affect the Vickers Hardness test that we have seen. First of all, the polishing process is a key process.

A non-flat surface can lead into bad results. We have spent a lot of time on ensuring the good performance of the samples' surface but, at the same time, it has been very difficult to confirm due to the limited resources we have.

We have also learnt the importance of non-applying an ultrasonic batch to the samples in order to clean the alumina solution of the polishing process. That is because the ultrasonic waves can lead into cracks in the ITZ.

It is also important to know that the original concrete of the recycled aggregates (the mortar adhered) is dominant factor in the micro-hardness results of them.

Chapter 7

FUTURE RESEARCH LINES

In the light of the obtained results and the several problematic that have appeared during this thesis development, it seems plausible to think that the future research lines have to follow not only the direction of getting a better definition on the ITZ mechanical properties, but also they should try to solve and enhance the actual test procedures.

Hence, in what testing concerns, is necessary to emphasize efficient solutions for the polishing process. A process whose influence is determinant in the micro-hardness indentation results.

In respect to the ITZ properties, one possible research line could be the nano-indentation test. It could provide a better characterisation of the ITZ and its transition between the aggregate and the bulk paste. Unfortunately, that test will imply the need of quantify the real scope of the ISE effect. A crucial step to collect reliable data of hardness.

Another interesting test that could be applied in the future is the Scratch test. This test could allow us to see, for example, the exact point of transition between the two main medium and to observe how the aggregates and the paste work under load until they break forming micro-cracks.

Finally, another interesting research branch could be to study the ITZ behaviour in concretes which are under chemical attack, for example sulphates, with the main goal of determining their microscopic behaviour.

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