THESIS

Prepared as a joint PhD between
IMT Lille Douai and Liège University

presented for the degree of

DOCTOR

in

Engineering science and technology

by

Charlotte Colman

DOCTORATE OF LIEGE UNIVERSITY
DOCTORATE OF LILLE UNIVERSITY
DELIVERED BY IMT LILLE DOUAI

Gypsum residues in fine recycled aggregates: effects on mechanical and microstructural properties of cementitious composites

Defended on December 7th, 2020 for the jury:

President	Pr. Frédéric Collin, Université de Liège
Examinator	Pr. Benoît Bissonnette, Université Laval
Examinator	MdC-HDR Jean-Michel Mechling, Université de Lorraine
Member	Pr. Stéphanie Lambert, Université de Liège
Member	MdC Marie Salgues, IMT Mines Alès
Member	Dr. Elie Valcke, SCK•CEN
Thesis promotor	Pr. Luc Courard, Université de Liège
Thesis co-promotor	Pr. David Bulteel, IMT Lille Douai
Invited	Pr. Sébastien Rémond, Université d'Orléans

Laboratories: CERI Matériaux et Procédés at IMT Lille Douai & Laboratory of Construction Materials at Liège University
Doctoral schools: SMRE 104 (IMT Lille Douai: GEPO) & Collège de doctorat en Architecture, Génie civil et Géologie

THESE

Préparée dans le cadre d'une cotutelle entre
IMT Lille Douai et L'Université de Liège

présentée en vue
d'obtenir le grade de

DOCTEUR

en

Sciences de l'ingénieur et technologie

par

Charlotte Colman

DOCTORAT DE L'UNIVERSITE DE LIEGE
DOCTORAT DE L'UNIVERSITE DE LILLE
DELIVRE PAR IMT LILLE DOUAI

Résidus de plâtre dans les sables recyclés : effets sur les propriétés mécaniques et microstructurales des composites cimentaires

Soutenue le 7 décembre 2020, pour le jury d'examen :

Président	Pr. Frédéric Collin, Université de Liège
Rapporteur	Pr. Benoît Bissonnette, Université Laval
Rapporteur	MdC-HDR Jean-Michel Mechling, Université de Lorraine
Membre	Pr. Stéphanie Lambert, Université de Liège
Membre	MdC Marie Salgues, IMT Mines Alès
Membre	Dr. Elie Valcke, SCK•CEN
Directeur de thèse n°1	Pr. Luc Courard, Université de Liège
Directeur de thèse n°2	Pr. David Bulteel, IMT Lille Douai
Invité	Pr. Sébastien Rémond, Université d'Orléans

Laboratoires d'accueil : CERI Matériaux et Procédés de IMT Lille Douai & Laboratoire des Matériaux de Construction de l'Université de Liège
Ecoles Doctorales : SMRE 104 (IMT Lille Douai : GEPO) & Collège de doctorat en Architecture, Génie civil et Géologie

Acknowledgements

First of all, I would like to thank my promotors: professors Luc Courard and David Bulteel, for welcoming me into their respective research departments. It's thanks to them that I could start my research and thanks to their direction that I could finish it. My PhD was filled with very educational experiences and collaborations, which would not have been possible without them.

My thanks are also due to professor Benoît Bissonnette and MdC Jean-Michel Mechling, for the detailed evaluation of my thesis and their comments and suggestions. To professor Frédéric Collin for presiding over the jury and to the jury members - Stéphanie Lambert, Marie Salgues and Elie Valcke - themselves: thank you for taking the time to examine my work and pose thought-provoking questions.

This work was possible thanks to the funding provided by Interreg to the VALDEM project. This funding allowed me to properly conduct my research with the right techniques and materials, and let me valorize it at conferences or in journals. I also want to thank my VALDEM colleagues from other institutions for their interest, input and the occasional *tarte au riz*.

Both in Liège and Douai I was surrounded by a team of pleasant colleagues. A coffee break, help in the lab, bowling nights or just some discussions: they all directly or indirectly contributed to my finished thesis, so thank you very much to my fellow researchers and lab technicians.

Last but not least, many thanks to my friends and family who took the effort to watch my defense at a distance. Your support and words of encouragement meant the world to me. Above all, thanks to my parents and grandparents who were my biggest supporters throughout: your unwavering pride was my encouragement from beginning to end.

Abstract

Fine recycled aggregates are an important waste stream coming from the demolition of old concrete structures. They are up to now not valorized because of an increased water absorption, lower density and higher fines content compared to natural aggregates. Moreover, they often have a high sulfate concentration. These sulfates could have originated from plaster in a demolished building, or from the residual cement that is commonly present in these materials. The sulfate level of recycled aggregates is recommended to stay under 0.2 mass% by standard EN206, to limit the risk on sulfate attack: the reaction between cement components, water and sulfates results in the formation of expansive minerals such as ettringite. This expansion can eventually lead to cracking of the material and a general loss in mechanical performances.

Fine recycled aggregates from recycling plants did contain 0.15 to 0.80 % of sulfates which is more than allowed, but these amounts did not cause any swelling or degradation when the aggregates were incorporated into mortars. A very elevated sulfate content of 3 % was needed to observe significant expansion, and even this level of contamination could be mitigated by increasing the alkalinity of a mix. Concretes made with varying sulfate levels either expanded or they didn't: the absolute swelling amount was not proportional to its sulfate content. The actual threshold concentration that started the swelling reaction was dependant on the type of coarse aggregate. The results of this study provide recommendations for the use of fine recycled aggregates contaminated with gypsum residues: a sulfate content of at least 0.3 % could be possible, and even more if certain parameters and mix compositions can be adjusted accordingly. The current limit of 0.2 % seems too strict and hinders the valorization of fine recycled aggregates in high quality construction applications.

Keywords: Fine recycled aggregates; sulfate attack; construction and demolition waste; secondary ettringite formation; microstructure; expansion

Résumé

Les sables recyclés représentent un flux important de déchets provenant de la démolition d'anciennes structures en béton. Ils ne sont jusqu'à présent pas valorisés à cause d'une absorption d'eau élevée, d'une densité plus faible et d'une teneur en fines plus importante que dans les granulats naturels. De plus, ils sont souvent contaminés par des sulfates. Ces sulfates pourraient provenir du plâtre du bâtiment démoli ou du ciment résiduel qui est couramment présent dans ces matériaux. Le taux de sulfate recommandé pour les granulats recyclés est inférieur à 0,2 % en masse selon la norme EN206, afin de limiter le risque d'attaque sulfatique : la réaction entre les composants du ciment, l'eau et les sulfates entraîne la formation de minéraux expansifs comme l'ettringite. Cette expansion peut éventuellement conduire à une fissuration du matériau et à une perte générale des performances mécaniques.

Une étude systématique a permis de mettre en évidence que les sables recyclés provenant des centres de recyclage contenaient de 0,15 à 0,80 % de sulfates ce qui est plus que ce qui est autorisé. Néanmoins, ces quantités n'ont pas engendré de gonflement ni de dégradation lorsque les granulats contaminés ont été incorporés dans des mortiers. Une teneur en sulfate très élevée de 3 % a été nécessaire pour observer une expansion significative ; toutefois, l'expansion a pu être contrôlée en augmentant l'alcalinité d'un mélange. Des bétons fabriqués avec différents niveaux de sulfates ont présenté des gonflements ou non : l'ampleur d'expansion n'était pas proportionnelle à la teneur en sulfate. Le seuil qui a déclenché la réaction de gonflement dépendait aussi du type de granulat. Les résultats de cette étude fournissent des recommandations pour l'utilisation de sables recyclés contaminés par des résidus de gypse : une teneur en sulfate jusque 0,3 % pourrait être possible, et même plus en fonction de certains paramètres et compositions de mélange. La limite actuelle de 0,2 % semble trop stricte et freine la valorisation de sables recyclés dans des bétons durables et résistants.

Mots clés : Sable recyclé; attaque sulfatique; déchets de démolition; formation d'ettringite secondaire; microstructure; expansion

Contents

General introduction

The construction industry is one of the biggest consumers of energy and natural resources. In a world where sustainability is of an evergrowing importance, waste recycling is a focus point for many. The construction industry is not an exception. A period of rapid urbanization after the second world war created a massive amount of concrete structures that are now ready to be demolished. The challenge today exists in valorizing this enormous volume of Construction and Demolition Waste (C&DW): by 2020, 70% of these materials need to be recycled according to European legislation.

The largest part of C&DW is an inert mineral fraction that lends itself excellently to a re-utilization in the form of recycled aggregates. Some roadblocks for their valorization are legislation, properties like water absorption and density, and the fact that they are mixed with other types of construction materials such as bricks, gypsum, soil, ... Most countries encourage 'deconstruction' practices that permit a separation of the different material flows, which largely facilitates their recycling. Nevertheless, the consumption of natural aggregates stays important and certain fractions of C&DW remain largely unvalorized.

The Interreg project VALDEM aims to identify, in collaboration with different industrial partners, the specific material flows that have trouble getting valorized. The 'mixed' C&DW that contains recycled concrete aggregates in addition to other construction materials, could be decontaminated by various techniques: jigging, selective crushing, or even by an on-site treatment machine. Other material flows are too fine for these treatments and will need alternative solutions.

One of the hesitations for the re-use of fine recycled aggregates (FRA) is a potential contamination with gypsum residues from plaster walls. Gypsum is an important contaminant in this context, because water soluble sulfates coming from these residues could induce internal sulfate attack. This is a reaction where sulfates react with cement components to form expansive minerals such as ettringite. The result of this reaction is an expansion of concrete, that can lead to cracking of the material and losses in mechanical performances.

Within the context of the VALDEM project, this thesis will be oriented towards the valorization of FRA contaminated with gypsum residues. The ability to incorporate this FRA into cementitious composites without a risk for deterioration by sulfate attack would be a valuable step towards a sustainable building sector: using recycled aggregates reduces the amount of C&DW disposed in landfills, reduces the rate of natural resource depletion, and will provide energy, cost and transport savings.

To approach this research, the thesis is constructed in 3 parts:

Part I will analyse the available literature about the different research subjects. A first chapter handles the practice of recycling C&DW, and the properties and valorization problems of (fine) recycled aggregates. In a second chapter, the different types and sources of sulfate attack are explained. These two subjects come together in a third chapter, where sulfate attack caused by contaminations in recycled aggregates is discussed. After this literature review, several research needs came to light. The thesis objectives are tuned to those needs, and the methodology is presented afterwards.

In Part II, the materials and techniques are explained that will be used in the experimental parts. The different types of FRA – either industrial samples or a laboratory-made 'model' FRA - are presented in Chapter 4. The design and mixing procedure of mortars and concretes is described in Chapter 5. Lastly, the tests that were conducted on these cementitious composites to follow the development of internal sulfate attack, are chosen and elaborated in Chapter 6.

Part III discusses the results of the experimental steps defined previously in the methodology:

Chapter 7 handles the valorization of industrial FRA. Samples were collected from recycling centres, characterized and incorporated into mortars. Those mortars then underwent swelling tests to evaluate whether internal sulfate attack is a concern for these materials. This chapter will give valuable information to industrials about the type of materials on the market and their properties.

In Chapter 8, the internal sulfate attack reaction is researched on a model (laboratory-made) material. This is done by defining and varying certain mortar composition or mixing parameters. The goal of this part was to evaluate if the swelling reaction could be influenced by factors other than sulfate contents. This chapter gives insights into the mechanism of sulfate attack in this specific context. It provides on the one hand solutions for mitigating high sulfate contents, and on the other hand attention points for not creating aggravating factors.

The 'sulfate limit' is analyzed in Chapter 9 on concrete with both natural and recycled coarse aggregates. The parameters that proved to be relevant in the previous chapter were evaluated too. This research part is terminated with several conclusions and recommendations about the use of (contaminated) FRA in cementitious composites, such as a proposal for maximal sulfate contents and mixing parameters to take into account.

At the end of the thesis, a general conclusion will be completed with future research perspectives.

Part I

Literature review

Introduction

Demolishing a concrete structure and reprocessing the resulting C&DW yields recycled aggregates, that can be re-used in a new concrete mix. However, as will be discussed in Chapter 1, these aggregates and especially the finer size fractions are of a lower quality than their natural counterparts. While coarse recycled aggregates are used in concrete under certain conditions, the incorporation of FRA is up to now generally avoided.

An important factor to keep in mind when designing a concrete is its long term behavior. The durability of a structure can suffer from different deteriorating reactions, described in Chapter 2. The secondary formation of ettringite, a sulfate containing mineral, can cause the swelling of a concrete with cracking of the structure as a result. This reaction, called sulfate attack, has different forms and mechanisms depending on the concrete design and the source of the sulfates.

Chapter 3 combines the use of FRA and the problem of sulfate attack. The gypsum residues present in FRA act as an internal source of sulfates, which is different from the types of sulfate attack that have been described. Strict legislation or the wariness of construction companies ensure that this (contaminated) material is hardly valorized.

1 | Recycled aggregates

This chapter discusses the impact of the construction industry on the environment, and different ways to reduce it. The focus will be on the re-use of demolished concrete inside a new structure, as a replacement for natural aggregates. The properties and characteristics of these recycled aggregates - and the concrete where they were incorporated - are discussed.

1.1 Sustainable development in the construction sector

The building sector is infamously known as the 40 %-industry, using 40 % of global energy and resources, and is responsible for a third of our greenhouse gas emissions [1]. Nowadays 1 m^3 of concrete, corresponding to more or less 2 tonnes, is being produced per person per year. Only fresh water as a resource is used more, and that's only because the largest part of it is being wasted [2]. Concrete in itself is not necessarily a material with a high environmental impact, but the enormous quantities that are produced make its manufacturing contribute to 5 % of our annual anthropogenic CO_2 emissions [3].

The part of the concrete production process with the highest ecological footprint would be the fabrication of cement [4]. The production of 1 kg CEM I releases 0.8 kg CO_2 into the atmosphere [3]. This value is so high firstly because CO_2 is a reaction product of the clinker fabrication, and secondly because very high temperatures are needed in the kiln for this reaction. Next to CO_2, SO_2 emissions are also an important byproduct [4] of cement production. The environmental impact of the cement industry can be limited by the use of alternative raw materials [5, 6], or alternative binders [7]. Design-wise, the construction sector can choose mixes that limit the use of cement, such as "Green Concrete" [8], self-compacting concrete or ultra-high performing concrete [9].

A second way to reduce the impact of concrete production is on the aggregate level. Aggregates play a crucial role in concrete compositions as they occupy about 60 to 70 % of the total volume [10]. The climate impact of the construction industry can be reduced by 77 % by core material separation and its recycling or re-use [11]. Recycled aggregates (RA) are reprocessed materials that were previously used in construction, including C&DW [12]. As can be seen in Figure 1.1, the aggregate market has an enormous turnover of materials, but only a very select part of the aggregates produced in 2016 came from recycled sources. The use of recycled aggregates as a replacement for natural aggregates in a new concrete has many benefits. The practice reduces the amount of debris disposed of in landfills, reduces the rate of natural resource depletion, and provides energy, cost and transport savings [13].

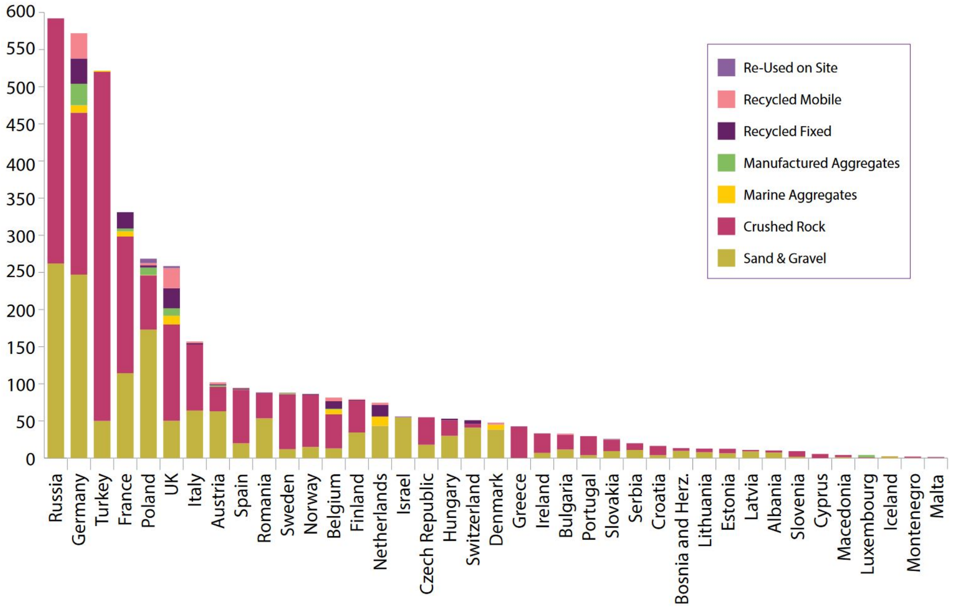


Figure 1.1: Aggregate production by type and country in 2016, in million of tonnes. From *European Aggregates Association* [12].

With the demand for cement-based materials expected to increase by a factor of 2.5 by 2050 [14], it is of an ever growing importance for the construction sector to increase its sustainability.

1.2 Recycled aggregates

1.2.1 Production from construction and demolition waste

Accounting for approximately 25 - 30 % of all waste generated, C&DW is one of the heaviest and most voluminous waste streams in the EU, and as such has been identified as a priority waste stream by the European Union [15]. C&DW consists of numerous materials, including concrete, bricks, gypsum, wood, glass, metals, plastic, and excavated soil. The major fraction of C&DW however is mineral waste, which has a high potential for recycling and re-use [16]. One of the objectives posed in the Waste Framework Directive (WFD) of the European Union (2008/98/EC) is to re-use a minimum of 70 % of C&DW by 2020, either by recovering materials, recycling them as aggregates, or using them for backfilling [17]. Conform to this WFD, most countries make an effort to not landfill their C&DW. However, presented in Figure 1.2, some of them are relying to a large extent on backfilling to meet the 2020 target. Even though it is mentioned as an acceptable treatment of C&DW in the WFD, the question could be asked if backfilling can be seen as 'quality recycling', especially for mineral wastes such as aggregates [18]. Of the 315 Mton of inert C&DW generated per year in Europe, 204 Mton ton of recycled aggregates are produced from it [12], but the percentage of recovery varies a lot between different countries.

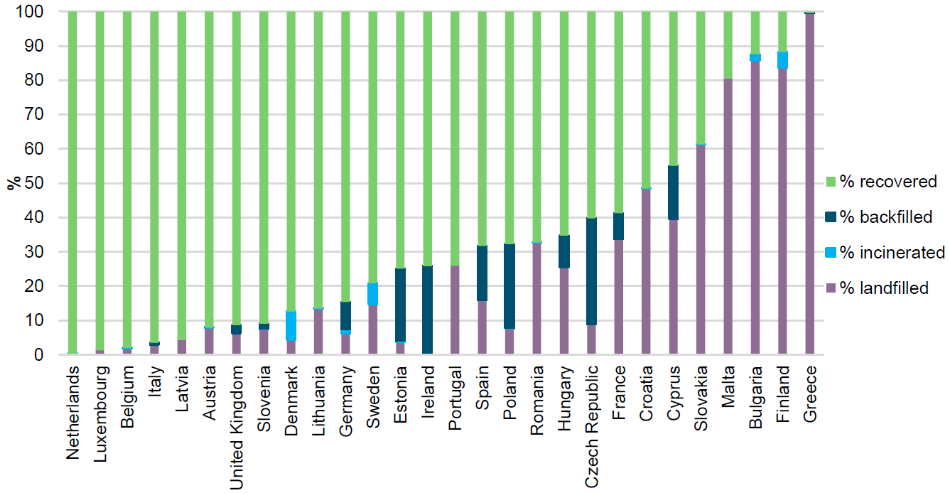


Figure 1.2: The treatment of C&DW in European countries in 2012. From *Deloitte, Study on resource efficient use of mixed wastes* [16].

Technology for the separation and recovery of construction and demolition waste is well established, readily accessible and in general inexpensive.

The recovery of C&DW has to be planned in advance of the demolition of the structure: a selective *deconstruction*, where material streams like wood, glass, plaster or hazardous wastes are separated before demolishing, ensures a higher quality of RA. A second step in the recovery of RA from C&DW is a separation and size reduction of the mineral phase, either by on-site crushers or at a recycling center. On-site processing has some constraints such as available space or legislation (permit needs) [18], but limits the need of transport which is a very impacting step of the recycled aggregate production [19]. In order to fulfill the desirable properties of RA (composition, size distribution, ...), an additional treatment of the stony fraction is necessary, which is typically performed in a recycling center. Each of these centers have their own processes optimized for the separation of their most abundant flows. Ceramic, asphalt, brick or concrete flows can be isolated by jigging [20], magnetic separation [21, 22], density [23], color [24], etc.

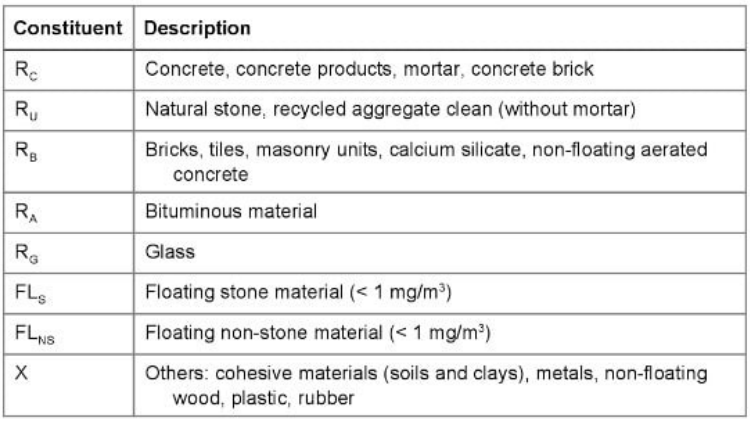
The traceability and quality assurance of the materials at every stage of the process is of great importance, especially for recycled aggregates that will be used in high-end applications or in large volumes [18]. Different countries have voluntary certification and waste audit systems in place to track material flows trough the whole process: Tracimat in Belgium [25], *Beoordelingsrichtlijn Veilig en Milieukundig Slopen* (assessment guideline for safe and environmental demolition) in the Netherlands [26], and the Construction Federation in Sweden [27] are some examples.

1.2.2 Characterization of recycled aggregates

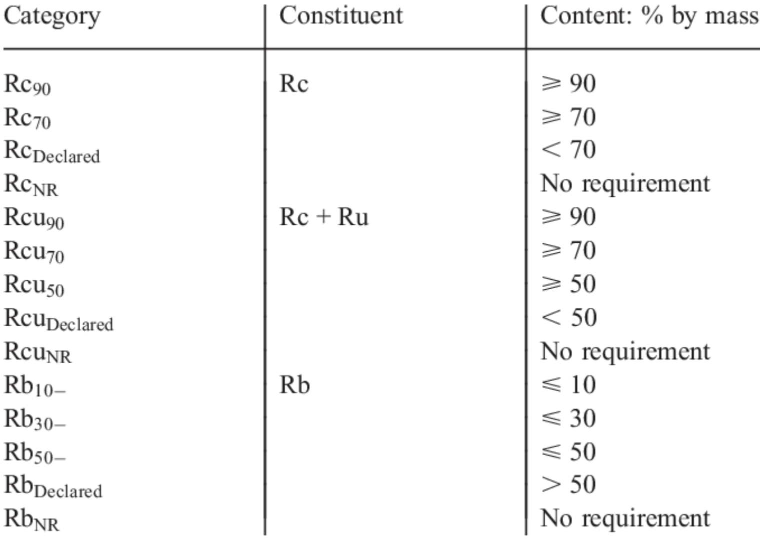
Heterogeneity and classification

As a general principle, results in literature about the properties of RA vary a lot. Because mechanical results depend largely on the effective water in a mix, the composition of the original concrete [28], or the crushing process, the heterogeneity of RA that is established [29, 30] makes it difficult to compare results of different studies.

The relative proportions of the main constituents within RA can vary widely and it is generally assumed that, as a result, the performance of concrete containing RA can vary significantly [31]. Standard EN12620 [32] classifies RA according to its different constituents, which should make it faster to judge their composition and related properties (Figure 1.3). The highest quality RA - defined as Rc_{90} and above - can be used in high performance applications [33]. This classification is however a visual method, and can therefore not be used for smaller size fractions of RA.



Constituent	Description
R_C	Concrete, concrete products, mortar, concrete brick
R_U	Natural stone, recycled aggregate clean (without mortar)
R_B	Bricks, tiles, masonry units, calcium silicate, non-floating aerated concrete
R_A	Bituminous material
R_G	Glass
FL_S	Floating stone material (< 1 mg/m^3)
FL_{NS}	Floating non-stone material (< 1 mg/m^3)
X	Others: cohesive materials (soils and clays), metals, non-floating wood, plastic, rubber



Category	Constituent	Content: % by mass
Rc_{90}	Rc	$\geqslant 90$
Rc_{70}		$\geqslant 70$
$Rc_{Declared}$		< 70
Rc_{NR}		No requirement
Rcu_{90}	Rc + Ru	$\geqslant 90$
Rcu_{70}		$\geqslant 70$
Rcu_{50}		$\geqslant 50$
$Rcu_{Declared}$		< 50
Rcu_{NR}		No requirement
Rb_{10-}	Rb	$\leqslant 10$
Rb_{30-}		$\leqslant 30$
Rb_{50-}		$\leqslant 50$
$Rb_{Declared}$		> 50
Rb_{NR}		No requirement

Figure 1.3: The different constituents used in the classification of RA (from EN12620 [32]) and their physical appearance (from *Medina et al.* [34]).

Adherent mortar and cement

The most distinguished property of RA derived from C&DW, is their adherent mortar content. Figure 1.4 shows how a RA particle consists of smaller natural aggregates connected by cement - both hydrated and unhydrated - coming from the original concrete. The volume of this residual mortar in RA has been found to vary between 20 and 60 %, with higher contents found in the smaller size fractions of RA [28, 35, 36]. The crushing procedure and the mechanical strength of the original concrete also play a role in the amount of adherent mortar [37], but not as significantly as the particle size.

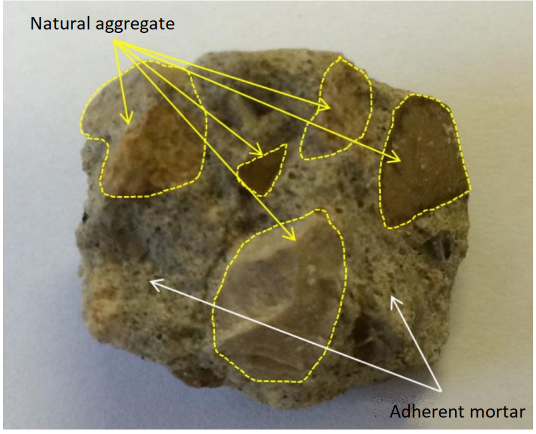


Figure 1.4: Recycled aggregates consist of smaller natural aggregates and adherent mortar paste. From *Le et al.* [38].

Water absorption, porosity and density

The adherent mortar is directly responsible for the high water absorption found in RA [39]. Because of the higher mortar content and specific surface area in finer particles, the water absorption of FRA will be higher than for coarse RA.The water absorption of CRA has been found to be 2 to 3 times higher than natural aggregates, and ranging up to 12 or even 15 % for FRA [36]. Another consequence of the adherent mortar is a higher porosity and lower bulk or apparent density [40]. Especially durability issues are affected by the porosity and high water absorption of RA [41].

Knowing the water absorption of RA is essential since the effective water in a mix will largely determine its workability and mechanical properties [29]. However, the measurement of this value is based on a 'surface saturated dry' state, which is difficult to obtain for FRA. Characterization techniques for natural aggregates described in EN1097 [42], while they can be used for CRA, consistently underestimate the water absorption of FRA because of

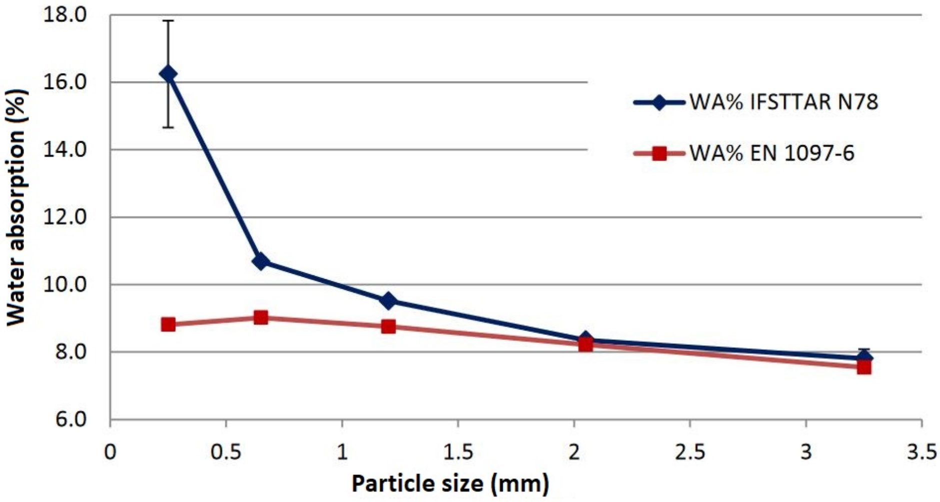


Figure 1.5: A comparison between the water absorption determination via the EN1097-6 or the IFSTTAR n°78 method shows a large disparity for small size fractions. From *Le et al.* [38].

the fineness and agglomeration issues between these particles. The method - designed in response to this difficulty - by IFSTTAR [43] on the other side seems to overestimate the water absorption of FRA but also works well for larger particles (Figure 1.5). Thanks to the very good correlation between water absorption and cement content, a method has been developed by *Zhao et al.* where the water absorption of larger particles is measured experimentally via the IFSTTAR method, and that of the finer particles is calculated via extrapolation [44]. This technique of determining the water absorption for each size fraction separately (either measured or calculated), gives more accurate results than measuring it for the whole RA bulk [45].

Another method to determine the water absorption of fine materials was developed by *Mechling et al.* and is based on evaporation kinetics. A porous and fine material is submerged in water and placed in an oven at 45 °C. An experimental setup is necessary where a balance is connected to the sample inside the oven and to a computer to regularly record the mass change. The drying of the sample proceeds at different rates: external water will evaporate at a constant speed, but water inside the porous particles will evaporate with a decreasing speed. The slope of the mass lost by evaporation over time reaches a critical point where it is considered that the particles are saturated with their absorbed water (Figure 1.6) [46].

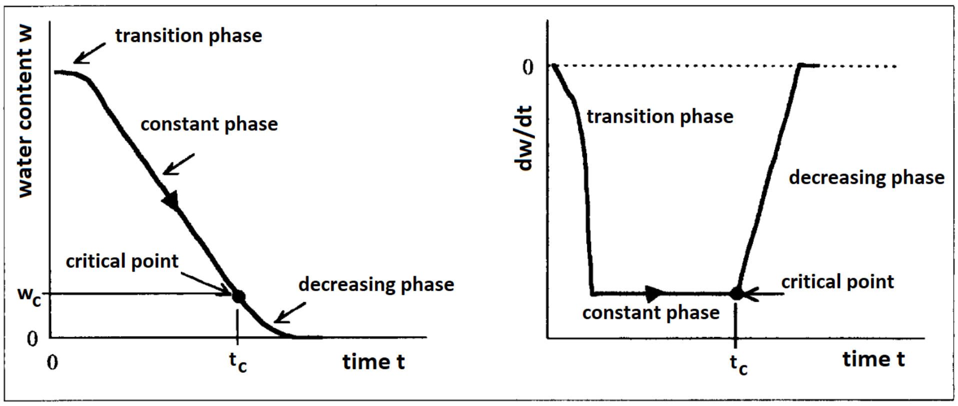


Figure 1.6: The evaporation of water from a porous fine material reaches a critical point at the SSD state. From *Mechling et al.* [46].

Form and size distribution

RA have a higher quantity of very fine material, which is often seen as a negative characteristic. These fines cause a decline in workability, have a higher and more difficult to measure water absorption, and are more difficult to separate from contaminations.

The RA particles themselves have an old interfacial transition zone (ITZ) between its natural aggregate and adherent mortar. This original ITZ is weak in nature because of the porosity of the mortar and cracks or fissures that were developed during the crushing process [47].

RA have a rough surface texture and irregular shape: they are more angular and elongated than NA (Figure 1.7). This requires more cement paste to compensate for the higher void content, and more water to counteract the effect on workability. Furthermore, flatter particles can stratify in such a way that they weaken the strength and durability of concrete [48].

Impurities

Another difficulty with the characterization and subsequent incorporation of RA is the potential presence of impurities. As discussed in section 1.2.1, guidelines are in place to separate different material streams during the demolition and processing. Nevertheless, RA often contain amounts of wood, plastic, brick, glass, ... which have a negative impact on concrete strength. More importantly, chemical contaminations in RA such as chlorides or sulfates have a significant effect on concrete durability [41].

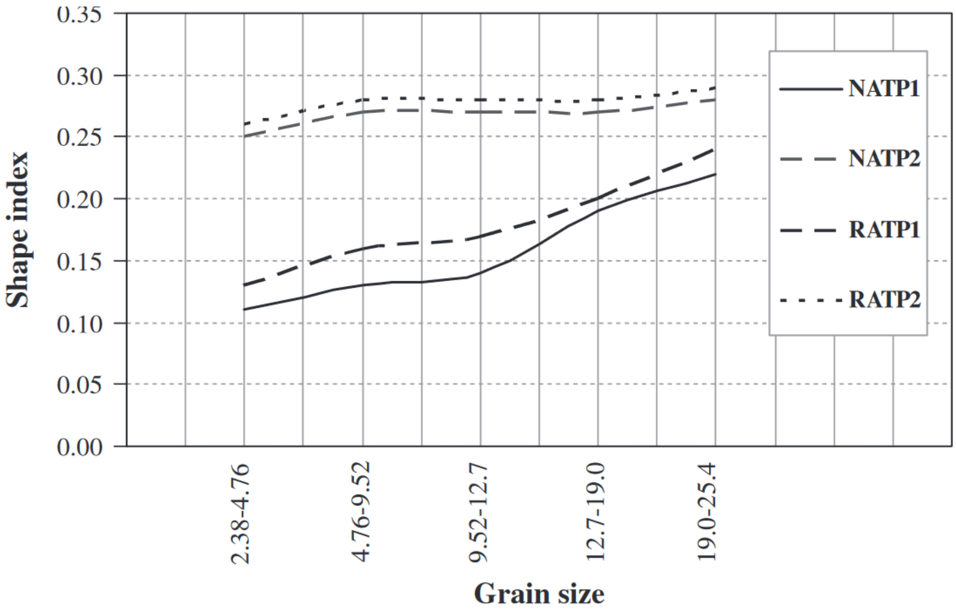


Figure 1.7: A higher shape index indicates more elongated and angular particles. Natural aggregates (NA) are more rounded than recycled aggregates (RA). From *Matias et al.* [48].

1.2.3 Properties of concrete with recycled aggregates

Although the potential for the use of RA has been acknowledged, some factors hinder the large scale use of RA in concrete, as it affects the performance in terms of workability, strength and durability.

Workability and fresh properties

The workability of concrete gets affected by physical parameters of the aggregate such as porosity, surface texture and aggregate size [49]. Even keeping the same W/C ratio (meaning taking into account the water absorption capacity of the aggregates) RA require about 10% more water to obtain the same slump as NA, due to their shape [50].

The high water absorption of mixes with RA is mostly due to the porosity of the adherent mortar paste, absorbing free water during the mixing process. This workability problem can be compensated by presaturating the RA, which is found to vastly improve the slump and other fresh properties [45, 51, 52, 53].

Hardened properties

In general, most researchers find a systematic reduction in long-term strength when NA are replaced by RA. Losses in compressive strength from 8 to 40 % were determined (Figure 1.8). This range is very high because of the variability of methods and materials used by researchers. After all, compressive strength depends on many parameters such as the replacement level of RA, the W/C ratio, and the physical properties of the aggregates.

Especially important when it comes to mechanical performance, is the old ITZ in the RA, between a natural aggregate and its adherent mortar. It is the dual performance of this old ITZ and the new one (between the RA and the new cement paste) that will determine concrete strength (Figure 1.9). The old ITZ is very weak, and will be responsible for the strength loss of concrete made with RA instead of NA [54]. Another reason why the incorporation of RA often leads to a loss in compressive strength, is the increased air content they generate in the cement matrix. These voids are caused by the angularity of the RA particles, entrapping air during the mixing process [55, 56].

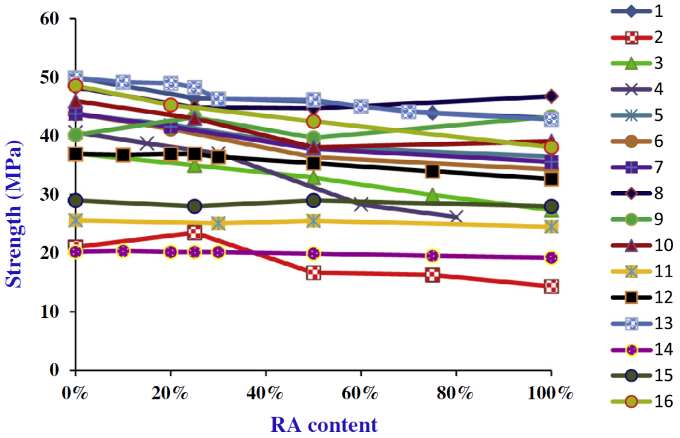


Figure 1.8: Compressive strength in function of coarse aggregate replacement percentage. These results are collected from a review by *Behera et al.* of 16 different studies [37].

It is established that the concrete made with RA has a lower quality than one with NA, nevertheless there is a certain percentage of coarse aggregate replacement where there is no loss of strength or durability (Figure 1.8). Most studies place this limit around 20-30% [37, 57, 58, 59], a value that has been adopted by the recommendations in international standards. In concretes where there is an existing risk on any chemical deterioration (such

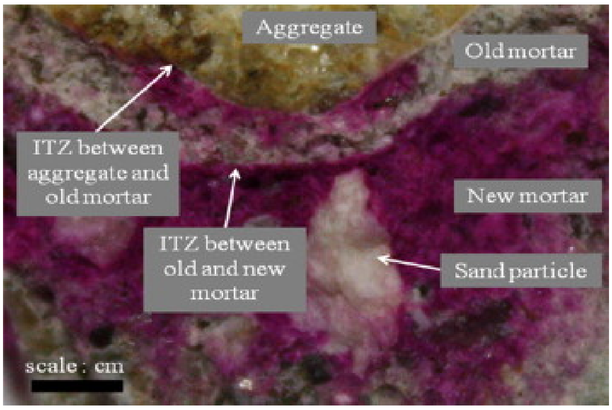


Figure 1.9: The mechanical performance of concrete with recycled aggregates depends on the dual performance of the old and new ITZ. From *Lee et al.* [54].

as corrosion), EN206 permits only 20-30 % of coarse RA, depending on the exposure level of the environment [60]. The French National Project RECYBETON concluded that, with the right adaptations to the mix formulation, replacements of up to 60 % are possible [61]. It goes without saying that a thorough characterization of the RA and knowledge about the exposure conditions of the concrete are necessary to know which measures to take. The W/C ratio or the amount of superplastifier can be considered to improve the properties of concrete made with 100 % RA [62].

1.2.4 Valorization of fine recycled aggregates

FRA are variably defined by different authors as particles below 4, 4.8 or 5 mm. Typically, they are seen as the less valorizable fraction of the processed C&DW [63]. FRA are a byproduct of the crushing and not made on purpose [64], but nevertheless make up 50 % of the C&DW weight [65]. The negative properties of RA discussed above become worse with a smaller particle size: more adherent mortar, higher water absorption, more contaminations [53]. Properties like water absorption become more difficult to measure with fineness, which makes special the techniques like those discussed above necessary. Where coarse RA can be processed to remove some adherent mortar or impurities, this is not possible for FRA. FRA vary even more in their characteristics - due to heterogeneity - than seen for coarse particles [66].

While some authors measure a decline in compressive strength after the incorporation of FRA (like with coarse RA) [67], others note an increase. In those cases, it is assumed that the high fines content acts as a filler, increasing the compacity of the mix and its mechanical performance [68]. The high cement content in FRA could also ensure a better bond [53]. Another reason why some authors find an increase in compressive strength, is because they failed to compensate for the extra water demand of the aggregates, thereby effectively lowering the W/C ratio of their mix.

While the incorporation of coarse RA is viable, the use of FRA is discouraged by strict standards and recommendations. Recent studies however conclude that substitutions with FRA are very possible, provided they are characterized correctly and the mix design is subsequently adapted to it [53]. Nevertheless, most research is focused on the incorporation of coarse RA, leaving FRA largely unvalorized by industrials.

2 | Sulfate attack

This chapter discusses the long term durability of concrete subjected to deteriorating reactions. The focus will be on sulfate attack, a reaction between sulfates and cement that causes the swelling and cracking of structures. The different types of sulfate attack and their proposed mechanisms are discussed.

2.1 Concrete durability

The degradation of concrete by various chemical or physical processes endangers its structural safety and increases maintenance and repair costs. A structure can lose integrity because of physical or chemical mechanisms, which are summarized in Table 2.1 and 2.2. In general, porosity/permeability and moisture content are the common points defining the resistance of a structure to these types of deteriorations [69].

Many physical and chemical deteriorations can occur simultaneously and different reactions can have similar effects, as can be deduced from Table 2.1 and 2.2. Besides that, cracking induced by one reaction can facilitate the ingress of aggressive solutions, thereby worsening the degradation even further. Durability studies are thus difficult to simulate in a laboratory where possible interactions are overlooked. For example, both the alkali-aggregate reaction and sulfate attack can be classified as a chemical process where expansive products are formed, and have comparable macroscopic results. In these instances, microstructural investigations can distinguish between the two. The discussion of some case studies later on will prove the complexity of this issue.

Mechanism	Examples	Consequences
Exchange reactions between aggressive fluids and components of hardened cement paste	Acidic solutions solubilizing Ca^{2+} ions	Increase in permeability and porosity: • loss of alkalinity, • loss of mass, • increase in other deterioration processes.
	Substitutions of Ca^{2+} by Mg^{2+} in seawater	
Reactions involving hydrolysis and leaching of the components of hardened cement paste	Presence of soft water	
Reactions involving the formation of expansive products	Sulfate attack	Increase in internal stress: • loss of strength and rigidity, • deformation and cracking.
	Alkali-aggregate reaction	

Table 2.1: Chemical reactions responsible for concrete deterioration. Summary adapted from *Mehta et al.* [70].

Consequences	Causes
Surface wear	Abrasion
	Erosion
	Cavitation
Cracking	Volume change: due to temperature and moisture, or a chemical degradation.
	Structural loading: either cyclic or overloading.
	Exposure to extreme temperatures: fire damage or freeze-thaw cycles.

Table 2.2: Physical causes of concrete deterioration. Summary adapted from *Mehta et al.* [70].

2.2 Degradations caused by ettringite or thaumasite

Sulfate attack is an important deteriorating reaction that manifests in two forms: as an expansion and subsequent cracking, and/or the progressive decrease in concrete strength and cohesiveness of the hydration products [70].

The key aspect of sulfate attack is the formation of expansive minerals like ettringite or thaumasite. While macroscopically the effects of both are comparable, XRD or microstructure analyses can confirm the presence of one and/or the other.

Ettringite is formed by the reaction between aluminates from cement, sulfates and water (Reaction 2.1) [71]. *Primary* ettringite is a normal hydration product necessary for the early strength development of concrete and to prevent premature setting. It is expansive, but crystallizes in the fresh and deformable paste. Only *secondary* ettringite, formed in an already rigid cement matrix and leading to a heterogeneous swelling, can lead to cracking [72, 73].

$$3(CaSO_4 \cdot 2H_2O) + 3CaO \cdot Al_2O_3 \cdot 6H_2O + 20H_2O \\ \rightarrow 3CaO \cdot Al_2O_3 \cdot 3(CaSO_4) \cdot 32H_2O \quad (2.1)$$

There are several ways in which the reaction can take place after hardening, and all are based on the delayed release of sulfates: a sulfate ingress from an aggressive environment (section 2.3.2), from the cement itself after the destruction of primary ettringite (section 2.3.3) or by a contamination of the aggregates (Chapter 3).

Next to ettringite, thaumasite is another expansive mineral that can be formed by the action of sulfates on the cement hydrates (Reaction 2.2) [71]. The damage it incurs is heavier than conventional sulfate attack, but thaumasite is not formed as often as ettringite. The conditions for thaumasite formation - presence of carbonates and a low temperature of 5 to 10 °C - are not as commonly met [74].

$$CaSO_4 \cdot 2H_2O + CaCO_3 + CaSiO_3 \cdot H_2O + 12H_2O \\ \rightarrow CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O \quad (2.2)$$

Self compacting concrete, containing limestone filler, is one example where thaumasite can be formed. Cement compositions with carbonates such as the CEM II types are also susceptible [75]. In these cases, it has been shown that thaumasite is formed out of the ettringite from the early stages of sulfate attack [76]. This means that thaumasite formation should not be seen as a separate type of sulfate attack, but as a continuation of the reaction in specific circumstances [77].

Characteristic symptoms of sulfate attack include an enlargement of the concrete, and the development of (microscopic and sometimes also macroscopic) cracking (Figure 2.1). Concrete undergoing sulfate attack suffers a general loss in mechanical strength and dynamic elastic modulus. The cohesiveness of the cement paste is diminished, and in extreme cases the concrete becomes crumbly and soft [78].

Figure 2.1: Examples of 2 different bridges in France that underwent sulfate attack. The damage appeared as a network of widely-spaced multidirectional cracks, only at places that were accesible by water. From *Divet et al.* [79].

Because the occurence of thaumasite sulfate attack is low, ettringite formation will be the focus of the following pages.

2.3 Sources of sulfates and associated mechanisms

2.3.1 General mechanism

It is agreed upon that the swelling caused by sulfate attack is due to the formation of ettringite, but the exact mechanism by which the expansion occurs is still under discussion [69]. One hypothesis - and the most commonly accepted one - is the exertion of pressure by the growing ettringite crystals in restricted spaces [78, 80]. In this reaction, the crystallization is constrained by the available porosity [77]. Another possibility is a homogeneous paste expansion by the absorption of water that happens in alkaline environments when ettringite is poorly crystallized [81].

Microstructure investigations show that ettringite is often formed in existing spaces like air bubbles, pores and microcracks. Next to its characteristic needle form, massive and semi-crystalline ettringite deposits are also possible, pointing to a formation in a confined space (Figure 2.2) [77, 82]. From these places of formation, networks of cracks are formed, running trough the cement paste or partly along aggregate peripheries (Figure 2.3, 2.4). The crack propagation is local and heterogeneous [78].

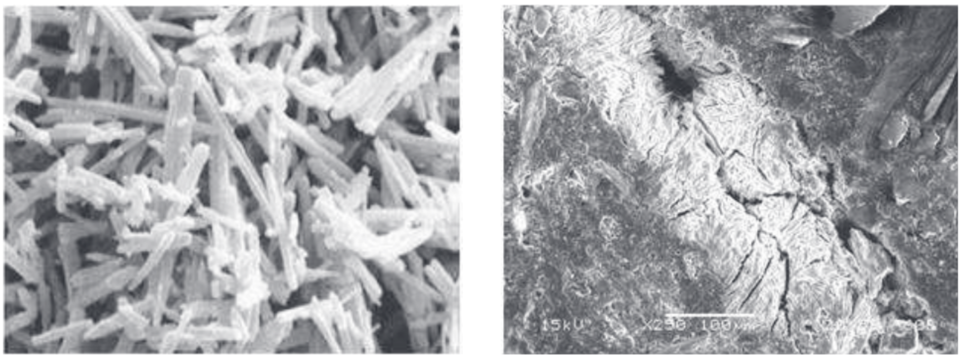


Figure 2.2: SEM images showing ettringite in its non-constrained needle form or in a massive deposit. From *Salgues et al.* [82].

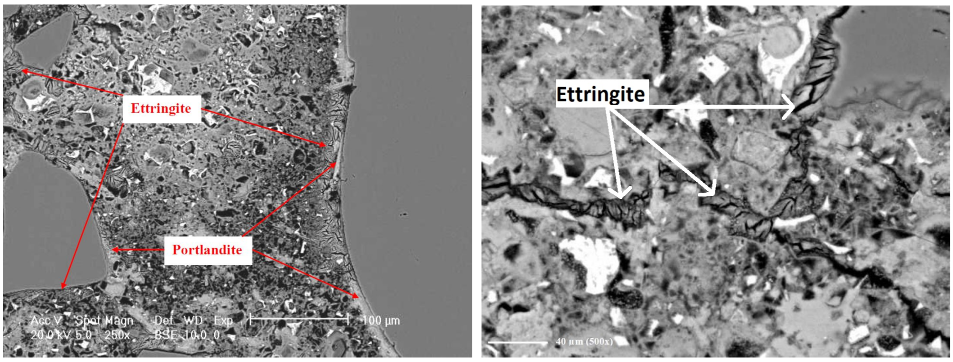


Figure 2.3: SEM images showing the formation of ettringite around aggregates and in crack networks. Adapted from *Brunetaud et al.* [73].

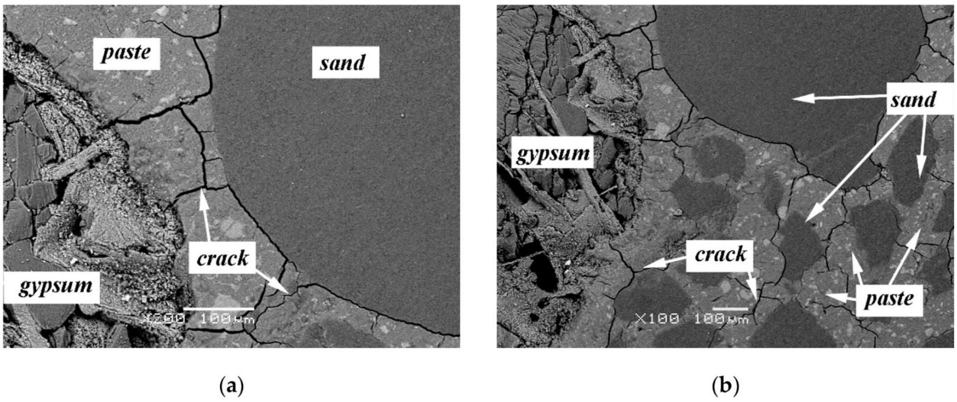


Figure 2.4: SEM images showing the propagation of cracking behavior at 120 (a) and 240 (b) days. The fracture first extends from the gypsum to the paste. The crack extended around the aggregate until finally, the aggregate separated from the paste completely. From *Chen et al.* [83].

Sulfate attack can have endo- or exogenous origins depending on the source of the sulfates. In both cases, there is the *secondary* formation of ettringite.

2.3.2 External sulfate attack

A common type of sulfate attack is where there is an ingress of sulfates from an aggressive environment such as sulfate containing soils or liquids. These sulfates can be part of the natural composition of the environment, or come from an industrial pollution [84]. Some examples of sulfate containing environments are seawater, agriculture soils, acid rain or certain sulfate producing bacteria [70].

Since the sulfates have to diffuse inwards, the main factor determining the extent of the external sulfate attack reaction is the permeability of the material via pores or microcracks [69, 72]. This means that porous or poorly compacted concretes will be more vulnerable [77]. The difference in mechanism with internal sulfate attack is that here, the reaction is very diffusion dependant: the damage starts on the surface and moves slowly inwards. Once microcracks have been formed, the reaction will go progressively faster. This will also mean that prevention of external sulfate attack is easily achievable by creating impermeable concretes [80].

2.3.3 Internal sulfate attack

To experience internal sulfate attack, the sulfates are introduced together with the mix components and not by an environment. The sulfates themselves can be associated with the aggregates (discussed in Chapter 3), or with the cement. This last case is explained here.

Early on, sulfate attack problems have been identified within precast railroad beams. These beams are steam cured, and it was discovered that this heat (>70 °C) destroyed the ettringite that was initially formed in the hydration process [85]. The sulfates and aluminates that have been released by this dissolution react again after some weeks to form ettringite anew, only this time in a rigid cement matrix that will swell, crack and degrade as a consequence (Figure 2.5). This specific mechanism of the sulfate attack reaction was labelled Delayed Ettringite Formation (DEF) and has since been researched a lot. Not only steam cured samples are subject to DEF, but massive concrete structures such as bridges or dams with a hydration heat >70 °C are also at risk [78, 86].

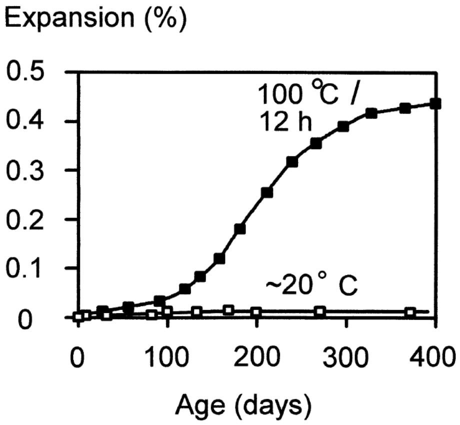


Figure 2.5: The same concrete, when subjected early to high temperatures, will showcase large amounts of swelling after a few months. From *Taylor et al.* [85].

Unlike the situation discussed for external sulfate attack, the sulfates in the DEF reaction do not come from outside, but are introduced with the cement. Cement contains sulfates which are added to prevent a 'flash set': a gypsum addition gives the best strength development and minimizes shrinkage while avoiding premature setting. The quantity of gypsum in cement required increases with increasing C_3A content, alkali content, and fineness of cement. A higher sulfate content in cement is associated with increased early (1 to 3 day) strengths [87].

The early temperature treatment of concrete is essential for DEF, where primary ettringite crystals are dissolved or even inhibited to grow in the first place. The sulfates from cement are thereby adsorbed onto the CSH matrix, in the form of monosulfate (Figure 2.6). This adsorption is completely reversible, and the sulfates are released back into solution after some weeks [88]. This desorption is however a slow reaction, explaining why it takes some months or even years to observe DEF swelling in heat cured samples. The ettringite-CSH equilibrium is indeed temperature dependent: at 20 °C, ettringite precipitates already at a concentration of 0.4 mmol/L, but at 85 °C 5 mmol/L is is possible in solution [89].

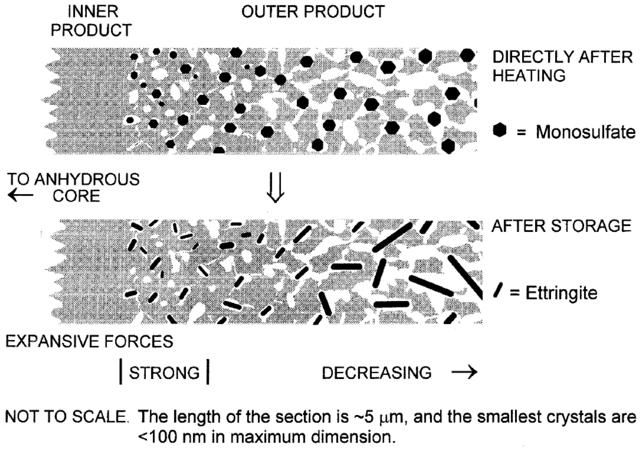


Figure 2.6: The adsorbed monosulfates will release and contribute to ettringite formation in microcracks and pores. From *Taylor et al.* [85].

According to *Collepardi et al.*, the DEF reaction is based on three elements: a late sulfate release, the presence of microcracks, and exposure to water. This means that preventing or controlling either of these could theoretically mitigate the DEF-induced damage [90]. A slower temperature rise during curing can also limit the expansion [91]. Some aspects of the concrete composition can be adapted: the use of lithium nitrate [92], a cement with a lower sulfate content, or the addition of fly ash [93] are some examples.

Interaction with AAR

The DEF reaction is remarkably often observed together with the alkali-aggregate reaction (AAR). This last reaction is also developed from the concrete mix itself: the cement alkali's in the pore water and the siliceous compounds in aggregates produce a type of gel. This gel swells after contact with water, causing tensile stresses and internal cracking. The final result is a deformation of the concrete with a crack network on the surface [94]. This reaction has been noticed already in the 1940's and has been studied extensively since then [69]. AAR is easily avoidable by keeping the relative humidity of the concrete/surroundings as low as possible (80 % or less) or by the use of mineral admixtures [95].

In many cases of DEF, there is a simultaneous or concurrent AAR [78]. The outward pathology of these two reactions is very similar and difficult to distinguish without a microstructural analysis, which is not always easy in the field. While DEF is less common than AAR, it can potentially be more damaging: AAR expansions are typically around 0.3 - 0.5 % where DEF can go to 1 - 2 % [73, 96]. AAR occurences reduce the alkalinity of the pore solution. As the formation of ettringite is heavily linked to this parameter - DEF is triggered at lower pH - naturally these reactions will be intertwined.

There have been a number of cases involving deteriorated concrete columns in North America where there was considerable controversy surrounding the respective contributions of AAR and DEF to the observed damage. Although the columns were not deliberately heat-cured, it was estimated that the peak internal temperature would have exceeded 70 °C. The forensic investigation of the columns by *Thomas et al.* included scanning electron microscopy with energy-dispersive X-ray analysis and expansion testing of cores extracted from the structure. Their conclusion was that DEF attributed for a far greater part to the deterioration than previously thought, and in most columns AAR and DEF worked hand in hand (Figure 2.7) [97].

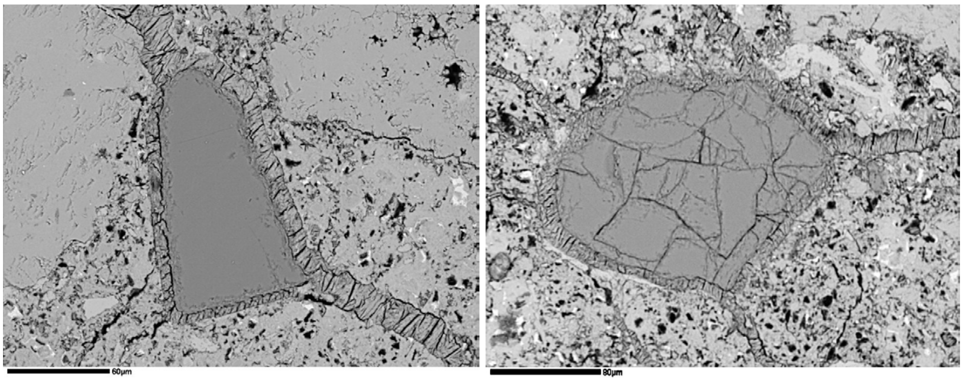


Figure 2.7: BSE images of concrete columns originally suspected to be deteriorated by AAR. Ettringite filled gaps are present around the reactive particle. From *Thomas et al.* [97].

A concrete dam in Spain had multiple diagnoses to explain its degradation, that kept changing throughout the years according to the evolution of the behavior observed. 2D and 3D models were used to analyze these diagnoses and determined that the conclusion of AAR did not justify the magnitude of displacements observed. The main cause of degradation was then considered to be an internal sulfate attack (figure 2.8) [86].

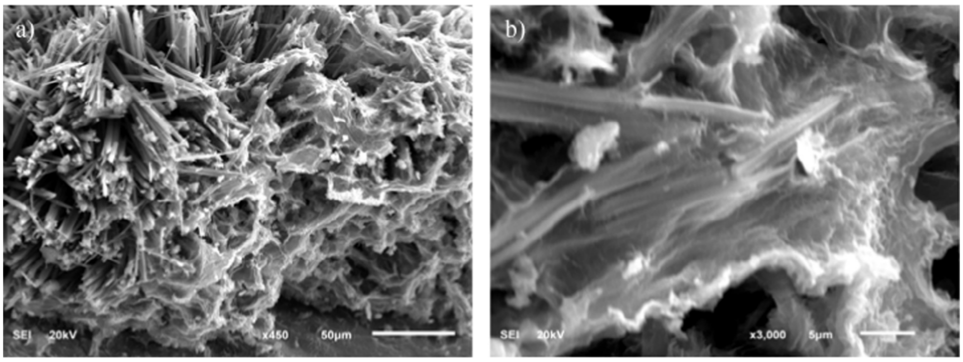


Figure 2.8: SEM images from a damaged dam: (a) ettringite crystals and gel of the AAR, (b) detail of the gel covering the ettringite crystals. From *Campos et al.* [86].

2.4 Important parameters

Many authors show the important role of the alkalinity of the interstitial solution, as it interferes with the equilibrium between the different sulfate phases. The alkali's in cement (from potassium or sodium salts which dissolve and raise the pH) are often expressed as a Na_2O equivalent (Reaction 2.3).

$$Na_2O_{eq.}\% = Na_2O\% + 0.658 \cdot K_2O\% \tag{2.3}$$

A higher alkalinity favors the existence of monosulfate and the absorption of sulfur on the CSH matrix instead of the formation of ettringite [73, 98], so ettringite formation triggers as pH lowers. This is because the alkali content largely influences the availability of Ca^{2+} ions (Figure 2.9). Alkali's are not necessary in the ettringite formation reaction, but play a role in the availability of the reactants [82]. This was also relevant in the interaction between sulfate attack and the alkali aggregate reaction (section 2.3.3). Nevertheless, a higher swelling due to ettringite formation is often found in mixes with a higher alkalinity [96, 98, 99, 100, 101] which seems contradictory. While alkalinity speeds up hydration and increases early compressive strength [102], it leads to lower mechanical performances in a sulfate presence [96, 98].

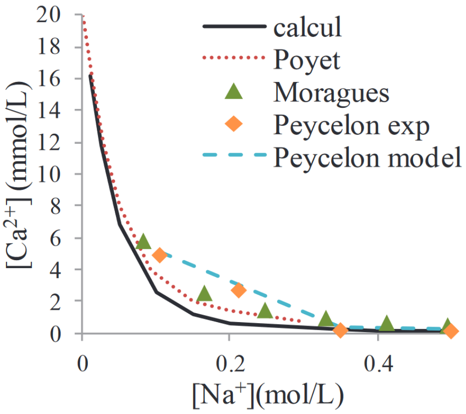


Figure 2.9: An elevated alkalinity influences the availability of necessary reactants for ettringite formation. Modellisations (black, blue) compared to experimental results (colored). From *Salgues et al.* [82].

Using a sulfate-resisting cement allows the concrete to be exposed to a high sulfate content [103]. These types of cement contain less C_3A, one of the reactants needed to form ettringite. Moreover, fewer gypsum is added to this cement type as a setting retarder, compensating for the additional sulfate source to which the mixture will be exposed. The SO_3/Al_2O_3 ratio of a cement is a limiting factor regarding its potential to form ettringite [73, 91, 104]. Figure 2.10 calculates, based on the reaction equations of cement hydration, the SO_3/Al_2O_3 ratio of cement required to consume all C_3A and convert it to monosulfoaluminate (the secondary ettringite precursor).

The most commonly accepted theory about the cause of expansion is the heterogeneous crystal pressure exerted by the growing ettringite crystals [69, 72, 78]. In this sense, a lower porosity means more confinement and a higher internal pressure. On the other hand, in the case of external sulfate attack (and numerous other deteriorating reactions), a lower porosity was recommended, to prevent the inwards diffusion of sulfates [105]. In general, a lower water to cement ratio of a concrete mix - thus a lower porosity - is found to have a positive effect on mechanical performances and durability.

For sulfate attack, it is important to have a source of sulfates that becomes available after the initial cure. Only water soluble sulfates can contribute to sulfate attack: characterization techniques for sulfates such as acid dissolutions also capt sulfates fixed into cement hydration products which do not pose a risk. Depending on the form of the sulfates ($MgSO_4$, Na_2SO_4, $CaSO_4$), the swelling response can change [96, 98].

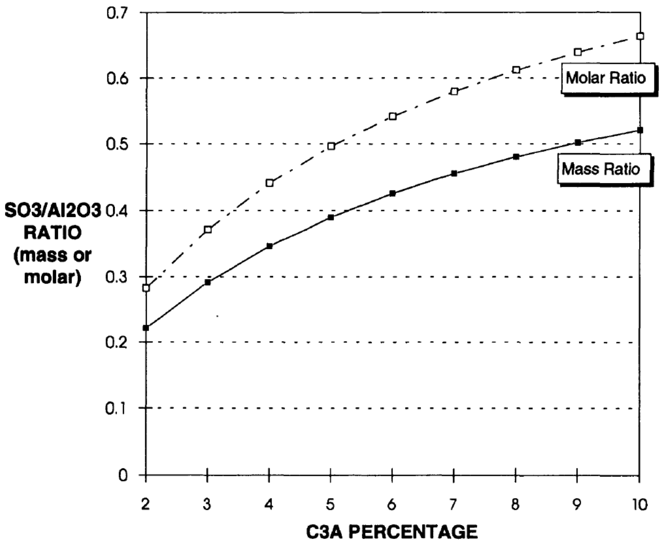


Figure 2.10: SO_3/Al_2O_3 ratio required to react with all C_3A to form monosulfoaluminate. From *Day et al.* [91].

Next to these identified parameters, other specific factors can also influence the course of the sulfate attack reaction, such as the presence of carbonates and low temperatures to form thaumasite. Numerous researchers also found that pre-existing cracks (for example from other deteriorating reactions) facilitate the reaction [72], as well as certain curing conditions like temperature treatments or wetting/drying cycles [89].

3 | Gypsum in recycled materials

This chapter discusses the combination of the two complicating factors discussed previously. FRA are often contaminated with gypsum residues from the demolition site, which can act as an internal source of sulfates to facilitate sulfate attack in recycled materials. With the goal of valorizing these contaminated FRA in mind, the objectives of the thesis are discussed.

3.1 Gypsum as a source of sulfates

Gypsum is used as a generic name for several types of calcium sulfate. These compounds are classified according to the number of hydrogens present in the crystal structure: calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), and calcium sulfate anhydrite ($CaSO_4$) [106]. Transformation between these different types is a reversible process of hydration and evaporation (Reaction 3.1). From here on out, 'gypsum' will refer to the calcium sulfate dihydrate form.

$$CaSO_4 \cdot 2H_2O \overset{p,T}{\rightleftharpoons} CaSO_4 \cdot 0.5H_2O + 1.5H_2O \overset{p,T}{\rightleftharpoons} CaSO_4 + 2H_2O \quad (3.1)$$

The primary occurrence of gypsum is as a soft white mineral found in massive sedimentary deposits, but it can also crystallize as selenite. It is used for many applications in medicine, agriculture or construction.

Gypsum is only moderately soluble: depending on the pH and ionic strength of water, gypsum has a solubility between 0.015 and 0.055 mol/kg (corresponding to 2.6 and 9.5 g/L) [107]. Exceptionally, gypsum also exhibits a retrograde solubility, where a rise in temperature does not equal a rise in solubility. The different types of calcium sulfate hydrates have different stabilities in solution as well. The solubility changes in function of these parameters can be seen in Figure 3.1.

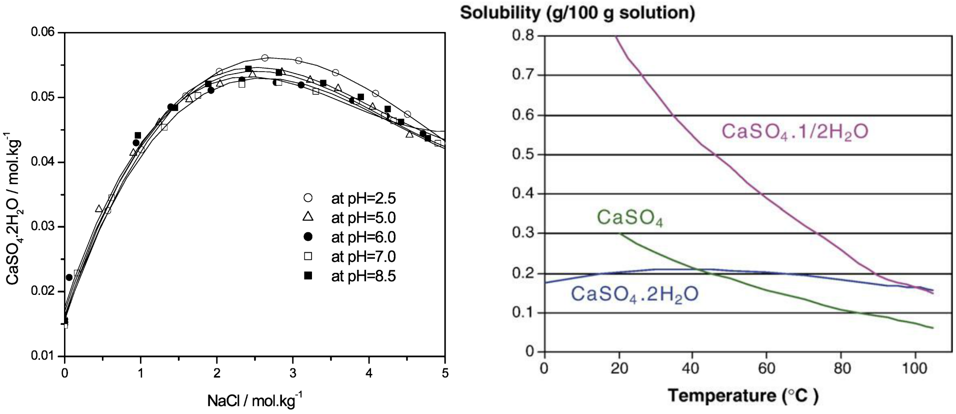


Figure 3.1: The solubility of $CaSO_4.2H_2O$ in aqueous NaCl solutions at 35 °C and at various pH values, and the solubility of the different calcium sulfate types in function of temperature. From *Shukla et al.* [107] and *Colas et al.* [108].

3.1.1 Use of gypsum in the construction industry

Gypsum is used in the construction industry as the major constituent of drywall boards for interior walls and ceilings which contain mostly gypsum and some small part cardboard. Plaster also consists of gypsum powder that has formed a paste with water and subsequently hardened. Plaster is not a strong material and is easily crushed. Naturally, when a building is demolished, the resulting C&DW will be contaminated with plaster residues. This increased water soluble sulfate content is a limiting factor for the reuse of recycled aggregates, because of the risk on internal sulfate attack.

To avoid these gypsum residues as much as possible, the *deconstruction* of a building is favored over its demolition. Plaster is taken out of the building in a systematic way, to be reused in future construction applications. The 'Gypsum to Gypsum' study of the European Commission on the reuse of gypsum products eventually lead to the publication of the 'European Handbook on best practices in deconstruction techniques' [109] [110]. In Figure 3.2 is shown how, before the demolition of an apartment building in Roubaix (France), plaster is collected to be recycled. Nevertheless, traces of gypsum were still to be found on most walls, which will end up in recycled aggregates after demolition.

The reversibility of the hydration reaction of calcium sulfates lends itself excellently to recycling: in theory, a closed loop is indefinitely possible. Studies prove indeed that multiple cycles of grinding and burning gypsum

Figure 3.2: Plaster is being collected before demolition (a) of an apartment building, but gypsum residues are still present on walls (b-d) and will end up in recycled aggregates.

waste can be completed without discernible differences in plaster properties [111]. The energy and temperatures needed for this recycling do have a larger environmental impact than the mining of new gypsum. However, a complete life cycle analysis shows that recycling is still the best option. Gypsum waste products in landfills can decompose to hydrogen sulfide gas by sulfate reducing bacteria, creating an environment where methanogenic bacteria thrive [112]. Next to this methane production, sulfates can also leach into the environment causing ecotoxicological problems [113, 114].

Even without a plaster contamination, RA will still contain water soluble sulfates because of their unreacted cement particle content. Gypsum is used as a setting retarder in cement, to limit the rapid hydration of calcium aluminates. When water first contacts cement there is an initial rapid dissolution of anhydrous aluminates and subsequent rapid crystallization of these hydrated calcium aluminates. This occurs before the solution becomes saturated with lime and/or gypsum and corresponds to the first peak in the hydration heat curve. When more and more gypsum gets dissolved, the formation of aluminates slows down. The subsequent formation of sulfoaluminates starts to deplete the amount of sulfates in solution, and the rapid aluminate reaction will begin again (Figure 3.3) [115].

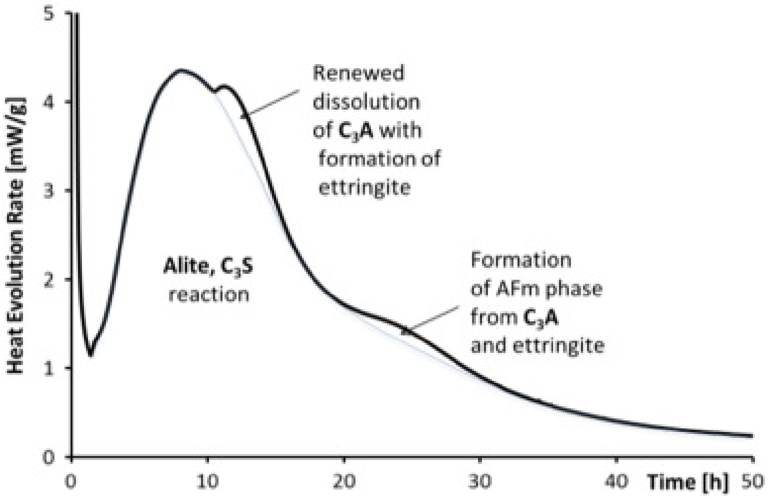


Figure 3.3: A calorimetric curve of Portland cement, showing the stages of cement hydration. From *Scrivener et al.* [115].

3.1.2 Sulfate attack with recycled aggregates

The gypsum contamination of recycled aggregates can cause internal sulfate attack. Larger concrete and gypsum particles can be separated from each other based on a difference in color [24] or density [23], but these techniques are mostly visual and thus not applicable on the smallest size fractions of RA. In FRA, gypsum is an important contaminant to be considered: the water soluble sulfates coming from the gypsum particles strongly limit their valorization potential [116]. There is a clear variability between different recycling centres: in industrial samples, values of 0.03 to 0.25 % of sulfates have been found in one study [117], but up to 1.52 % in another [118].

Laboratory made concrete that was crushed and manually contaminated with gypsum particles is a good way to simulate contaminated recycled aggregates with exact knowledge of their composition but without other interfering impurities. The substitution of natural aggregates with these materials, shown in Figure 3.4, prove that the sulfate content in RA provokes a swelling of the concrete samples [119]. While the same trend of increased expansion with sulfate contents is seen in other studies, the absolute swelling amounts do not seem reproducible. Mortars made with an acid soluble SO_3 content of 2.9 or 4.3 % by weight of cement, showed expansions of 0.04 to 0.12 % respectively [120]. An SO_3 content of 1.8 % however gave rise to 0.04 % of expansion in another study [121].

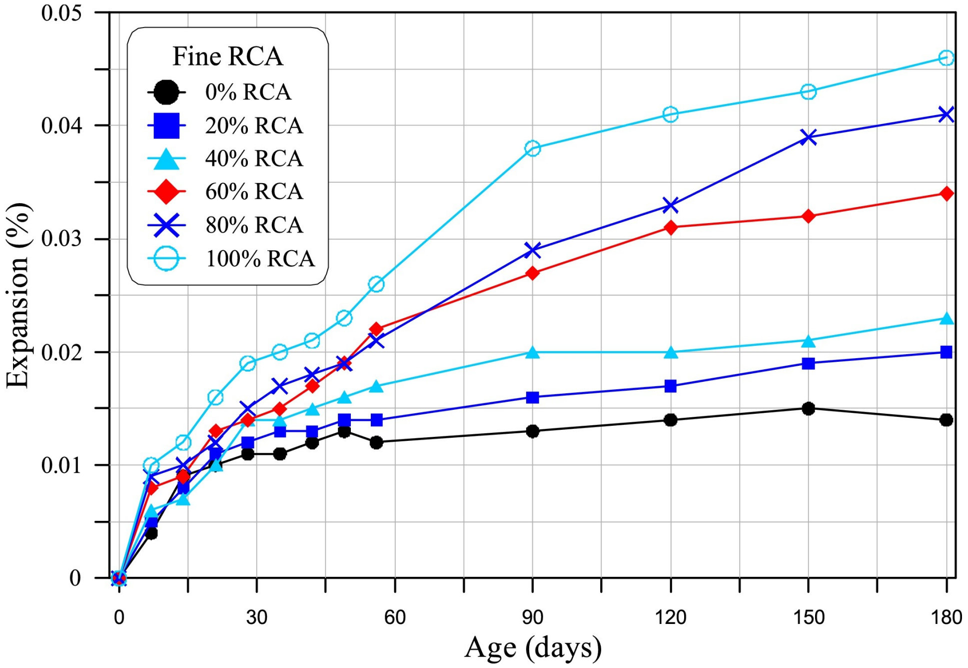


Figure 3.4: Swelling behavior of concrete made with contaminated fine recycled aggregates. The FRA had an acid soluble SO_3 content of 1.5%. From *Abid et al.* [119].

Next to the sulfate content, other parameters can influence the swelling response. An early work on the use of contaminated recycled aggregates found that the C_3A content of cement and the particle size of gypsum changed the swelling results. Gypsum particles from the 0/4 mm fraction were more reactive and lead to a larger swelling response. For a concrete made with a standard CEM I, the swelling limit was exceeded for plaster contents above 1.5% (Figure 3.5), while cements with lower C_3A contents - like CEM III - could handle up to 3% of plaster [122]. When accounting for their molar mass ratio, these amounts of plaster correspond to respectively 0.87 % and 1.74 % of SO_4^{2-}. The use of an accelerated aging protocol in this study and a W/C of 1 could make it difficult to compare these results to industrially realistic scenarios.

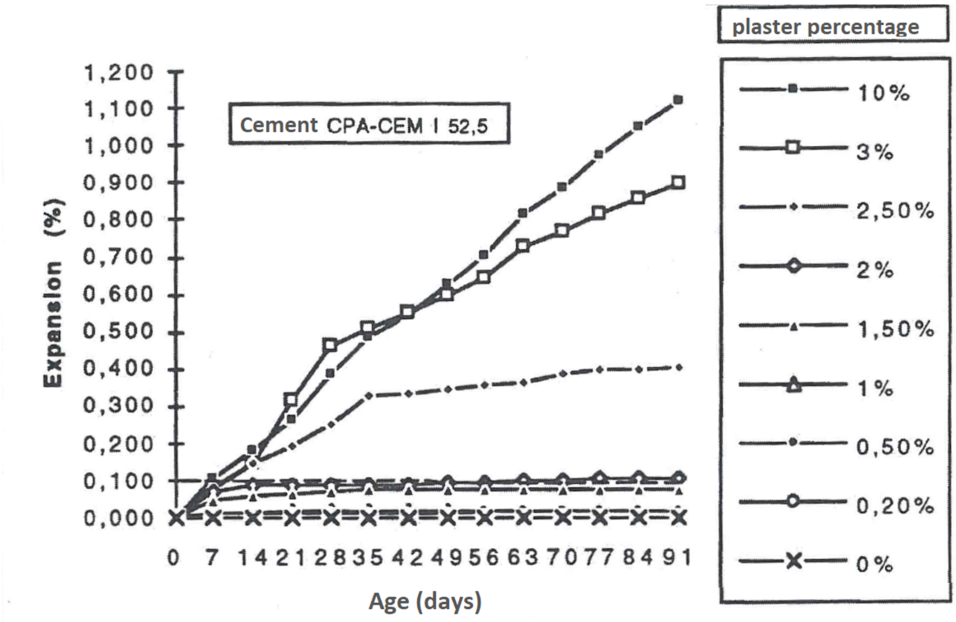


Figure 3.5: Swelling behavior of 7x7x28 cm concrete samples, made with contaminated recycled aggregates. From *Orsetti et al.* [122].

A heavy contamination of aggregates does not necessarily mean they cannot be used: several possible solutions exist to compensate for sulfate attack. A case study about the reuse of excavated materials as aggregates in concrete showed that they were contaminated with 1.6 to 4.3 % of SO_3. The sulfates in these aggregates did not come from plaster residues from a construction site but rather from the gypsum content of the soil. The swelling caused by these amounts of sulfates was indeed important and two possible solutions were suggested. A first proposal would be - for very large projects such as these - to order a custom cement where gypsum had not been added as a setting retarder. The sulfates in the aggregates would take on the role of setting retarder. If this is not possible, some sulfate resisting cements also had good results limiting the swelling reaction. A second solution was on the level of the aggregates. Washing the aggregates lead to a decrease from 3.5 to 2.5 % of sulfates. Eliminating the finer fraction (0/0.315 mm) reduced the sulfate content even more, to 1.1 %. These fine particles contained most of the sulfates, which leached very quickly [108].

In most of these discussed studies, there is not a uniform definition for 'the sulfate content'. They were expressed as a percentage of SO_3 or plaster, all of which have a different molar mass and correspond to a different SO_4^{2-} content in the mix. To make it even more confusing, this mass percentage referred sometimes to the aggregate but at times also the cement weight. The percentages were often specified as being determined by acid dissolution, which will misinterpret the risk on sulfate attack because only water soluble sulfates will react to form secondary ettringite. It is, as a consequence, very hard to compare these results or try to correlate a sulfate content to a swelling response in general. The most important distinction in these studies however, is that they researched the influence of the gypsum contamination as an additional internal source of sulfates, without doing any heat treatments to provoke the DEF reaction. This makes the problem much more prevalent as it can happen in every concrete - not just precast or massive structures.

3.2 Limits, legislation and standards

3.2.1 Limitations for recycled aggregates

To keep the risk on sulfate attack at a reasonable level, the current water soluble sulfate limit in coarse recycled aggregates is established at 0.2% by EN206 [60], with no mention of FRA. EN206 also states a replacement percentage of 30 % coarse RA in concrete is feasible, but there again does not discuss the incorporation of FRA. Other recommendations state that RA with water absorptions above 7 % for coarse and 13 % for fine particles are not suitable to be used in concrete [37].

These limits can be seen as very strict and will exclude the use of a big part of C&DW, and especially FRA. Because these regulations also require numerous analyses to be run before use, small sites with a high stock rotation will have difficulties valorizing RA [16]. There is a general lack of confidence from industrials regarding the quality of RA perpetuated by these strict recommendations [12], but this position is more and more seen as too conservative by researchers [53]. Recent durability studies mention the possibility of increasing the sulfate limit [103]. The previously mentioned French National Project RECYBETON specifically proposes a sulfate limit of 0.3 % [123].

3.2.2 Recommendations for swelling due to DEF

The recommendations on allowable compositions are in turn based on a swelling limit. Expansions above 0.1% lead to a reduction in compressive strength of 60 to 70 %, and a decrease in elasticity of 60 % [96]. This value of 0.1 % is also seen as a threshold for the cracking of concrete, while others place that limit at 0.2 % [100, 121]. As soon as this threshold is passed, existing microcracks facilitate the reaction and the needed crystal pressure to cause deformations will be smaller.

In a protocol to assess damage by DEF by the *Laboratoire Central des Ponts et Chaussées* [124], the following swelling limits are established for concrete formulations that are considered 'safe':

- After 12 months, the average expansion is below 0.04 % with no individual sample passing the 0.06 % mark. After the third month, the expansion did not increase by more than 0.004 %.

- If expansion after 12 months should be comprised between 0.04 and 0.07 %, three additional months of testing are necessary. The formulation is safe if in those 3 extra months, the expansion did not increase by more than 0.004 %.

Brunetaud et al. proposed, based on his experimental results on DEF (Figure 3.6), a classification of expansions depending on the swelling amounts and the form of the swelling curve [73]:

- Negligible (<0.04 %): 0.04 % is the usual limit used for the diagnosis of sulfate attack. This type of swelling had no macroscopically visible effects.

- Weak (0.04-0.2 %): the swelling increased linearly, but had no effect on mechanical properties.

- Important (>0.4 %): these swelling curves had sigmoid shapes. The material was damaged which in turn caused even more swelling, and increased more in mass than was necessary for the hydration reaction. There were noticeable effects on mechanical properties.

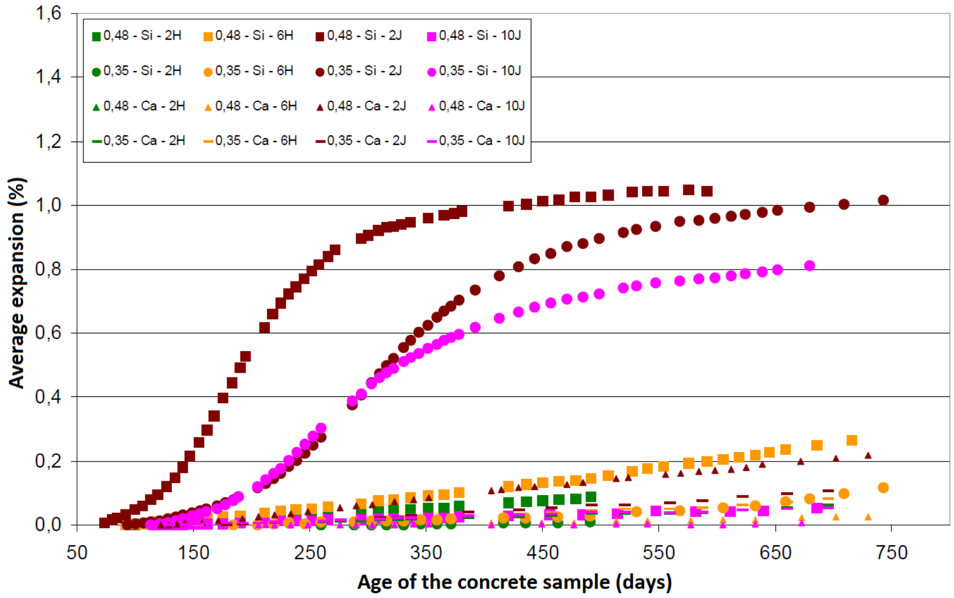


Figure 3.6: The expansions of different concrete formulations - tested according to a DEF protocol - could be classified in three groups: negligible, weak and important. From *Brunetaud et al.* [73].

From these results, 0.2 % could be seen as the threshold for 'dangerous' expansions, but even the so called 'weak' swelling can still have effects on a structure. Here, a problem arises with the translation of swelling limits to sulfate limits. Methodology and materials play a big part in the measured absolute amount of swelling: certain sulfate contents will, depending on the followed protocol, give rise to different swelling amounts. These discussed limits and protocols are specifically set up for DEF on concrete, and not for all mechanisms of sulfate attack.

Conclusion, problem definition and methodology

Using recycled aggregates coming from C&DW is a good practice that would majorly impact the environmental burden of the construction sector, but it still needs traction in the industry. Recycled aggregates need some processing and characterization before their incorporation has satisfactory results, and especially fine recycled aggregates are up to now not valorized in high quality applications.

Sulfate attack is a real concern for concrete: significant damage can occur depending on its composition or environment. It has a complex mechanism depending on many parameters and other deteriorating reactions. In this context, sulfate contaminated aggregates are definitely a risk factor for degradation.

Depending on the source of fine recycled aggregates, they can be contaminated with non-negligible amounts of gypsum. Standards and limits are in place to restrict their use because of the risk they pose for sulfate attack. However, research points out that these limits could be too strict, and that they are hindering the valorization of FRA.

From the available literature, several problems were pointed out that could be addressed in new experimental work:

- Studies about sulfate attack focus on one of the two better known mechanisms, being DEF or external sulfate attack. Research about the presence of an internal source of sulfates without heat curing samples is very scarce.

- Most authors acknowledge that the finer fraction of RA is often overlooked in research. Perpetuated by older studies and strict regulations, there is a lack of confidence in the quality of FRA, which inhibits its valorization.

- A lot of research about the incorporation of RA highlights mechanical performance, and more work needs to look at long term durability issues. Durability is especially a concern with recycled materials, as they are less dense and less resistant to aggressions.

This research was conducted in the framework of the VALDEM project, which aims to identify and valorize 'problematic' material flows derived from C&DW. One of the focus points was the valorization of FRA contaminated with gypsum residues. Within that context, this thesis started with two questions: how much sulfates are actually contaminating industrially available FRA? Do these amounts of sulfates cause any significant damage and if so, which parameters could influence this result?

The ultimate objective of this work was to provide new scientific results about the internal sulfate attack reaction, that at the same time also inform industrials about the use of contaminated FRA.

To obtain answers to the research questions posed above, the following experimental steps were envisaged:

- Fabricating an uncontaminated FRA, to serve as a reference material against industrial sources of FRA;
- Developing different protocols, to measure water soluble sulfates in FRA, and to monitor the degradation of mortar or concrete over several months;
- Collecting FRA from different recycling centres to characterize them and incorporate them into mortars to undergo swelling tests;
- Varying different composition or mixing parameters to assess their effect on the swelling result, regardless of the sulfate contamination;
- Evaluating whether the results found on mortars in the previous steps are applicable to concrete.

These steps are displayed schematically in Figure 3.7.

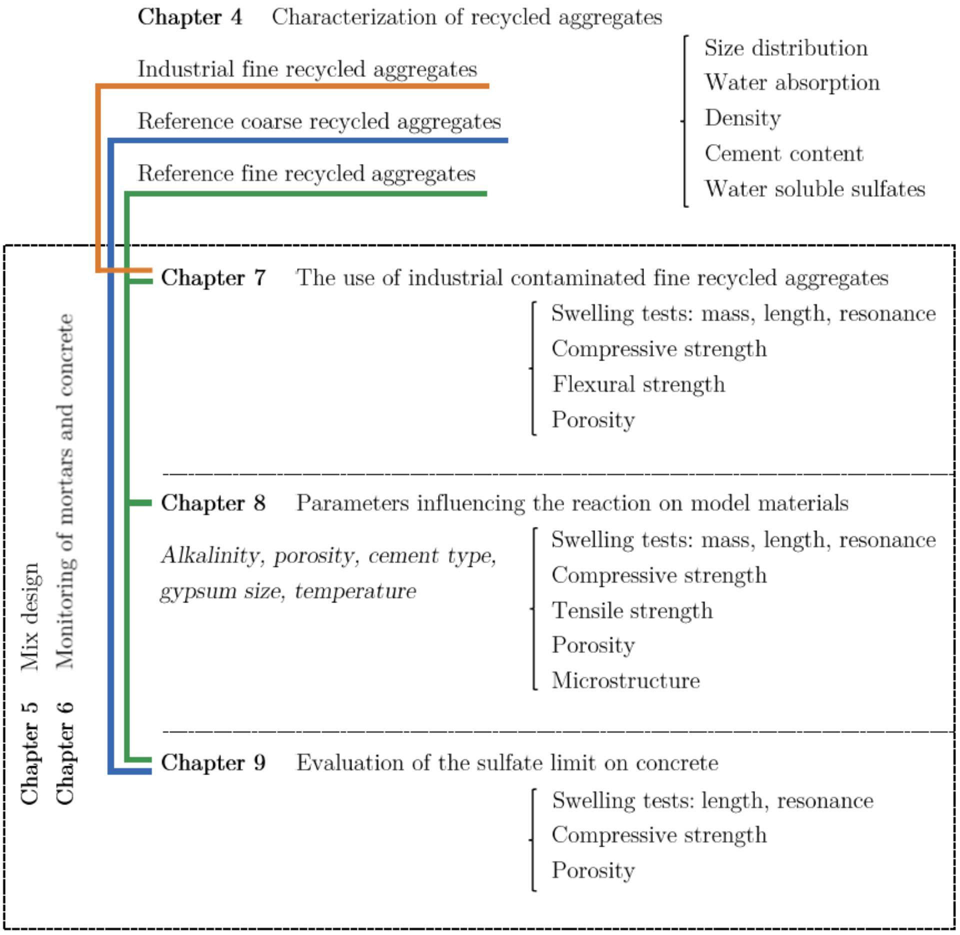


Figure 3.7: Schematic representation of the different materials and the experimental steps in which they were used.

Part II

Materials and methods

Introduction

The experimental work in Part III all makes use of the same protocols and materials, which are summarized in these following chapters.

The fine recycled aggregates that were the subject of this study are described in Chapter 4. Different industrial samples of FRA have been collected from recycling centers. As a reference material, a laboratory-made concrete was crushed to obtain pure uncontaminated FRA. Their physical and chemical characteristics relevant for the following experiments are discussed: size distribution, water absorption, density, cement content and water soluble sulfate content.

Experimental work in this thesis is conducted on mortar or concrete bars, made with the materials from Chapter 4. The design of their compositions and mixing procedures are discussed in Chapter 5.

In Chapter 6, the different tests are described that will follow the development of sulfate attack in the samples. Because no heat curing is used to trigger DEF in this study, a ready-made testing protocol was not available. The relevant weekly swelling tests, periodic mechanical tests and microscopic examinations are defined.

4 | Characterization of recycled aggregates

This chapter discusses the different types of aggregates used, and their physical and chemical characteristics.

4.1 Recycled aggregates

To study the effect of gypsum residues in FRA, two types of recycled aggregates are used: industrial FRA coming from C&DW, and a laboratory-made FRA to act as a reference material.

4.1.1 FRA from recycling plants

Samples of recycled aggregates were collected in different size ranges from three different recycling centers in Belgium. These samples were named 'A' to 'F', and their original characteristics are shown in Table 4.1. To obtain FRA samples ready for characterization, they were dried at 40 °C and sieved to keep the 0/4 mm fraction. From the pictures in Table 4.1 a large variability between the different sources can be seen, and contaminations with soil, brick, wood, plastic or gypsum particles. Their impurity becomes especially clear when compared to pure crushed concrete, discussed later in Figure 4.1.

A	B	C	D	E	F
TRADECOWALL 0/4	SATEA 0/10	SATEA 0/32	SATEA 0/20	ELOY 0/90	SATEA 0/10
					

Table 4.1: The different samples of FRA, their source recycling center and original size distribution. Pictures shown are after drying at 40 °C and separating of the 0/4 mm fraction.

4.1.2 Production of a reference material

Next to industrial samples, a reference material was made by fabricating and crushing a standard concrete. The use of these 'model' recycled aggregates gave exact control over the chemical composition of the materials and removed any possible variability or contamination at the level of the aggregates by chlorides, organics, etc. These reference recycled aggregates could then manually be contaminated with gypsum when desired, to obtain a 'clean' material where only sulfates can contribute to a deteriorating reaction.

The composition and properties of the original concrete are given in Table 4.2. It was designed to obtain a consistency class S3 and strength class C30/37. The the mixing procedure and the method used to determine this composition are described in more detail in section 5.2, as well as a description of the used cement.

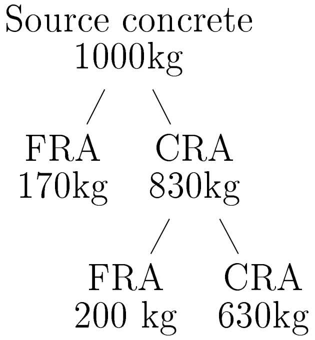
CEM I 52.5 N	Water	Limestone aggregates (mm)				Superplasticizer
		0/4	2/7	7/14	14/20	
350	175	216	658	436	612	0.4%

Slump	Fresh density	Compressive strength (90 days)
12 cm	2.45 (kg/m^3)	42 MPa

Table 4.2: Composition (in kg) of the original concrete, and its properties at a fresh and hardened state. This concrete was crushed after 90 days to obtain the reference recycled aggregates.

After 90 days of curing in a humid environment, 1000 kg of this concrete was crushed by a jaw crusher at the *Centre Terre et Pierre* in Belgium. A first crushing was carried out with a jaw opening of 15 mm. The remaining coarse recycled aggregates (CRA) were passed through the crusher again with a jaw opening of 8 mm, which yielded some extra FRA (Figure 4.1).

The two resulting loads of FRA differed slightly in their size distribution and cement paste content. They were homogenized by mixing the two batches and quartering them with the help of a riffle splitter (Figure 4.2). 10 samples taken after this homogenization showed no distinct differences in size distribution or cement paste content anymore.



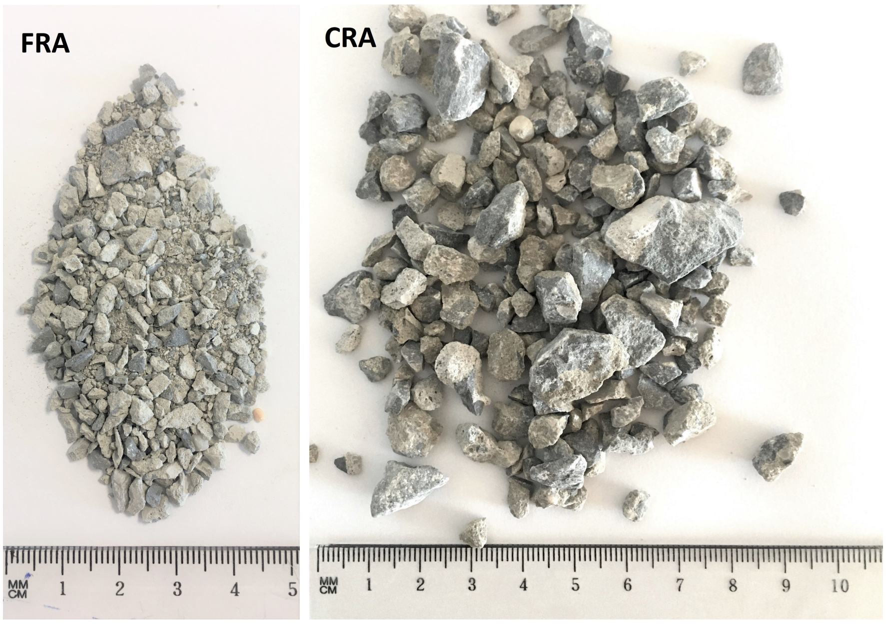


Figure 4.1: The crushing procedure of the original concrete in two steps: the first with a jaw opening of 15 mm and the second at 8 mm. The result was 370 kg of FRA and 630 kg of CRA.

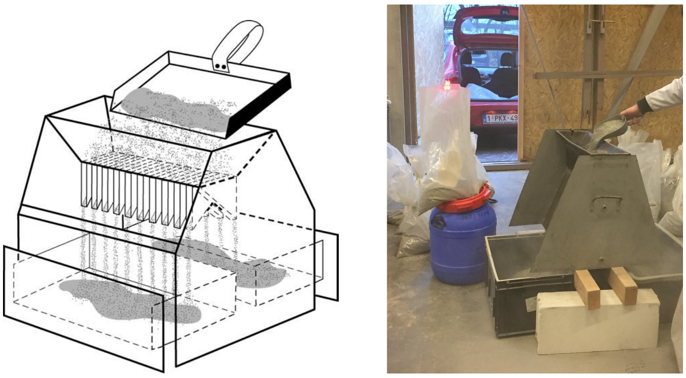


Figure 4.2: The homogenization process of the 2 obtained FRA fractions, with the help of a riffle splitter.

4.2 Physical characteristics

4.2.1 Size distribution

The size distribution of the industrial FRA samples as well as the reference FRA, are shown in Figure 4.3. They were determined by dry sieving according to standard EN 933-1 [125]. A high variability in fines content was found between the different industrial sources. The size distribution of the CRA fraction, obtained from the same crushing process as the reference FRA, is shown in Figure 4.4

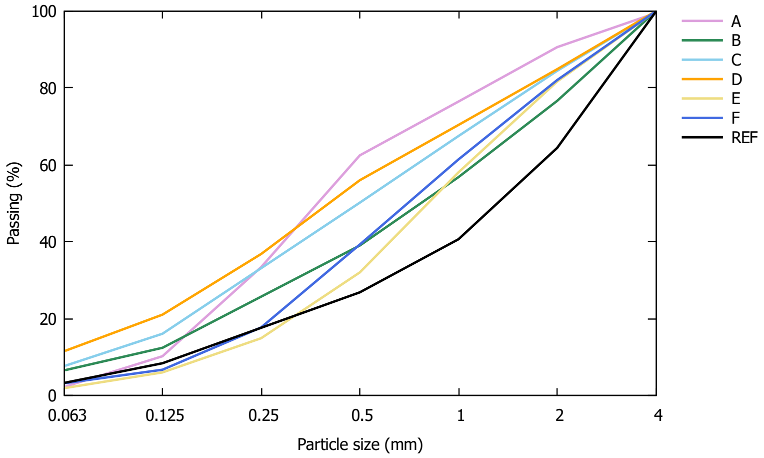


Figure 4.3: Particle size distribution of the used FRA: industrial sources or lab-made.

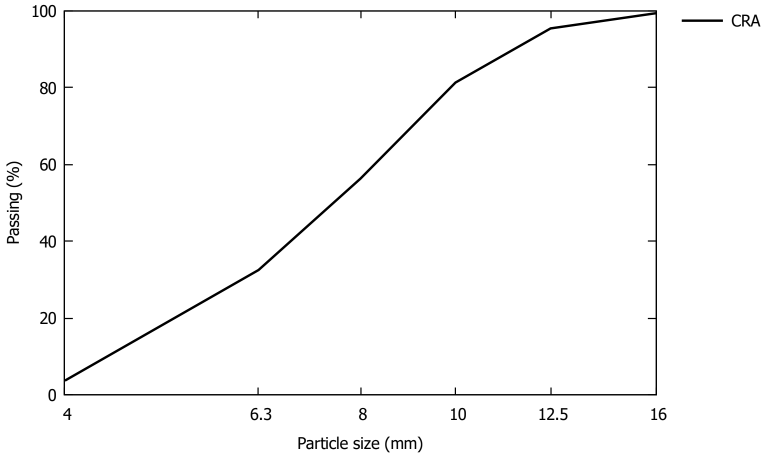


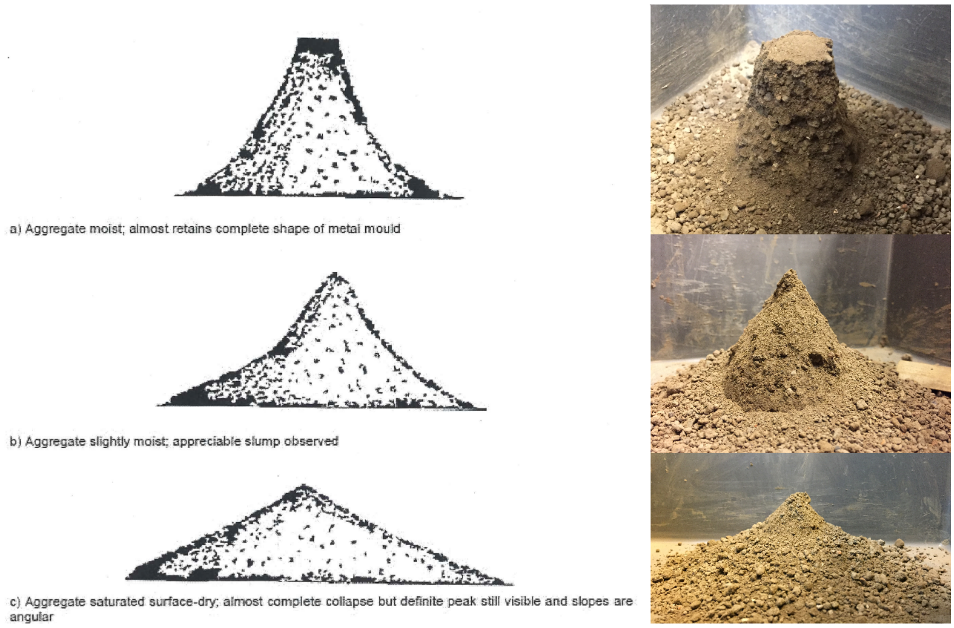
Figure 4.4: Particle size distribution of the used CRA, obtained by crushing concrete.

4.2.2 Water absorption

The water absorption of FRA is a notoriously difficult characteristic to measure [53]. Three techniques were used here to determine this value: the one according to standard EN1097-6 [42], the one designed by IFSTTAR [43], and an extrapolation method developed by *Zhao et al.* [44]. They are all based on finding the saturated surface dry (SSD) state of the aggregates, where the surface is dry but the intra-particle voids are filled with water. The water absorption coefficient is determined by comparing the weight of the aggregates in SSD condition to their weight when oven dried (Equation 4.1).

$$\text{WA } (\%) = \frac{M_{SSD} - M_{dry}}{M_{dry}} \tag{4.1}$$

The standard method consists of blowing warm air over a saturated aggregate to dry out the surface of its particles. A cone is used to test the slump, and the SSD state is here defined as a specific shape after removal of this cone (Figure 4.5). This technique is known to underestimate the water absorption of FRA, because the agglomeration between the fine particles means they need to be dried more before they reach the desired slump.



a) Aggregate moist; almost retains complete shape of metal mould

b) Aggregate slightly moist; appreciable slump observed

c) Aggregate saturated surface-dry; almost complete collapse but definite peak still visible and slopes are angular

Figure 4.5: Determination of the SSD state according to standard EN1097-6, in juxtaposition with observations on FRA.

The method developed by IFSTTAR determines the SSD state by drying the wet aggregates on absorbent paper until there are no traces of moisture visible anymore. While this technique works well for coarser particles, finer size fractions are very difficult to get in such a state without overestimating the water absorption or losing material (Figure 4.6).

Figure 4.6: Determination of the SSD state according to method n°78 by IFSTTAR, for the size fractions 2/4 and 0.5/1 mm respectively. The smaller the particle size, the more difficult it gets to measure the SSD state accurately.

A solution to the problem with these fine materials has been proposed by *Zhao et al*, by determining the water absorption for each size fraction separately. Water absorption has been found to correlate nicely with mass loss at 475 °C. This mass loss is associated with the cement content of a material, because the water bound in hardened cement paste will evaporate around this temperature (Section 4.3.1). The water absorption of the particle sizes from 0.5 to 4 mm is measured with the IFSTTAR method, and the resulting regression line makes it possible to extrapolate the water absorption of the fine particles (Figure 4.7). The size distribution, determined in Section 4.2.1, then permits to calculate the water absorption of the 0/4 mm bulk.

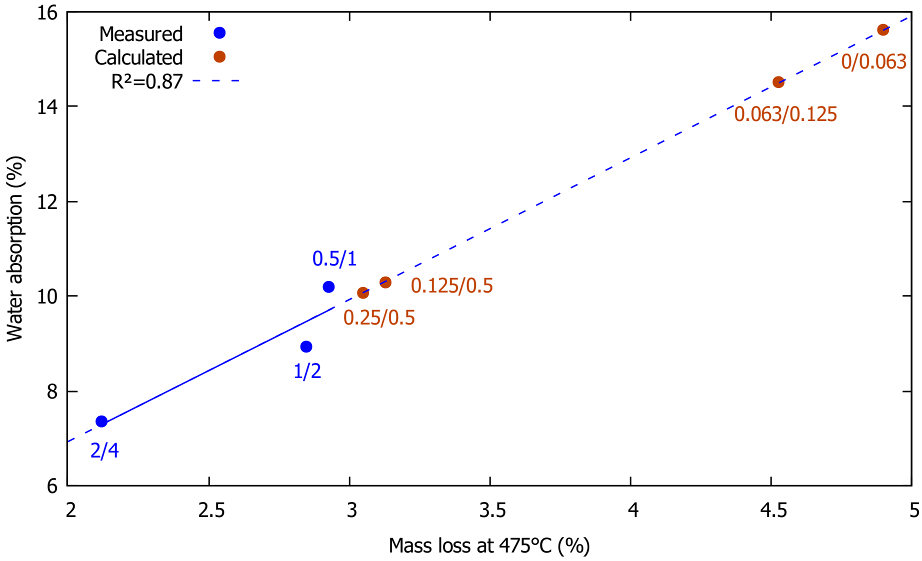


Figure 4.7: An example of how the water absorption of 0/4 mm aggregates is determined with the extrapolation method. The particle sizes in blue have been measured with the IFSTTAR method, the orange ones are calculated via the resulting regression line.

As an illustration, the 3 mentioned techniques have been applied on aggregate B. Table 4.3 shows how the extrapolation method yields a value between the standard and the IFSTTAR method. In terms of maniability, this value also seemed the most correct [45].

Norm EN1097-6	IFSTTAR n°78	Extrapolation
5.1 %	13.2 %	8.9 %

Table 4.3: The three methods of water absorption determination, applied on aggregate B.

The extrapolation method was then applied in triplicate for all (industrial and reference) aggregates (Figure 4.8, Table 4.4). The technique worked really well for a pure crushed concrete, and also obtained good results for most industrial FRA. Only two of them showed a weak correlation with the mass loss at 475 °C: A and C.

The water absorption of the coarse recycled aggregates could be measured without issues by the IFSTTAR method, and is also given in Table 4.4.

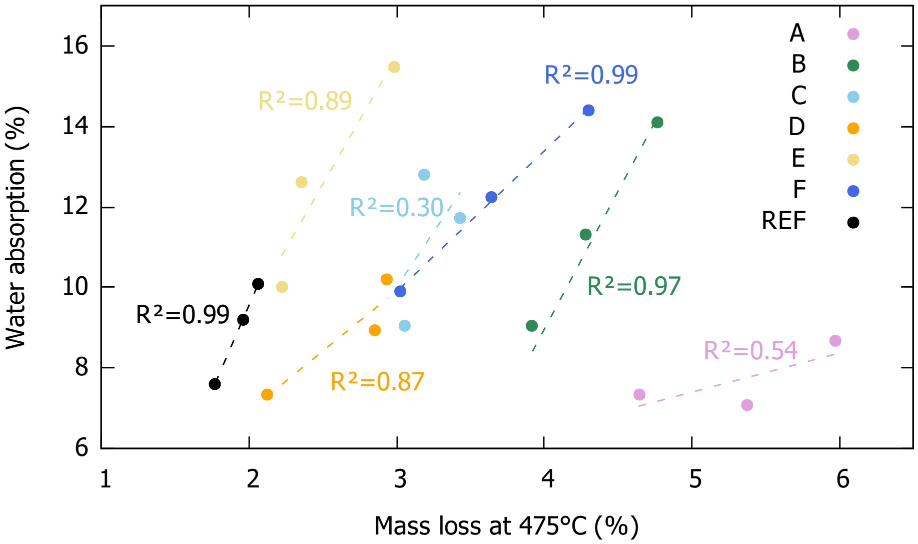


Figure 4.8: A summary of the correlation between the water absorption and mass loss at 475 °C for the coarser particles of FRA. This correlation was used to calculate the water absorption of the 0/4 mm fraction.

RA	WA (%)
A	6.1
B	8.9
C	11.5
D	10.6
E	14.6
F	13.0
REF	9.8
CRA	3.2

Table 4.4: The water absorption of all RA, for FRA determined by the extrapolation method and for CRA determined by the IFSTTAR method.

4.2.3 Density

The density of an aggregate is an important requirement to determine its total volume in a mix. Different types of densities can be measured. The apparent density ρ_{app} of a material is its mass per unit of volume, but without bringing into account the porosity of the grains. This value is determined with fixed-volume pycnometers according to standard EN1097-6.

The particle density ρ used hereafter to determine certain volumes of RA is calculated by equation 4.2. The porosity P is directly related to the amount of water an aggregate envelope holds in its SSD state, and is defined in equation 4.3.

$$\rho = \rho_{app}(1 - P) \tag{4.2}$$

$$P = \frac{WA}{WA + \frac{1}{\rho_{app}}} \tag{4.3}$$

The resulting particle densities, based on the water absorptions determined in section 4.2.2, are summarized in Table 4.5.

RA	particle density (g/cm^3)
A	2.14
B	2.10
C	1.99
D	2.00
E	1.97
F	1.96
REF	1.95
CRA	2.38

Table 4.5: The SSD-based particle density of all FRA samples, and the CRA.

4.3 Chemical characteristics

4.3.1 Cement content

The mass loss at 475 °C that is used in the determination of the water absorption, is a value that indicates the cement paste content of a sample. The water bound to hydrated cement will release at this temperature (Equations 4.4 and 4.5). To measure this value, FRA are ground until they pass a 200 μm sieve and dried at 105 °C. They are then placed, in triplicate, in crucibles in an oven and their weight difference between 105 and 475 °C is recorded.

$$Ca(OH)_2 \xrightarrow{T} CaO + H_2O \tag{4.4}$$

$$C - S - H \xrightarrow{T} C - S + H_2O \tag{4.5}$$

This mass loss for the recycled aggregates is pictured in Figure 4.9 for the 0/4 mm fraction, and in Figure 4.10 per particle size. For most sources of FRA the smaller size fractions contain more cement.

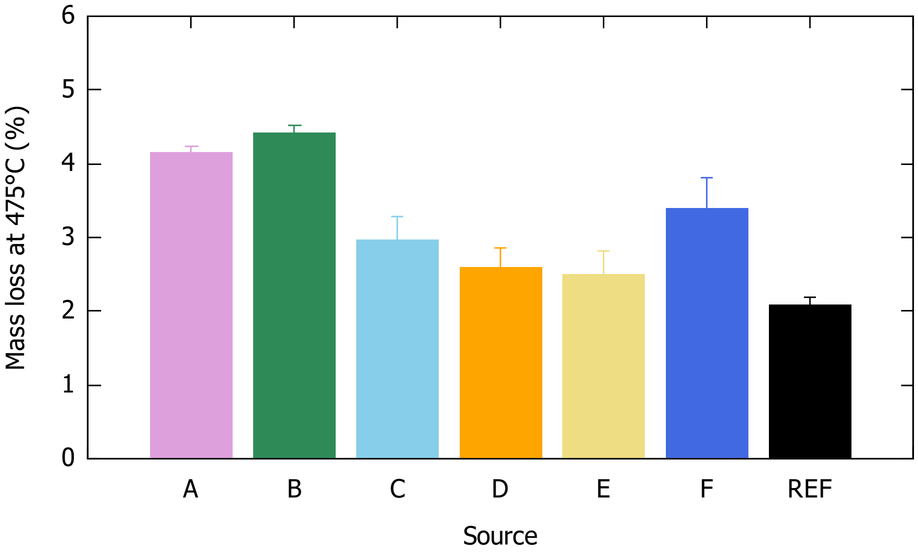


Figure 4.9: The mass loss at 475 °C for the 0/4 mm aggregate samples.

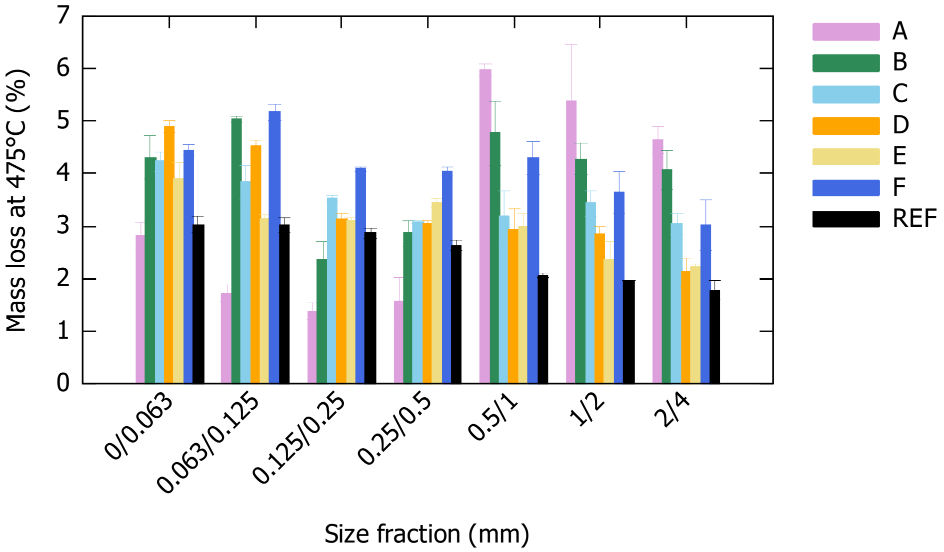


Figure 4.10: The mass loss at 475 °C per size fraction.

4.3.2 Water soluble sulfates

Only water soluble sulfates participate in the sulfate attack reaction. Standard EN1744-1 lays out the way to determine their concentration in either natural or recycled aggregates [126]. For recycled aggregates, it specifies to extract the sulfates in hot water, filter them, and buffer at a neutral pH. They are then precipitated with BaCl and quantified spectrophotometrically.

In this thesis, the water soluble sulfates are determined in a slightly different way. Firstly, the sulfates are brought into solution at room temperature and not at 60 °C, because in this context they originate from gypsum which exhibits a retrograde solubility. Secondly, the sulfate concentration was not determined via precipitation but via ion chromatography which is an easier, safer and more precise analytical technique.

2 grams of FRA were placed in 250 mL of demineralized water and stirred for 1 hour at room temperature. A sample was passed trough a 0.45 μm syringe filter, and tested for its sulfate concentration by ion chromatography (Dionex ICS-3000). These tests are all done in triplicate.

This method was first validated for different parameters, by mixing a certain amount of gypsum powder into a sample of FRA. Figure 4.11 shows that gypsum is dissoluted quickly enough to justify a time of 1 hour. Figure 4.12 shows that the method is very accurate, and only a slight underestimation for high gypsum contents.

Using this method, the water soluble sulfates in the used FRA samples were determined (Figure 4.13). Five out of six industrial samples surpassed the 0.2 % limit posed in standard EN206. The reference FRA, which is not contaminated, still contained 0.18 % of sulfates which originated from cement.

The sulfates shown in Figure 4.13 were not evenly divided over the different size fractions. Figure 4.14 shows how in most cases the sulfates are predominantly present in the finer particles. The finer particles are known to contain more cement paste which can in part explain the higher sulfate content. The brittleness of gypsum plaster is another reason why - after the demolition, crushing and handling - more sulfates are present in fine particle sizes.

The water soluble sulfates of CRA were measured in the same way. Similar to the reference FRA, this aggregate was uncontaminated and the sulfates here originated from cement. The low cement paste content of CRA lead to

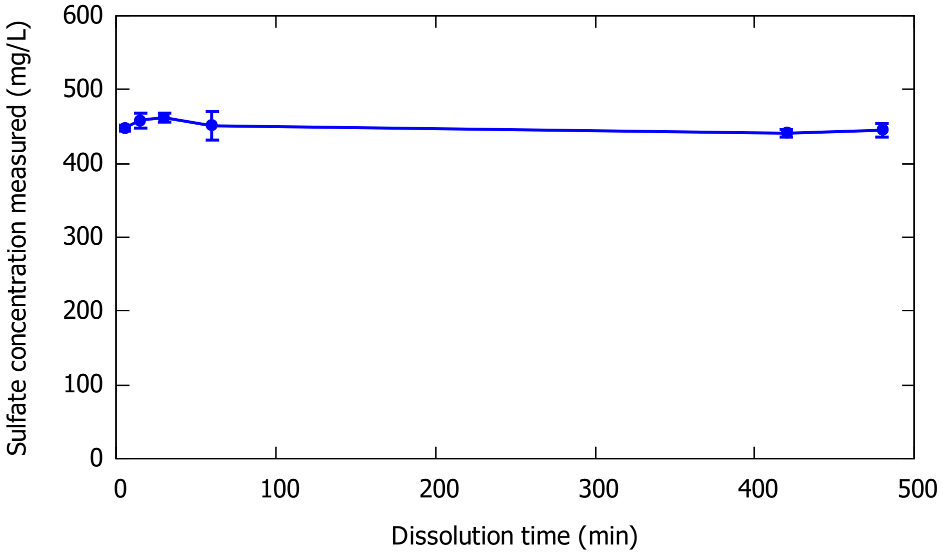


Figure 4.11: A leaching time of 1 hour was largely sufficient to take an accurate sample.

a sulfate content that was several orders of magnitude smaller than in found in FRA (Figure 4.15).

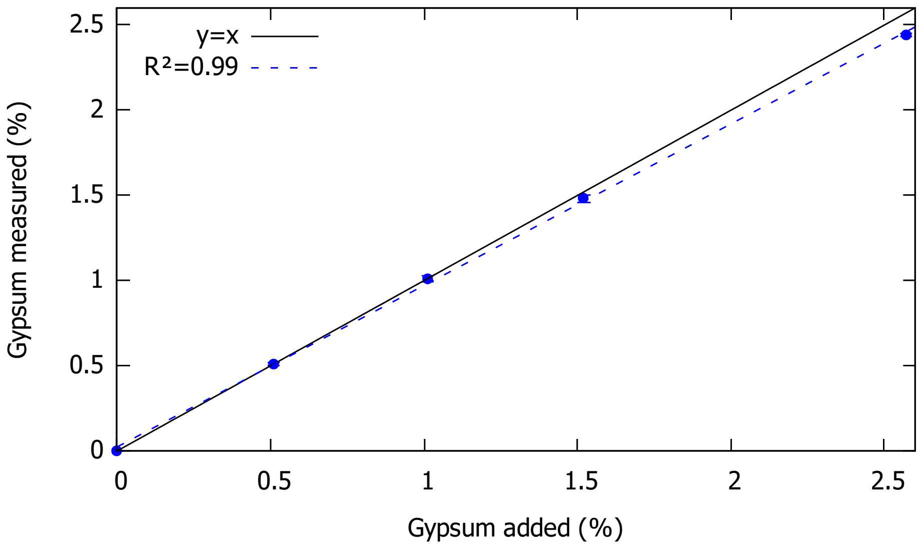


Figure 4.12: The sulfate determination technique shows to be very accurate and precise, especially for low gyspum contents.

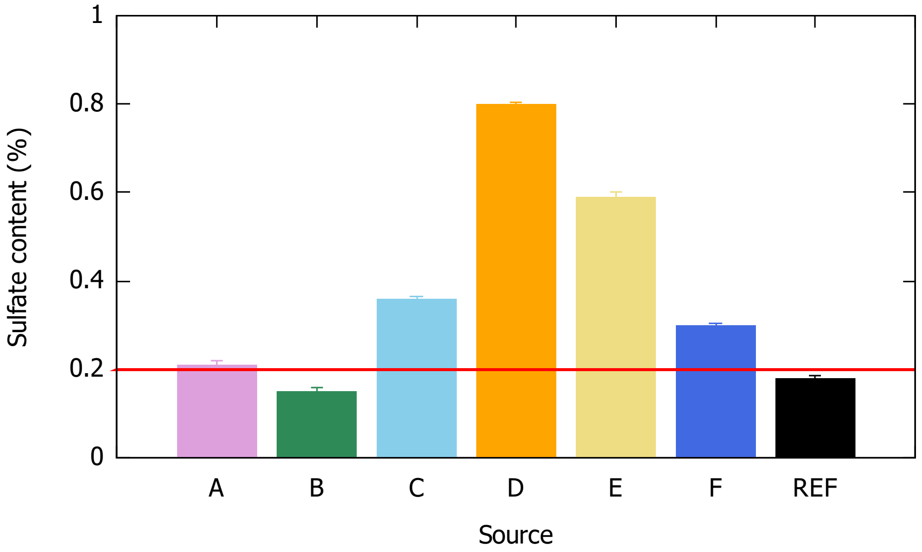


Figure 4.13: Sulfate content (by mass of aggregate) of the 0/4 mm fraction, in 5 out of 7 cases surpassing the 0.2 % limit posed in EN206.

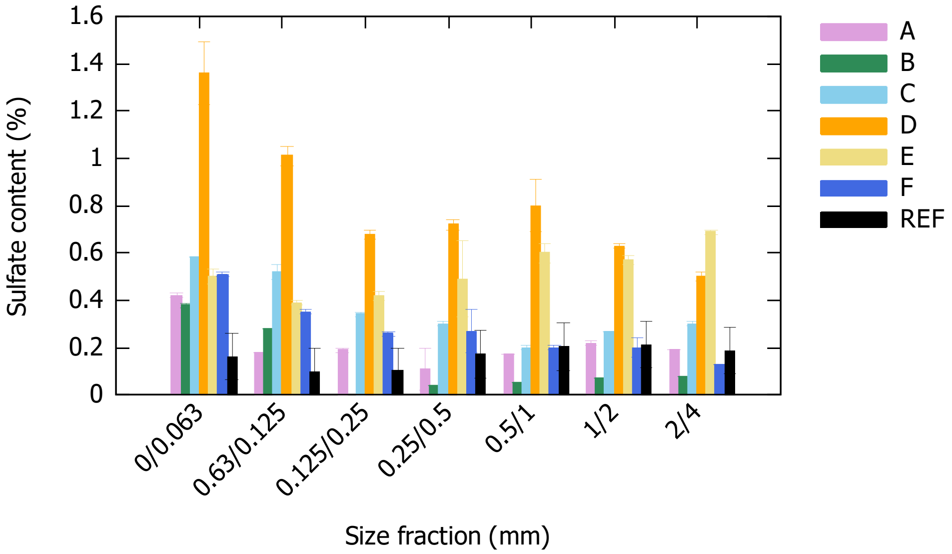


Figure 4.14: The distribution of the total sulfate content over the size fractions of the aggregates.

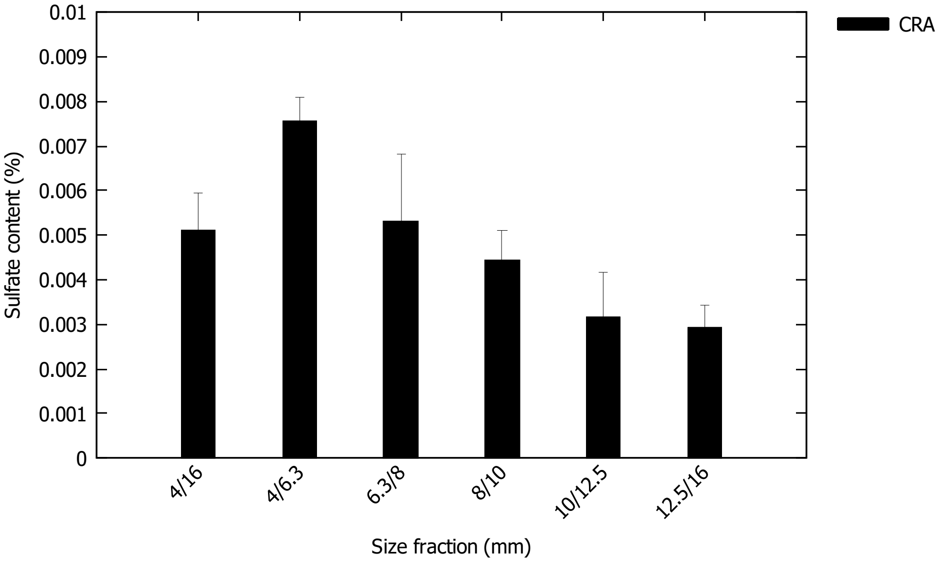


Figure 4.15: The sulfate content of CRA in the 4/16 bulk, and per size fraction.

5 | Mix design

In this chapter, the mixing procedure and materials for mortars and concrete are discussed.

5.1 Used materials

In some mixes, aggregates were manually contaminated with gypsum. This gypsum is a $CaSO_4.2H_2O$ powder (D50 13 μm) obtained from VWR Chemicals.

The cement types used in the following tests were a CEM I 52.5 N and in one case a CEM I HSR, both from Holcim in Belgium. A large quantity of the same batch was ordered and kept in airtight containers, to be used throughout all experiments. The chemical characteristics of both cements are shown in Table 5.1.

Next to recycled aggregates, natural limestone aggregates were sometimes used in a mix to act as a reference aggregate.

5.2 Mixing procedures

Experiments were mostly done on mortar bars to limit the quantity of necessary materials and storage room for the numerous samples. To evaluate the conclusions made on these mortars, an experimental series on concrete was also conducted afterwards.

5.2.1 Mortars

According to EN196-1, a standard mortar contains 1 part cement for 3 parts sand, and has a W/C ratio of 0.5 [127]. To account for their difference in density, a volumetric equivalent of FRA was added to the mortars instead of a mass equivalent, to keep the aggregate envelope volume constant.

	CEM I 52.5 N	CEM I HSR
CaO	64.3	64.6
SiO_2	18.3	21.4
Al_2O_3	5.2	3.7
Fe_2O_3	4.0	4.6
MgO	1.4	0.8
Na_2O	0.32	0.27
K_2O	0.43	0.40
SO_3	3.5	2.5
Cl^-	0.06	0.06
LOI	2.3	1.3
C_3A	6.6	2.4
C_4AF	12	14
C_3S	61.9	68.8
C_2S	11.2	9.4

Table 5.1: Chemical composition (mass%) of the used cement types

	Cement	Aggregate	Water
Normalized aggregate	450	1350	225

Table 5.2: Standard mortar composition, in g, as described in EN196-1 [127]. When switching to a recycled aggregate, its density, size distribution and water absorption needed to be taken into account.

To compensate for the increased water absorption of FRA compared to the normalized sand, the FRA were always presaturated with their absorbed water and 10 % of the mixing water. This technique to improve the properties of mortars made with recycled aggregates has been proposed by many researchers in Chapter 1. For the reference FRA, which contained a lot of cement, this week of presaturation ensured that this cement started to harden. As a consequence, the size distribution of the FRA on mixing day was slightly different than the one measured in section 4.2.1 (Figure 5.1): the presaturated FRA contained less fine particles.

When different sources of aggregate were used in an experimental series with the intention of comparing the results to each other (Chapter 7 and 9), their size distribution was adapted to resemble one another. This way, a difference in swelling results could not be due to particle sizes. In the case of the reference FRA the size distribution *after* presaturation was considered, not the one from before.

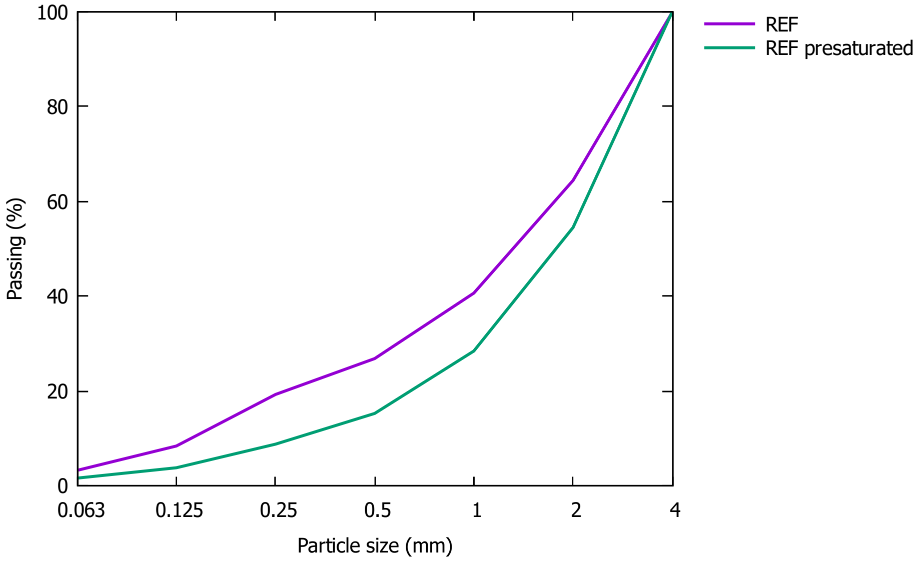


Figure 5.1: Presaturating the reference FRA hardened its residual cement particles. The size distribution of the FRA on mixing day changed to contain less fines.

If gypsum was used to contaminate the mix, it was added to cement. The size distributions of cement and the gypsum powder were similar and this ensured a homogeneous mix. Nevertheless, sulfate/gypsum concentrations were always expressed as a mass% of the aggregate.

The standard mixing protocol from EN196-1 was followed (Table 5.3). The mixing water mentioned here needs to be substracted with the percentage that was used for presaturation.

Action	Speed	Time	Total time
Add cement and mixing water, mix	1	30"	30"
Add aggregates (0/4 mm), mix	1	30"	1’
Mix	2	30"	1’30"
Rest	0	1’30"	3’
Mix	2	1’	3’

Table 5.3: Mortar mixing procedure in function of mixer speed as described in EN 196-1 [127].

After this mixing procedure, the mortar is tested for slump according to EN196-1. The 4x4x16 cm moulds, coated with demoulding oil, are filled halfway and compacted on a shocking table. They are then topped up with mortar and compacted again. All samples were cured for 24 hours in a humid environment at room temperature before demoulding.

5.2.2 Concrete

The design of concrete compositions, either the original concrete that yielded the reference recycled materials or the concrete mixes in Chapter 9, was done with the Dreux-Gorisse method.

7x7x28 cm bars were cast for weekly swelling tests, and 15x15x15 cubes for the periodic mechanical measurements.

The mixing procedure for concrete is largely the same as for mortar. Because it takes a lot of time to introduce the large quantities of aggregates, they are first placed in the mixer after which cement is added. The mixing protocol is shown in Table 5.4. The slump of the concrete is checked with the help of an Abrams cone according to EN12350-8 (Figure 5.2). Depending on the envisaged slump value, sometimes it was necessary to add a little more superplastifier and mix for another several minutes. Because the volume of a sample is known, the density at a fresh state can easily be determined by weighing filled moulds.

Action	Time	Total time
Add aggregates (0/16 cmm), mix	30"	30"
Add half of the mixing water, mix	2'	2'30"
Rest	2'	4'30"
Add cement, mix	30"	5'
Add second half of mixing water and superplastifier, mix	1'30	6'30"

Table 5.4: Concrete mixing procedure in function of mixer speed.

5.3 Sulfate contents of standard mixes

A few preliminary mixes were made to check which sulfate contents had visible results, and could thus be used in further mixes. In this sulfate series, the comparison between recycled and natural aggregates was also made. The aggregates in these samples were contaminated with 0, 0.5, 1 and 5 mass% of gypsum respectively. Table 5.5 shows with which sulfate concentration

Figure 5.2: Testing the slump of a concrete mix with an Abrams cone

this corresponds, taking into account that FRA already contained 0.18 % of sulfates.

$CaSO_4.2H_2O$ (%)	SO_4^{2-} (%) FRA	FNA
0	0.18	0
0.5	0.47	0.29
1	0.76	0.58
5	3.08	2.90

Table 5.5: The mass% of gypsum in the aggregates corresponds to different actual sulfate concentrations, due to the residual sulfates in FRA originating from cement.

The mixing protocol described in Section 5.2 was followed, and the length measurements will be explained in Section 6.1. The swelling results can be seen in Figure 5.3 for the reference FRA, and Figure 5.4 for natural aggregates. For FRA, only the highest sulfate concentration gave a visible swelling result. The length change also stabilizes already after one month of testing. This is in contrast with the tests on natural aggregates, where more moderate amounts of sulfates also caused a significant swelling, and the expansion did not yet reach its maximum point after 7 months.

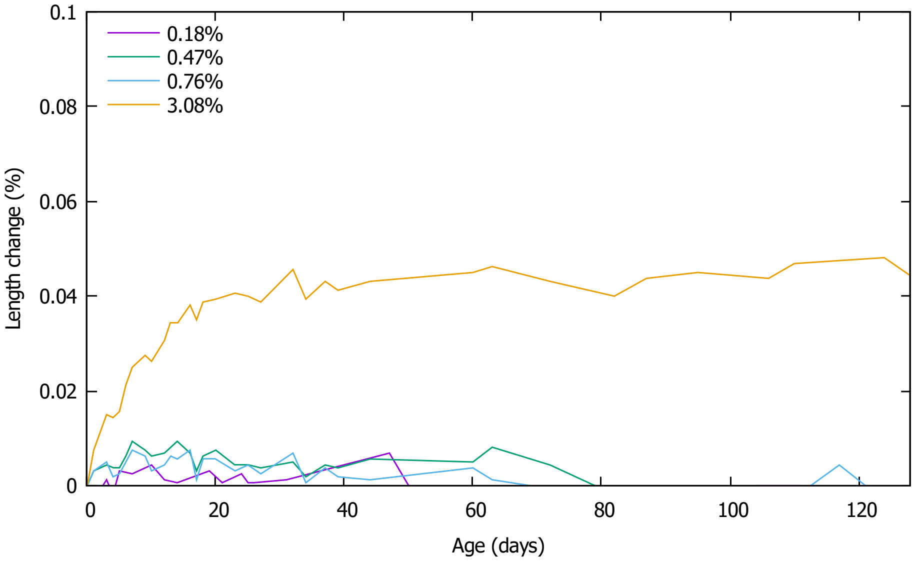


Figure 5.3: Swelling tests on mortars with FRA and varying gypsum contents.

With these swelling results in mind, a gypsum content of 5 % by mass of the aggregate was chosen for other preliminary tests, and for the parameter variations in Chapter 8.

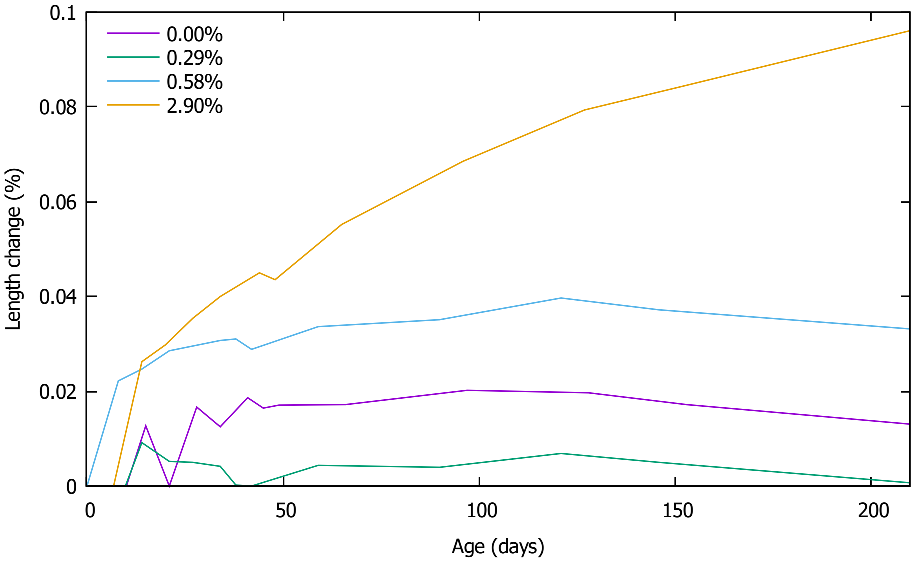


Figure 5.4: Swelling tests on mortars with FNA and varying gypsum contents.

6 | Monitoring of mortars and concrete

6.1 Swelling tests

A digital length comparator is used to measure the length of a mortar or concrete bar accurately up to 0.001 mm, relative to a reference rod. This reference rod is made of Invar - an alloy with a uniquely low thermal expansion coefficient - and does not expand or contract depending on temperature. The measurement works by fitting the bottom and top anvils of the apparatus into studs. These studs were specifically cast into the mortar or concrete during fabrication, by attaching them to the mould and pouring the material around it (Figure 6.1).

Figure 6.1: To register the length of a mortar or concrete sample with a length comparator, measuring studs need to be placed into the bars during fabrication.

This relative length change was measured weekly at early ages, and monthly when the swelling started to stabilize. To obtain the most accurate results, the pins are cleaned before performing the measurement, and the result is always registered when the bar is in the same position (writing in the front and right side up). Similarly, the Invar reference bar also has a front and top side. If the start of the hydration reaction is seen as day 0, the first length measurement (after demoulding) is carried out on day 1.

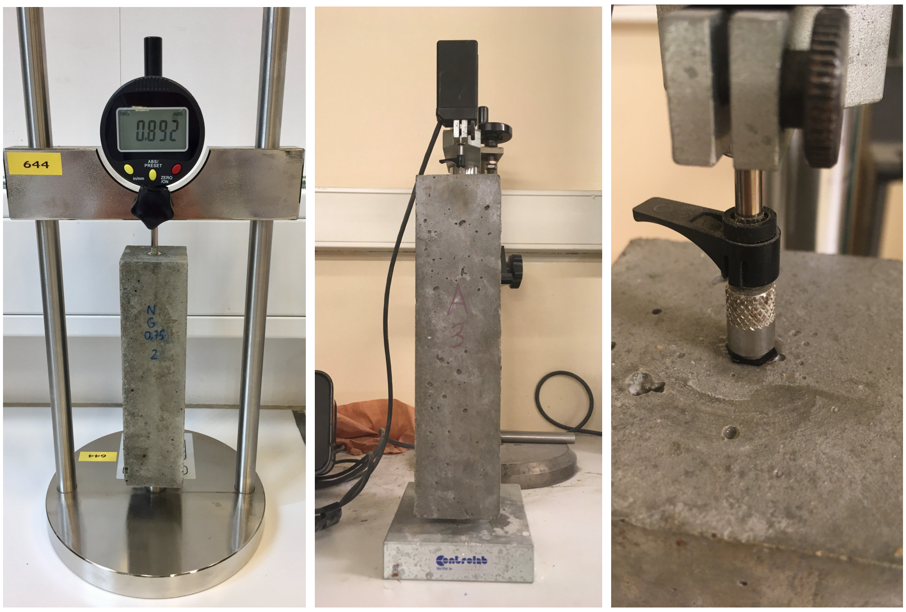


Figure 6.2: A swelling test on a mortar (4x4x16 cm) and a concrete (7x7x28 cm) bar respectively. The length value, relative to a reference rod, is measured by fitting the anvils into the measuring studs.

Next to a length change, the swelling reaction can also be recorded by the relative mass change of a sample. The bars were weighed after dabbing off excess water, before the length measurements. While the normal mass gain of samples submerged in water is about 1 %, for DEF experiments an increase of up to 5 % has been found [73]. However, different researchers found that a mass increase only correlates with length change for high swelling amounts [96].

A test often used to assess the internal damage caused by a swelling reaction is based on the propagation of ultrasonic waves trough the material [128, 129]. Two different methods have been used depending on available techniques, but the principle of the two tests stays the same. The experiments of Chapter 8 made use of the wave *velocity* (m/s), by measuring the time it takes for an ultrasonic wave to travel trough the mortar and be registered by a receiver. Dividing by the traveled distance gives the wavespeed. In Chapter 7 and 9, the *resonance frequency* (KHz) of a mortar or concrete bar is determined by measuring the vibrations caused by the impact of a hammer (Figure 6.3).

Sulfate attack is known as a slow process and most authors mentioned in Chapter 1 monitored their samples for a year or more. As can be seen on the

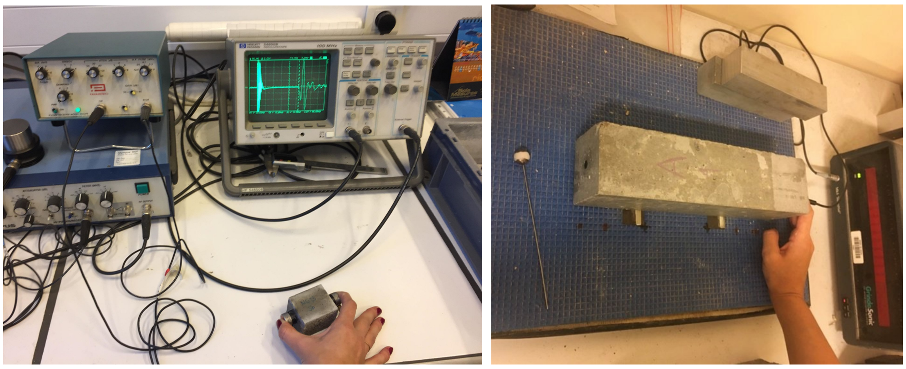


Figure 6.3: Assessing possible internal damage with 2 methods: the measure of wave velocity (left) and the measure of resonance frequency (right).

preliminary tests in section 5.3 and 6.2, the reaction for recycled materials goes noticeably quicker and a testing time of 6 months would be justified.

6.2 Storage

The storage of the mortar and concrete samples after curing was another point that could influence the swelling results. Results found in literature were often obtained by different storage conditions and sometimes by protocols trying to accelerate the reaction. Because sulfate attack is a slow reaction, a testing protocol where the response would be exaggerated and/or accelerated could be interesting. Three options were considered here, tested for mortar bars made with the reference FRA contaminated with 5 mass% of gypsum.

In a first procedure the mortar bars are placed in a conditioned chamber at 100 % humidity. The samples have access to the water needed for the sulfate attack reaction, but are not in direct contact with it so the sulfates cannot leach.

A second option would be a storage in water, where there is a possibility that sulfates are leached into the storage water and the sulfate concentration of the mix changes. To limit leaching when submerged, mortar bars are placed in very limited amounts of water, which are not changed during the testing time. Ion chromatography on samples of this storage water confirmed that the loss of sulfates into this solution was small. This procedure is the one most often found in literature and seems to give elevated swelling results.

The third treatment plan consisted of the drying/wetting cycles proposed in method n°66 by the *Laboratoire des ponts et chaussées* to assess the reactivity of concrete towards internal sulfate attack [124]. This method is designed for the DEF reaction and contains a curing program at high temperature which was not used here, only the wetting/drying cycles they propose before a storage in water were adopted. These cycles consisted of a placement in the oven at 38 °C for a week, and a submersion in water at room temperature for a week. This is then repeated once more. The temperature change of these cycles is represented in Figure 6.4, together with the length of the mortar during this treatment.

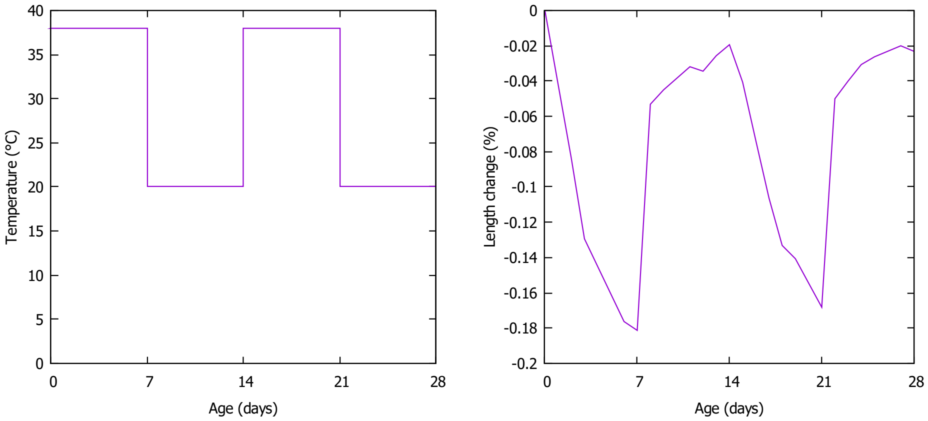


Figure 6.4: The wetting/drying cycles, and the length change of a mortar with FRA and 5 mass% of gypsum during these cycles.

After these 28 days of drying/wetting, the mortars are placed into water in the same way as the second procedure, where their length is monitored for the remainder of the test.

Figure 6.5 summarizes the results of the three tested storage protocols. For exactly the same mortar compositions, different expansions were found. A storage in water gave the highest results and - knowing that sulfate leaching was negligible - was thus used in the experiments in Chapter 7, 8 and 9.

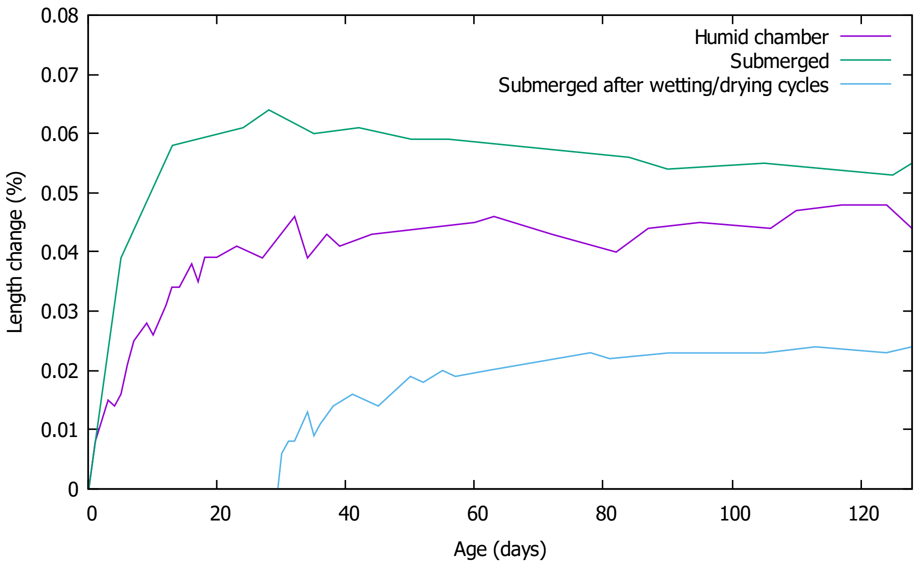


Figure 6.5: The swelling results of mortars made with FRA and 5 mass% of gypsum for the three tested storage protocols.

6.3 Periodic tests

At ages of 7, 28, 90 and 180 days of curing, mortar bars and concrete cubes are tested in triplicate for various hardened properties.

Compressive strength was universally used by authors to assess the quality of a mortar or concrete made with RA, and to follow its development (Chapter 1). The compressive strength was measured according to standard EN196-1.

On mortars, either the 3-point flexural (EN196-1) or tensile (NBN B15-211 [130]) strength were also determined. Both tests are based on the yield stress of the material.

The porosity of the mortars or concretes at these specific ages was measured by Mercury Intrusion Porosity. The porosimeter - a Mecromeritics Autopore IV - forces mercury into the voids of a 1 cm^3 porous substrate, at increasingly higher pressures ranging from 0 to 200 MPa. The porosity, pore size distribution, and pore volume can be characterized. This test was carried out to check whether pores would get filled up with ettringite over the course of the reaction.

From Chapter 2, it could be seen how ettringite can manifest in different microstructural forms: the location (cement paste, cracks, ITZ, pores, ...) and morphology of ettringite can give useful information about the mechanism of its formation. A microstructural analysis for the mortars in Chapter 8 was carried out at a sample age of 90 days. The samples were prepared according to routine procedures of embedding and polishing [131] using a 2020 resin from Huntsman and MD System from Struers with water-free diamond pastes and lubricants. Images in scanning electron microscopy were obtained on a Hitachi S-4300/SE-N. These images were coupled with Energy-dispersive X-ray spectroscopy (EDS) analyses to identify certain minerals or to map the distribution of sulfur throughout the sample.

Conclusion

From the literature study, the cement paste content, water absorption, density and sulfate contamination were proposed as important characteristics of FRA often hindering their valorization. These properties were determined, on industrial FRA as well as a reference material. This reference recycled aggregate was fabricated by crushing a standard concrete. A large variation in characteristics was found between FRA from different recycling centres, and even between different FRA batches from the same source. The sulfate contaminations in industrial sources of FRA were significant and surpassed the maximum allowable limit of 0.2 %. The reference FRA that was not contaminated also contained a certain concentration of sulfates, which must have come from its residual cement content.

Mortar and concrete compositions and mixing procedures were described in Chapter 5. A gypsum content of 5 %, corresponding to 3.1 % of sulfates, showed the most visible swelling results, and will be chosen as the standard value from here on out. An important distinction could be made between recycled and natural aggregates: mortars made with contaminated *natural* aggregates showed more variation in their swelling results, corresponding to their sulfate content. The swelling reaction also took longer: while the mortar with recycled aggregates had stabilized after one month, the one with natural aggregates continued swelling for at least 200 days.

The different characteristics - like length, compressive strength, and microstructure - that will be used to follow the development of internal sulfate attack in these samples were defined. A storage in water and no use of heat treatments or accelerated aging protocols was explained and justified by several validation tests in Chapter 6.

Part III

Experimental work

Introduction

After the characterization of the used materials and some preliminary tests, three experimental campaigns were envisaged. The following chapters are presented in the form of research articles, written about each of those three parts. They are supplemented with a short introduction to relate them to the thesis objectives, and an annex to show some additional results.

The first article, Chapter 7, researches the potential valorization of industrial FRA. It has been submitted to Materials.

In Chapter 8, several parameters that could influence - either negatively or positively - the amount of expansion due to internal sulfate attack were identified. It has been submitted to Construction and Building Materials.

The different proposed sulfate limits, and the parameters that proved to be relevant in Chapter 8, are tested on concrete in Chapter 9. It has been submitted to Journal of Building Engineering.

7 | Valorization of industrial contaminated FRA

This Chapter researches the valorization potential of FRA. As a starting point for this research, the first important issue was to determine the range of sulfate contents that are actually contaminating 'real-life' industrial FRA. Do they regularly surpass the maximum limit of 0.2 %? What is the variability between recycling plants or even different batches from the same plant?

A second matter was the influence of FRA on the properties of cementitious materials. With the contamination levels of FRA known, which amount of expansion can they cause? Does the incorporation of FRA affect other characteristics of the material?

To answer these questions, the FRA that were collected from recycling centres, and who were described and characterized in detail in Chapter 4, were used as a replacement for natural aggregates in mortars. As a comparison, mortars were also made with the reference FRA and natural aggregates. They were contaminated with the same amount of gypsum found in the industrial samples. To put the swelling results in perspective, one mortar was made that contained the token amount of 3.1% of sulfates, to show significant swelling. The length change and mechanical properties of the mortars were monitored.

While the industrial samples did show the negative characteristics that are often associated with FRA, the mortars were not affected in a major way. Most importantly, they did not show an important swelling reaction. This does not mean that sulfate attack caused by FRA doesn't exist: as proven by the very contaminated mortar, it just simply needs more sulfates than assumed by the norm.

materials

MDPI

Article

Valorization of Fine Recycled Aggregates Contaminated with Gypsum Residues: Characterization and Evaluation of the Risk for Secondary Ettringite Formation

Charlotte Colman [1,2,*], David Bulteel [1], Sébastien Rémond [3], Zengfeng Zhao [2] and Luc Courard [2]

[1] Laboratoire de Génie Civil et géo-Environnement, Université de Lille, IMT Lille Douai, ULR 4515-LGCgE, F-59000 Lille, France; david.bulteel@imt-lille-douai.fr

[2] Urban and Environmental Engineering, GeMMe Building Materials, University of Liège, 4000 Liège, Belgium; zengfeng.zhao@uliege.be (Z.Z.); luc.courard@uliege.be (L.C.)

[3] Laboratoire de Mécanique Gabriel Lamé (LaMé), Université d'Orléans, 45100 Orléans, France; sebastien.remond@univ-orleans.fr

[*] Correspondence: charlotte.colman@uliege.be

Received: 2 October 2020; Accepted: 26 October 2020; Published: 30 October 2020

Abstract: Fine recycled aggregates (FRA) (0/4 mm) are up to now not valorized on a high enough level because of characteristics like an elevated water absorption, higher fines content, and the presence of contaminations. Leftover gypsum residues from the construction site can cause internal sulfate attack when FRA are incorporated into new structures. Concern about this deteriorating reaction plays an important role in the rejection of FRA. In this study, samples of FRA from different recycling centers were characterized and incorporated into mortars. They were then subjected to swelling tests in order to evaluate the development of sulfate attack. Reference materials with different amounts of sulfates were used as a comparison. Results showed a variable sulfate content in industrial FRA, depending heavily on the source of the materials. In all but one case, the total amounts surpassed the acceptable sulfate contents specified in the European standard EN 206, meaning the FRA would be rejected for reuse in concrete. Nevertheless, swelling tests demonstrated that these contamination levels did not pose a risk for sulfate attack. These results indicated that the incorporation of FRA leads to acceptable mechanical performances and that the sulfate limit could be reviewed to be less strict.

Keywords: fine recycled aggregates; sulfate attack; construction and demolition waste; secondary ettringite formation

---

1. Introduction

The building sector is infamously known as the 40%-industry, using 40% of global energy and resources, and is responsible for one-third of our greenhouse gas emissions [1]. Nowadays, 1 m^3 of concrete, corresponding to more or less 2 tonnes, is being produced per person per year. The climate impact of the construction industry can be reduced by 77% by core material separation and its recycling or reuse [2]. Accounting for approximately 25–30 % of all waste generated, Construction and Demolition Waste (C&DW) is one of the heaviest and most voluminous waste streams in the EU and as such has been identified as a priority waste stream by the European Union [3]. C&DW consists of numerous materials, including concrete, bricks, gypsum, wood, glass, metals, plastic, and excavated soil [4]. The major fraction of C&DW however is mineral waste, which has a high potential for recycling and reuse [5]. One of the objectives posed in the Waste Framework Directive (WFD) of the European Union (2008/98/EC) is to reuse a minimum of 70% of C&DW by 2020 [6], either by backfilling as road bases or—the most preferrable high-quality application—reusing them in the form of Recycled Aggregates (RA). RA are reprocessed from C&DW and can be used in mortar or concrete as a replacement for natural aggregates (NA) [7,8]. This practice reduces the amount of debris disposed of in landfills, reduces the rate of natural resource depletion, and provides energy, cost and transport savings [9]; 1.7 tonnes of these recycled aggregates are produced per person per year in Europe, waiting to be valorized [10].

The use of coarse recycled aggregates has been shown to produce concrete with acceptable properties [11–15]. Fine recycled aggregates (FRA), however, have more nefarious characteristics and their incorporation into a new concrete is up to now generally avoided [16,17]. These properties include—among others—a higher water absorption [18,19]; a lower density; and the presence of contaminations from the construction or demolition site such as plaster, bricks, wood, etc. [20,21]. Existing studies often focus on mechanical properties, and research is needed on the durability aspects of the incorporation of FRA.

Gypsum ($CaSO_4 \cdot 2H_2O$) is used in the construction sector firstly as an addition to Portland cement, to regulate the setting time of cement and prevent a flash set [22]. Besides that, gypsum is the major constituent of plaster walls in buildings. Demolished concrete particles contain adherent cement and plaster, which will lead to a certain sulfate content in recycled aggregates after the crushing process. The effective sulfate concentration in RA will of course depend on the type of the source concrete but most stocks of RA in recycling centers are mixed from different sources and demolition sites: a sulfate contamination is a very realistic concern for RA. Larger concrete and gypsum particles can be separated from each other based on a difference in color [23] or density [24], but these techniques are not applicable on the smallest size fractions. Especially in FRA, gypsum is an important contaminant to be considered: the water-soluble sulfates coming from the gypsum particles strongly limit their valorization potential [25].

Sulfate attack is a deteriorating process where sulfates dissolve in water and react with aluminate hydrates in a hardened cement paste to form secondary ettringite. It is assumed that this mineral exerts a pressure on its surrounding cement paste and thereby causes a volumetric deformation [26]. Macroscopically, the concrete structure will show swelling behavior and the formation of (micro)cracks. Primary ettringite is a normal hydration product in the cement paste: it is only secondary ettringite, formed in an already rigid cement matrix, that risks causing a swelling reaction.

A distinction can be made between different types of sulfate attack. External sulfate attack happens when the sulfates diffuse into the concrete from an aggressive environment [27]. Another reaction called Delayed Ettringite Formation (DEF) occurs when primary ettringite is destroyed by high curing temperatures and formed anew in a hardened cement paste. The sulfates in this case come from cement, an internal source [22,26,28] .

While external sulfate attack and Delayed Ettringite Formation are well researched and understood, the reaction caused by the presence of gypsum in FRA is not. The gypsum residues contaminating FRA are another internal source of sulfates and unlike with the DEF reaction, high curing temperatures are not needed to observe the swelling effect of ettringite formation. The term "secondary ettringite formation" will be used to distinguish this reaction from DEF.

To keep the risk for secondary ettringite formation at a reasonable level, the current water soluble sulfate limit in coarse recycled aggregates is established at 0.2% by EN 206 [29], with no specific mention of FRA. The conclusions of recent durability studies indicate a higher level should be made possible [30], specifically up to contents of 0.3% [31].

In this study, different sources of FRA were characterized for their sulfate content, water absorption, and size distribution; this provided information about the variability in characteristics between industrially available FRA. The materials were then incorporated into mortars. Swelling tests performed on these mortars indicated whether or not the found contamination levels did indeed cause a deterioration. Ultimately, these results might provide a better understanding of the long term effects of sulfate attack in the context of construction and demolition waste and will promote the use of these recycled materials in the building sector.

2. Materials and Methods

Six samples of recycled aggregates were collected from recycling centres in Belgium, of which only the 0/4 mm fraction was characterized and used. They are named "A" to "F". In total, 3 recycling plants were sampled: of the six FRA samples, four were from different batches of the same recycling plant. As a reference sample, a pure FRA was also made in the laboratory by fabricating and crushing a standard concrete. This sample is called "REF". The composition of this original concrete was designed to obtain a consistency class S3 and strength class C30/37, and was made with CEM I and limestone aggregates. After 90 days of curing, this concrete was crushed by a jaw crusher and the resulting 0/4 mm fraction was used as FRA. The use of this "model" FRA as a reference gave exact control of the chemical composition of the materials and removed any possible variability or contamination at the level of the aggregates by chlorides, organics, etc. The results on FRA are compared with those from a natural limestone aggregate called 'NS'.

2.1. Characterization

All FRA samples were characterized for their size distribution according to EN 933-1 [32].

Only water-soluble sulfates contribute to secondary ettringite formation. The procedure described in EN 1744-1 [33] for the determination of water-soluble sulfates in recycled aggregates was followed with two adaptations to the testing protocol. First, an elevated temperature to extract the sulfates was not used because gypsum exhibits a retrograde solubility [34]. Second, sulfate concentrations were measured with ion chromatography instead of spectrophotometry, which is an easier, safer, and more precise analytical technique [35].

Water absorption and particle density of the FRA were determined via the method described by Zhao et al. [18]. Characterization techniques for natural aggregates, described in EN 1097-6 [36], consistently underestimate the water absorption of FRA because of the fineness and agglomeration issues between the particles. The method, designed in response to this difficulty, by IFSTTAR [37] seems to overestimate the water absorption of FRA, but works well for particles in the 0.5/4 mm range. Thanks to an excellent correlation between the hardened cement paste content or mass loss at 475 °C and the water absorption, the water absorption of the fines can then be extrapolated. Using the water absorption of each size fraction (either measured for the coarser particles or calculated for the fines) is more accurate than using either of the two mentioned experimental methods for the whole 0/4 mm bulk [38].

2.2. Swelling Tests

The industrial FRA were used in the manufacture of mortars, to monitor their swelling over the course of 6 months. Three extra mixes were prepared to serve as reference samples:

- Two mixes that will compare the industrial FRA with either a natural aggregate (named "NS") and a pure crushed concrete (the reference FRA named "REF"). Both the natural and the recycled aggregate are manually contaminated with 0.5 mass% of gypsum. This 0.5% of gypsum corresponds to to 0.29% of sulfates, which reflects the sulfate contents found in industrial FRA. In the case of FRA, this manual contamination is in addition to the water soluble sulfates already found during the characterization, bringing its total sulfate content to 0.47%.
- One mix made with the reference FRA and a very high gypsum content of 5 mass%—corresponding to 2.9% of sulfates—to exaggerate the consequences of sulfate attack. Again, this manual contamination is in addition to the sulfates already present in this FRA, bringing the total sulfate content to 3.08%.

The gypsum used to contaminate the aggregates was a $CaSO_4{\cdot}2H_2O$ powder (D50 13 μm) obtained from VWR Chemicals.

In order to compare only the influence of the different sulfate contents of the sands, other variations between the different aggregate types were reduced as much as possible:

- To account for their difference in size distribution, all aggregates were recomposed to match the size distribution of the reference FRA. This adaptation caused a slight change in the total sulfate content, water absorption, and density. These new values were recalculated.
- To account for their difference in density, a volumetric equivalent of every aggregate was added to the mortars instead of a mass equivalent, to keep the aggregate envelope volume constant.
- To account for their difference in water absorption, all aggregates were pre-saturated one week before mixing, with their absorbed water and 10% of the mixing water. This assures the same amount of effective water in all mixes, proven to be an important factor in the swelling process [39].

The standard procedure described in EN 196-1 [40] for mortar fabrication was followed. A CEM 52.5 N from HOLCIM in Belgium was used for all mortars.

To follow the development of the internal sulfate attack reaction, the mortar specimens were subjected to different tests. The mass, length [41], and resonance frequency were recorded weekly to observe features of sulfate attack such as swelling and possible internal cracking. Length measurements were performed with a digital length comparator, which gives the length of a mortar bar accurately up to 0.001 mm, relative to an Invar reference rod. At 7, 28, 90, and 180 days the mortars were characterized mechanically for their flexural and compressive strength [40]. One sample that showed significant swelling was analyzed with XRD using a Bruker D8 Advance diffractometer according to the powder diffraction method with a Co $K\alpha_1$ radiation, sweep from 10° to 200° 2θ. Every described test was done for 3 replicate mortars.

3. Results and Discussion

3.1. Characterization

Of the six collected FRA samples, four were from different batches of the same recycling plant. Because of their small particle sizes, it was not possible to obtain a detailed composition of these materials. The industrial sources named these samples "mixed aggregates", indicating that next to concrete also bricks and other construction materials can be present. Their original characteristics are shown in Table 1. To obtain FRA samples ready for characterization and subsequent incorporation into mortars, they were dried at 40 °C and sieved to keep the 0/4 mm fraction. From the pictures in Table 1, a large variability between the different sources can be seen, and contaminations with soil, brick, wood, plastic, or gypsum particles. Their impurity becomes especially clear when compared to the pure crushed concrete "REF".

The particle size distribution of the FRA samples is shown in Figure 1. A very high variability in characteristics was found between the different industrial sources.

In Figure 2, the water-soluble sulfate content of the FRA is shown for the total 0/4 mm sample as well as per size fraction. All but one source of FRA surpassed the maximum allowable sulfate limit of 0.2% specified by EN 206 [29], indicating they would be rejected for use in a new concrete. The reference FRA, which was a pure uncontaminated crushed concrete, also contained 0.18% of sulfates, which originated from the leaching of cement particles.

Sulfates are predominantly present in the smaller size fractions, except for sample E and REF. This is explained by the brittleness of gypsum during the handling process of construction and demolition waste, and by the increasing presence of cement particles in the finer size fractions [42–44]. The sulfates accumulating to the finer fractions partially explains why—contrary to coarse recycled aggregates—FRA are not valorized.

Table 2 summarizes other characterization results. Again, a large difference in characteristics was noticed, proving the necessity of a thorough characterization of FRA before incorporating them into a mix. An elevated water absorption is one of the key aspects of recycled aggregates, and these ranged from 6.1% to 14.6% over the different samples. No apparent correlation was found between this water absorption and the sulfate content (Figure 2) or the amount of fine particles (Figure 1).

Table 1. The different samples of aggregates and their original size distribution. Pictures shown are after drying at 40 °C and separating of the 0/4 mm fraction. The "model" FRA and natural aggregate that were used for reference mortars are also presented.

A	B	C	D
0/4	0/10	0/32	0/20
			
E	F	FRA	NS
0/90	0/10		
			

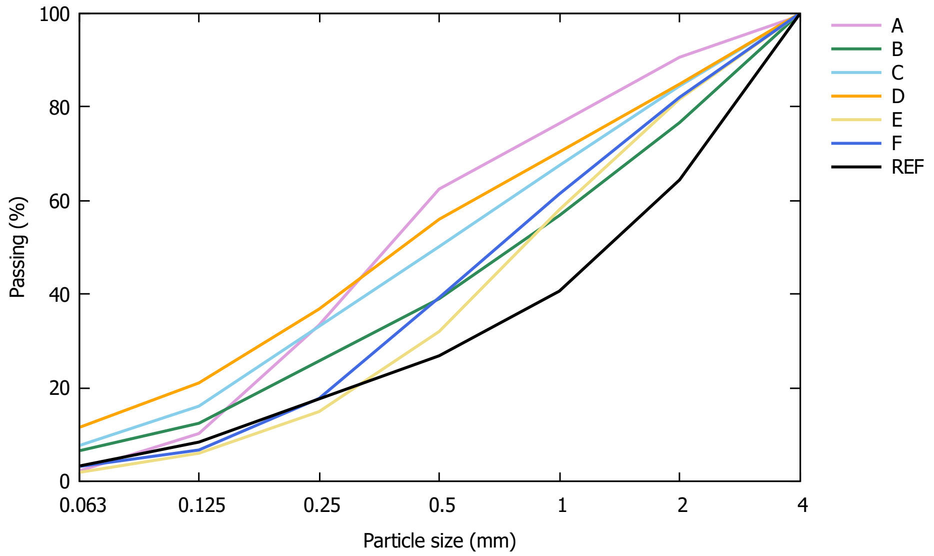


Figure 1. Particle size distribution of the used fine recycled aggregates (FRA).

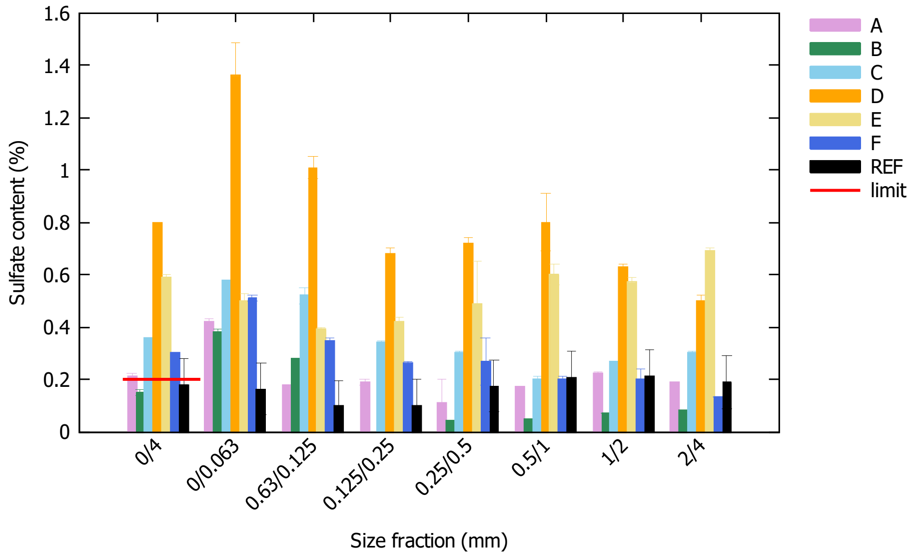


Figure 2. Water soluble sulfate content of the FRA in total and per size fraction.

Table 2. Characterization of the used FRA before recomposition and effective values in the mortars after recomposition.

	Water Absorption (%)		SSD Particle Density (g/cm^3)		SO_4^{2-} Content (%)	
Source	**Original**	**Recomposed**	**Original**	**Recomposed**	**Original**	**Recomposed**
A	6.1	7.1	2.14	2.15	0.21	0.19
B	8.9	9.7	2.10	2.00	0.15	0.08
C	11.5	10.6	1.99	1.97	0.36	0.29
D	10.6	8.8	2.00	1.92	0.80	0.62
E	14.6	12.6	1.97	1.92	0.59	0.61
F	13.0	11.8	1.96	1.85	0.30	0.18
REF	9.8		1.95		0.18	

3.2. Swelling Tests

Recomposing all aggregates to obtain a uniform size distribution slightly changed their total water absorption, density, and sulfate content. The recalculated values of these recomposed aggregates are shown in Table 2. Taking these values into account, the composition of the mortars was calculated and shown in Table 3. An amount of added gypsum was then recalculated into the corresponding amount of sulfates, giving the total water soluble sulfate content for each mortar in the sample name. These mixes were made in triplicate.

The 6-month swelling behavior of these mortars is shown in Figure 3. Except for "F-0.18%" which showed a lower expansion, no statistical differences ($p < 0.05$) were found between the length changes of the industrial FRA sources and the 2 reference mortars with similar sulfate contents. More information about statistical differences between the results can be found in Table S1 and Figure S1 in the Supplementary Information. There was also no correlation between the absolute swelling amount and the sulfate content of these mortar mixes. It was, however, very clear that sulfates do indeed cause a swelling reaction—as can be seen from the curve of REF-3.08%, but an exaggerated contamination level was needed for this result. The sulfates present in the industrial FRA were not enough to provoke a significant swelling reaction even though they largely surpassed the 0.2% limit. The length change curve of sample REF-3.08% stabilized after one month, which is a much faster reaction than seen in literature for other types of sulfate deteriorations like DEF or external sulfate attack, that often go on over multiple years [28,45–47].

The resonance frequency test is a measure for the internal damage in the mortar sample. If microcracks were formed, they would manifest as irregularities in their frequency curves, but this was not the case for these mortars. Even though significant swelling was attained for REF-3.08%, it was nevertheless not severe enough to cause internal fissuration.

Table 3. Compositions, in g, of the mortars, using the values of the recomposed FRA from Table 2. The samples are named after the source of their FRA, and the water soluble sulfate content in their mix expressed as a mass % of the aggregate fraction.

Name	Cement	Water		Aggregate (0/4 mm)	Extra Gypsum
		Effective	Absorbed		
A-0.19%	1350	675	79.15	1116.3	0
B-0.08%	1350	675	100.32	1038.5	0
C-0.29%	1350	675	108.22	1022.9	0
D-0.62%	1350	675	87.33	996.9	0
E-0.61%	1350	675	125.71	996.9	0
F-0.18%	1350	675	113.16	960.6	0
REF-0.47%	1350	675	98.52	1007.4	5.1
REF-3.08%	1350	675	94.07	961.9	50.6
NS-0.29%	1350	675	0	1343.2	6.8

The mass of the mortars kept steadily increasing each week, because of ingress of the water in which they were kept. The mortars made with the reference FRA gained more mass, because of their irregular shape which captures more air into the mixture than a round aggregate [30,48]. For the reference FRA specifically, a high air content in mixes with this material was already observed [49]. Industrially fabricated FRA are rounder by nature than laboratory crushed FRA [50], explaining why their results lie between those of the natural aggregates and the reference FRA.

An XRD analysis on "REF-3.08%" (Figure 4) at different moments shows how ettringite peaks become more intense with age, corresponding well to the observed swelling results. The biggest growth for the ettringite peaks is between 7, 28, and 90 days, after which the intensity stabilizes and even decreases slightly at 180 days.

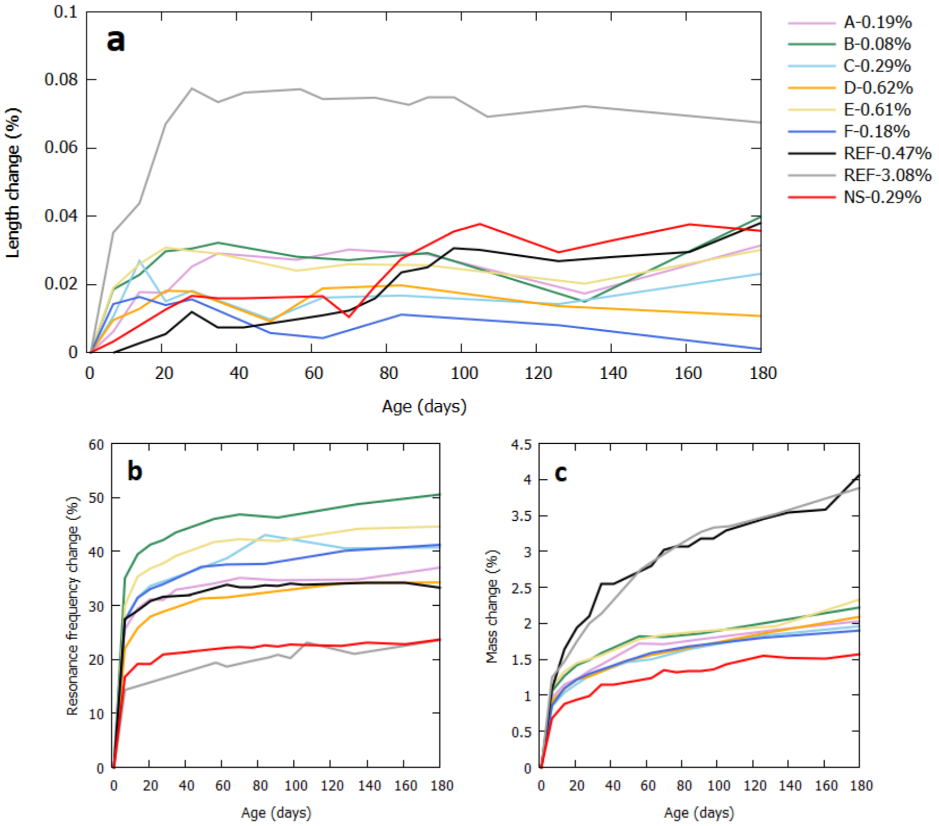


Figure 3. Six-month swelling behavior of the mortar samples, including their length change (**a**), resonance frequency change (**b**), and mass change (**c**).

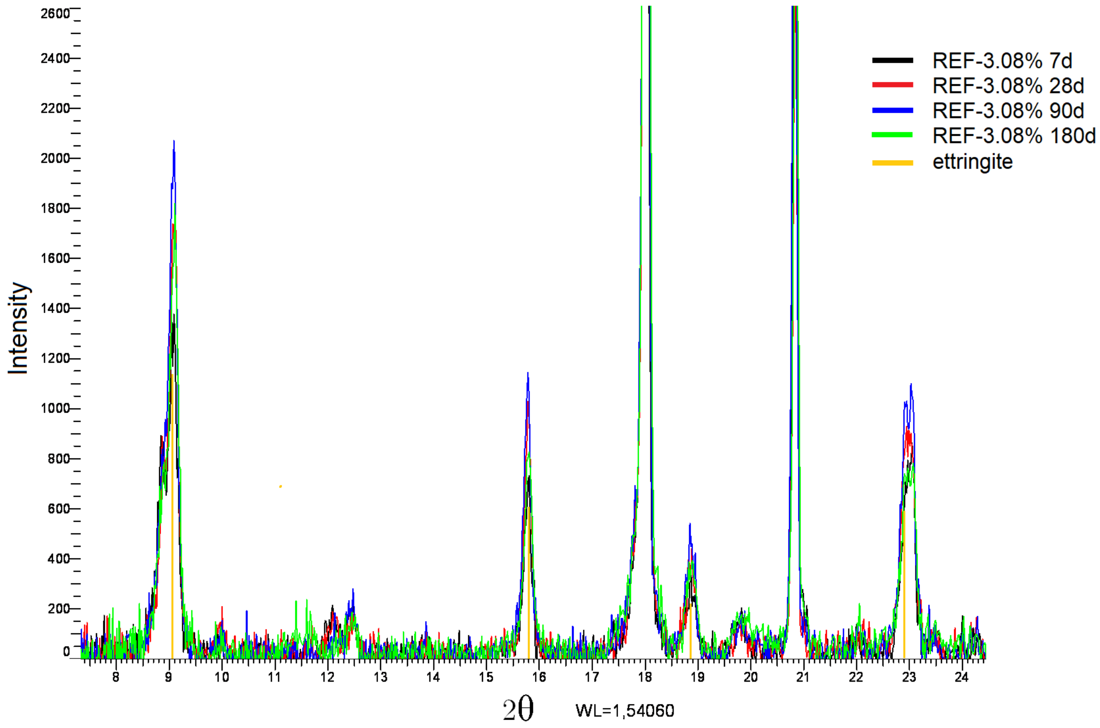


Figure 4. XRD analysis of "REF-3.08%" at 7, 28, 90, and 180 days.

Figure 5 shows the flexural and compressive strength of the mortar samples after 7, 28, 90, and 180 days. As expected, the mortar with natural aggregates has a better mechanical performance than those with the reference FRA. The heavily contaminated sample REF-3.08% showed a higher flexural and compressive strength than REF-0.47%, even though it underwent significant swelling. The samples with the industrial FRA performed between the natural aggregates and the reference FRA, confirming their higher quality compared to a pure crushed concrete. This could again be due to the irregular shape of the REF aggregates: the higher air content in these mixes affected their mechanical resistance.

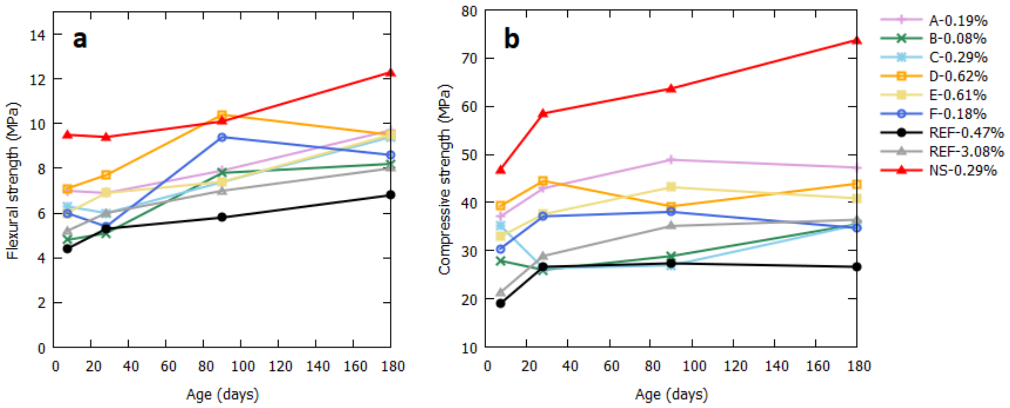


Figure 5. Flexural (**a**) and compressive (**b**) strength of the mortar samples after 7, 28, 90, and 180 days.

4. Conclusions

Between the three different sampled recycling centers and even between different samples from the same center, a large variability was found in the FRA they offered. Results showed their water absorptions ranging from 6.1% to 14.6% and sulfate contents from 0.15% to 0.80%. Both of these characteristics increased with particle fineness, explaining how small particles sizes can be more difficult to incorporate than coarser grains.

Pure, uncontaminated, crushed concrete had a sulfate content of 0.18%, showing that sulfates are not only originating from gypsum but also residual cement particles. Regardless of their source, all water soluble sulfates can contribute to sulfate attack. Mortars made with this reference recycled material showed a lower compressive strength than those with industrial FRA. Lots of research done on the incorporation of FRA in mortars or concrete is done with reference recycled materials, so this could mean that the quality of industrial FRA is underestimated.

Swelling tests on mortars showed that no harmful swelling occurred when industrial FRA were incorporated. While internal sulfate attack caused by contaminated FRA is definitely a relevant deteriorating reaction, exaggerated sulfate amounts were necessary to provoke any swelling. The sulfate contents found in industrial FRA, while still largely surpassing the 0.2% limit posed in EN 206, did not pose this threat to the mechanical stability of the mortar.

For these reasons, FRA from recycling centers should be considered as a viable material to incorporate in mortars, provided that the mix design is adapted to account for their lower density and higher water absorption. Future work should focus on upscaling these tests to concrete, to further evaluate the established sulfate limit.

Based on these results, the sulfate limit of 0.2% posed in EN 206 could be reconsidered to be less strict. Mortars made with sulfate contents of up to 0.6% did not show any significant deteriorating reaction.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/13/21/4866/s1, Figure S1: Swelling curve corresponding to Figure 3a, shown with error bars, Table S1: T-test results of the swelling curves. A red color means that samples differed significantly from each other for $p < 0.05$.

Author Contributions: Investigation, C.C.; writing—original draft preparation, C.C.; writing—review and editing, D.B., S.R., Z.Z., and L.C.; visualization, C.C.; supervision, D.B. and L.C.; project administration, D.B., S.R., Z.Z., and L.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was conducted in the framework of the Interreg project VALDEM "Solutions intégrées de valorisation des flux 'matériaux' issus de la démolition des bâtiments: approche transfrontalière vers une économie circulaire" (Convention n° 1.1.57 of Interreg France–Wallonie-Vlaanderen 2014–2020).

Conflicts of Interest: The authors declare no conflicts of interest. The funding source had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. United Nations Environment Programme. *Sustainable Buildings and Climate Initiative*; United Nations Environment Programme: Nairobi, Kenya, 2016.
2. Coelho, A.; De Brito, J. Influence of construction and demolition waste management on the environmental impact of buildings. *Waste Manag.* **2012**, *32*, 532–541. [CrossRef] [PubMed]
3. European Commission. On Resource Efficiency Opportunities in the Building Sector. COM/2014/0445fina. 2014. Available online: https://ec.europa.eu/environment/eussd/pdf/SustainableBuildingsCommunication.pdf (accessed on 6 August 2020).
4. Behera, M.; Bhattacharyya, S.; Minocha, A.; Deoliya, R.; Maiti, S. Recycled aggregate from C&D waste and its use in concrete: A breakthrough towards sustainability in construction sector: A review. *Constr. Build. Mater.* **2014**, *68*, 501–516. [CrossRef]
5. Deloitte. *Study on Resource Efficient Use of Mixed Wastes, Improving Management of Construction and Demolition Waste: Final Report*; Prepared for the European Commission; Deloitte: London, UK, 2017.
6. Council Directive 2008/98/EC of the European Parliament. On Waste and Repealing Certain Directives. Official Journal of the European Union L312. 2008. Available online: http://data.europa.eu/eli/dir/2008/98/2018-07-05 (accessed on 6 September 2020).
7. European Aggregates Association. Annual Review. 2017. Available online: https://uepg.eu/mediatheque/media/AR_2017-2018.pdf (accessed on 6 September 2020).
8. Thormark, C. Conservation of energy and natural resources by recycling building waste. *Resour. Conserv. Recycl.* **2001**, *33*, 113–130. [CrossRef]
9. Wilburn, D.; Goonan, T. *Aggregates from Natural and Recycled Sources: Economic Assessments for Construction Applications, a Materials Flow Analysis*; Technical Report; U.S. Department of the Interior: Washington, DC, USA, 1998.
10. Delvoie, S.; Zhao, Z.; Michel, F.; Courard, L. Market analysis of recycled sands and aggregates in NorthWest Europe: Drivers and barriers. In Proceedings of the IOP Conference series: Earth and Environmental Science, Brussels, Belgium, 5–7 February 2019; pp. 1–8. [CrossRef]
11. Oikonomou, N. Recycled concrete aggregates. *Cem. Concr. Compos.* **2005**, *27*, 315–318. [CrossRef]
12. Bravo, M.; De Brito, J.; Pontes, J.; Evangelista, L. Mechanical performance of concrete made with aggregates from construction and demolition waste recycling plants. *J. Clean. Prod.* **2015**, *99*, 59–74. [CrossRef]
13. Gutierrez, P.; Sanchez de Juan, M. *Utilization of Recycled Concrete Aggregate for Structural Concrete*; Service Life Design for Infrastructures: Delft, The Netherlands, 2018.
14. Rao, A.; Jha, K.; Misra, S. Use of aggregates from recycled construction and demolition waste in concrete. *Resour. Conserv. Recycl.* **2007**, *50*, 71–81. [CrossRef]
15. Zhao, Z.; Courard, L.; Groslambert, S.; Jehin, T.; Léonard, A.; Xiao, J. Use of recycled concrete aggregates from precast block for the production of new building blocks: An industrial scale study. *Resour. Conserv. Recycl.* **2020**, *157*, 104786. [CrossRef]
16. Evangelista, L.; De Brito, J. Concrete with fine recycled aggregates: A review. *Eur. J. Environ. Civ. Eng.* **2014**, *18*, 129–172. [CrossRef]
17. Khatib, J. Properties of concrete incorporating fine recycled aggregate. *Cem. Concr. Res.* **2005**, *35*, 763–769. [CrossRef]
18. Zhao, Z.; Rémond, S.; Damidot, D.; Xu, W. Influence of hardened cement paste content on the water absorption of fine recycled concrete aggregates. *J. Sustain. Cem. Based Mater.* **2013**, *2*, 186–203. [CrossRef]

19. Tam, V.; Tam, C.; Le, K. Removal of cement mortar remains from recycled aggregate using pre-soaking approaches. *Resour. Conserv. Recycl.* **2007**, *50*, 82–101. [CrossRef]
20. Bravo, M.; de Brito, J.; Pontes, J.; Evangelista, L. Durability performance of concrete with recycled aggregates from construction and demolition waste plants. *Constr. Build. Mater.* **2015**, *77*, 357–369. [CrossRef]
21. Braymand, S.; Roux, S.; Deodonne, K.; Mihalcea, C.; Feugeas, F.; Fond, C. *Les Granulats RecycléS de BéTons: Un MatéRiau à Fort Potentiel de Valorisation Dans Les BéTons*; Matériaux: Montpellier, France, 2014.
22. Collepardi, M. A state of the art review on delayed ettringite attack on concrete. *Cem. Concr. Compos.* **2003**, *25*, 401–407. [CrossRef]
23. Asakura, H.; Watanabe, Y.; Ono, Y.; Yamada, M.; Inoue, Y.; Alfaro, A.M. Characteristics of fine processed construction and demolition waste in Japan and method to obtain fines having low gypsum component and wood contents. *Waste Manag. Res.* **2010**, *28*, 634–646. [CrossRef] [PubMed]
24. Ambrós, W.; Sampaio, C.; Cazacliu, B.; Miltzarek, G.; Miranda, L.R. Separation in air jigs of mixed construction and demolition waste. In *Advances in Recycling and Management of Construction and Demolition Waste*; Delft University of Technology: Delft, The Netherlands, 2017; pp. 25–28.
25. Agrela, F.; de Juan, M.S.; Ayuso, J.; Geraldes, V.; Jiménez, J. Limiting properties in the characterisation of mixed recycled aggregates for use in the manufacture of concrete. *Constr. Build. Mater.* **2011**, *25*, 3950–3955. [CrossRef]
26. Diamond, S. Delayed Ettringite Formation: Processes and Problems. *Cem. Concr. Compos.* **1996**, *18*, 205–215. [CrossRef]
27. Breysse, D. Deterioration processes in reinforced concrete: An overview. In *Non-Destructive Evaluation of Reinforced Concrete Structures: Deterioration Processes and Standard Test Methods*; Maierhofer, C., Reinhardt, H., Dobmann, G., Eds.; Woodhead Publishing: Sawston, UK, 2010.
28. Taylor, H.; Famy, C.; Scrivener, K. Delayed ettringite formation. *Cem. Concr. Res.* **2001**, *31*, 683–693. [CrossRef]
29. European Committee for Standardization. *EN 206 'Concrete: Specification, Performance, Production and Conformity: Annex E.3 on Recycled Aggregates'*; European Committee for Standardization: Brussels, Belgium, 2014.
30. Yammine, A.; Nordine, L.; Choinska, M.; Bignonnet, F.; Mechling, J. DEF damage in heat cured mortars made of recycled concrete sand aggregate. *Constr. Build. Mater.* **2020**, *252*. [CrossRef]
31. Rougeau, P.; Schmitt, L.; Nai-Nhu, J.; Djerbi, A.; Saillio, M.; Ghorbel, E.; Mechling, J.M.; Lecomte, A.; Trauchessec, R.; Bulteel, D.; et al. Durability-related properties. In *Concrete Recycling : Research and Practice*; De Larrard, F., Colina, H., Eds.; CRC Press: Boca Raton, FL, USA, 2019.
32. European Committee for Standardization. *EN 933 'Tests for Geometrical Properties of Aggregates. Part 1: Determination of Particle Size Distribution'*; European Committee for Standardization: Brussels, Belgium, 2012.
33. European Committee for Standardization. *EN 1744-1 'Tests for Chemical Properties of Aggregates. Part 1: Chemical Analysis';* European Committee for Standardization: Brussels, Belgium, 2014.
34. Bock, E. On the solubility of anhydrous calcium sulphate and of gypsum in concentrated solutions of sodium chloride at 25 °C, 30 °C, 40 °C and 50 °C. *Can. J. Chem.* **1961**, *39*, 1746–1751. [CrossRef]
35. Colman, C.; Zhao, Z.; Michel, F.; Rémond, S.; Bulteel, D.; Courard, L. *Gypsum Residues in Recycled Materials: Characterization of Fine Recycled Aggregates*; Service Life Design for Infrastructures: Delft, The Netherlands, 2018.
36. European Committee for Standardization. *EN 1097-6 'Tests for Mechanical and Physical Properties of Aggregates. Part 6: Determination of Particle Density and Water Absorption'*; European Committee for Standardization: Brussels, Belgium, 2001.
37. IFSTTAR. *Test Method No. 78:2011. Tests on Aggregates for Concrete: Measurement of Total Water Absorption by a Crushed Sand*; IFSTTAR: Paris, France, 2011.
38. Le, T.; Remond, S.; Le Saout, G.; Garcia-Diaz, E. Fresh behavior of mortar based on recycled sand: Influence of moisture condition. *Constr. Build. Mater.* **2016**, *106*, 35–42. [CrossRef]
39. Delobel, F.; Bulteel, D.; Mechling, J.; Lecomte, A.; Cyr, M.; Rémond, S. Application of ASR tests to recycled concrete aggregates: Influence of water absorption. *Constr. Build. Mater.* **2016**, *124*, 714–721. [CrossRef]
40. European Committee for Standardization. *EN 196-1 'Methods of Testing Cement. Part 1: Determination of Strength'*; European Committee for Standardization: Brussels, Belgium, 2014.

41. Colman, C.; Zhao, Z.; Michel, F.; Rémond, S.; Bulteel, D.; Courard, L. *Internal Sulfate Attack Caused by Gypsum Contamination of Recycled Aggregates: Development of a Swelling Test Protocol*; Journées Scientifiques RF2B: Anglet, France, 2018.
42. Hansen, T.; Narud, H. Strength of recycled concrete made from crushed concrete coarse aggregate. *Concr. Int.* **1983**, *5*, 79–83.
43. Nassar, R.; Soroushian, P. Strength and durability of recycled aggregate concrete containing milled glass as partial replacement for cement. *Constr. Build. Mater.* **2012**, *29*, 368–377. [CrossRef]
44. Poon, C.; Shui, Z.; Lam, L. Effect of microstructure of ITZ on compressive strength of concrete prepared with recycled aggregates. *Constr. Build. Mater.* **2004**, *18*, 461–468. [CrossRef]
45. Pavoine, A.; Brunetaud, X.; Divet, L. The impact of cement parameters on Delayed Ettringite Formation. *Cem. Concr. Compos.* **2012**, *34*, 521–528. [CrossRef]
46. Aubert, J.; Escadeillas, G.; Leklou, N. Expansion of five-year-old mortars attributable to DEF. *Constr. Build. Mater.* **2009**, *23*, 3583–3585. [CrossRef]
47. Batic, O.; Milanesi, C.; Maiza, P.; Marfil, S. Secondary ettringite formation in concrete subjected to different curing conditions. *Cem. Concr. Res.* **2000**, *30*, 1407–1412. [CrossRef]
48. Mehdipour, I.; Khayat, K. Understanding the role of particle packing characteristics in rheophysical properties of cementitious suspensions: A literature review. *Constr. Build. Mater.* **2018**, *161*, 340–353. [CrossRef]
49. Colman, C.; Bulteel, D.; Thiery, V.; Rémond, S.; Michel, F.; Courard, L. Internal sulfate attack in mortars containing contaminated fine recycled concrete aggregates. *Constr. Build. Mater.* Unpublished.
50. Matias, D.; De Brito, J.; Rosa, A.; Pedro, D. Mechanical properties of concrete produced with recycled coarse aggregates: Influence of the use of superplasticizers. *Constr. Build. Mater.* **2013**, *44*, 101–109. [CrossRef]

Annex

The fresh mortars showed a similar slump and density right after mixing (Table 7.1), except for 'B' and 'F' which were less maniable than the other aggregates. The determination of their water absorption was however done via a very good correlation (Section 4.2.2), and their fresh densities were in line with the other mortars.

	Slump (mm)	Fresh density (g/cm^3)
A-0.19%	27.9	2.14
B-0.08%	14.9	2.05
C-0.29%	24.5	1.98
D-0.62%	31.3	2.07
E-0.61%	27.9	2.10
F-0.18%	16.7	2.07
REF-0.47%	30.5	1.78
REF-3.08%	20.6	1.95
NS-0.29%	29.5	2.27

Table 7.1: Fresh properties of the mortar mixes.

The porosity of the mortar mixes is shown in Figure 7.1. As expected, the sample with natural aggregates is less porous than those with recycled aggregates. The porosities of the mortars with FRA were not proportional to their swelling results. The fact that the mortar with FRA 'A' is a little bit below the others might be explained by its higher fresh density, approaching that of the mortar with natural aggregate.

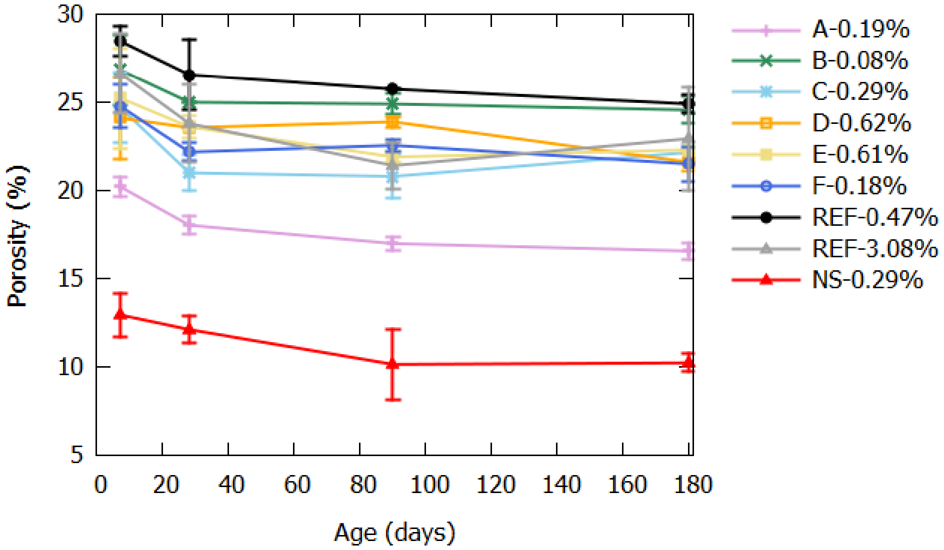


Figure 7.1: Porosity by mercury intrusion of the mortars made with industrial FRA, 'model' FRA, or natural fine aggregates.

8 | Parameters influencing the reaction on model materials

When dealing with contaminated FRA, some expansion can be expected depending on its sulfate content. This chapter aimed to identify which parameters of a mix could be adapted to try to limit sulfate attack when the gypsum content is a given. This way, even heavily contaminated FRA could be valorized provided that the composition or mixing procedure can be adapted accordingly.

The literature study in Chapter 2 revealed several factors that can play a role in the internal sulfate attack mechanism. In this experimental part, they were analyzed in a qualitative way, which means with exaggerated low or high values. While varying, all other parameters were kept constant so the response could be isolated.

In Chapter 5, it was determined that a gypsum contamination of 5 mass% gave the best visible swelling results. That gypsum content - corresponding to 3.1 % of sulfates in the reference FRA - was used in these experiments.

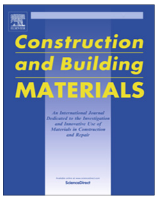
Three factors came to light that altered the swelling results of a mortar with 3.1 % of sulfates significantly. The possibility for thaumasite formation was the most damaging, and after that the lowering of the W/C ratio. On the other hand, the swelling caused by a very high sulfate content could be completely mitigated by increasing the alkalinity of the mix. Surprisingly, other parameters that were thought to have an influence - like the cement type or the gypsum particle size - did not change the swelling results. These results were interpreted with the help of microstructure observations, that showed where and how ettringite was being formed, and how these parameters could have influenced the expansion of the mortars.

Construction and Building Materials 272 (2021) 121851

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat



Internal sulfate attack in mortars containing contaminated fine recycled concrete aggregates

C. Colman [a,c,*], D. Bulteel [a], V. Thiery [a], S. Rémond [b], F. Michel [c], L. Courard [c]

[a] Univ. Lille, IMT Lille Douai, ULR 4515 – LGCgE, Laboratoire de Génie Civil et géo-Environnement, F-59000 Lille, France
[b] Univ Orléans, Univ Tours, INSA CVL, LaMé, EA 7494, France
[c] University of Liège, Urban and Environmental Engineering, GeMMe Building Materials, 4000 Liège, Belgium

HIGHLIGHTS

- Gypsum residues in fine recycled aggregates can cause internal sulfate attack.
- Limited porosity or thaumasite formation had an aggravating role on the swelling.
- Increased alkalinity or limited sulfate contents inhibited the swelling response.

ARTICLE INFO

Article history:
Received 15 April 2020
Received in revised form 12 August 2020
Accepted 25 November 2020

Keywords:
Recycled aggregates
Sulfate attack
Microstructure
Waste management
Secondary ettringite formation

ABSTRACT

Internal sulfate attack can be caused by the gypsum residues present in fine recycled aggregates (FRA). As opposed to the better known external sulfate attack or Delayed Ettringite Formation (DEF), the sulfates in this context are provided by a gypsum contamination of the aggregates. Mortars made with contaminated FRA were subjected to different conditions, to assess which parameters had an influence on the sulfate attack reaction. Their mechanical properties and microstructure are investigated. Results showed that gypsum content, porosity, temperature and alkalinity influenced the consequences of sulfate attack. However, the gypsum size distribution and cement type did not.

1. Introduction

1.1. Gypsum in fine recycled concrete aggregates

One of the key points within the framework of a sustainable construction sector is the recycling of its waste products, completing the life cycle of these materials. Recycled concrete aggregates (RCA), obtained by the demolition or deconstruction of older concrete structures, can be used in a new concrete as a replacement for natural aggregates [1]. 1.7 tonnes of these RCA are produced per person per year in Europe, waiting to be valorized [2]. Gypsum ($CaSO_4.2H_2O$) is used in the construction sector firstly as an addition to Portland cement, to regulate the setting time of concrete and prevent a flash set [3]. Besides that, gypsum is the major constituent of plaster walls in buildings. RCA, as a consequence, will contain a certain amount of gypsum. Larger concrete and gypsum particles can be separated from each other based on a difference in color [4] or density [5], but these techniques are not applicable on the smallest size fractions of RCA. In fine recycled aggregates (FRA), gypsum is an important contaminant to be considered: the water soluble sulfates coming from the gypsum particles strongly limit their valorization potential [6].

1.2. Sulfate attack: sources and mechanisms

Sulfate attack is a deteriorating process where sulfates react with water and aluminate hydrates in a hardened cement paste to form secondary ettringite. It is assumed that this mineral exerts a pressure on its surrounding cement paste and causes a volumetric deformation [7]. Macroscopically, the concrete structure will show swelling behavior and the formation of cracks. Ettringite is a normal hydration product in the cement paste: its formation only becomes dangerous when it occurs after setting, in a rigid cement matrix. Depending on the source of the sulfates responsible for the reaction, a distinction can be made between an external and an

---

* Corresponding author at: Univ. Lille, IMT Lille Douai, ULR 4515 – LGCgE, Laboratoire de Génie Civil et géo-Environnement, F-59000 Lille, France.
E-mail address: charlotte.colman@uliege.be (C. Colman).

https://doi.org/10.1016/j.conbuildmat.2020.121851
0950-0618/

internal reaction. To experience *external* sulfate attack, the structure is submerged in a sulfate rich environment such as soil or seawater. Diffusion mechanics and microcrack propagation from the surface inwards are determining factors here [8]. *Internal* sulfate attack happens when there is a delayed release of sulfates from the hardened cement matrix. In this sense, an internal source of sulfates eliminates the diffusion and microcrack necessity of external sulfate attack, possibly accelerating the reaction. Delayed Ettringite Formation (DEF), which occurs when high curing temperatures have destroyed the sulfate hydrates that were initially formed [7], has been known for some time. The current situation, where FRA is contaminated with gypsum residues, is a relatively new problem that has not been studied extensively.

The following aspects of the internal sulfate attack reaction were selected to be elaborated in this study:

Alkalinity Many authors show the important role of the alkalinity of the interstitial solution, as it interferes with the equilibrium between the different sulfate phases. A higher alkalinity favors the existence of monosulfate and the absorption of sulfur on the C-S-H gel instead of the formation of ettringite [9], so ettringite formation triggers as pH lowers. Nevertheless, a higher swelling due to ettringite formation is often found in mixes with a higher alkalinity [9–13]. While alkalinity speeds up hydration and increases early compressive strength [14], it leads to lower mechanical performances in a sulfate presence [9,10]. Besides a possible interaction with sulfate attack, alkalinity is also a risk factor for the alkali-silica reaction and other durability issues.

Cement type Using a sulfate-resisting cement allows the use of FRA with a high sulfate content [15]. These types of cement contain less C_3A, one of the reactants needed to form ettringite. Moreover, fewer gypsum is added to this cement type as a setting retarder, compensating for the additional sulfate source to which the mixture will be exposed. The SO_3/Al_2O_3 ratio of a cement is an important factor regarding its potential to form ettringite [16].

Porosity The most commonly accepted theory about the cause of expansion is the heterogeneous crystal pressure exerted by the growing ettringite crystals [7,3,17]. In this sense, a lower porosity means more confinement and a higher internal pressure. On the other hand, in the case of external sulfate attack, a lower porosity would prevent the inwards diffusion of sulfates and thus limit the swelling potential [18].

Sulfates Before dissolution, sulfates can be associated with different cations. It has been found that the sulfates originating from Na_2SO_4 lead to more swelling than those from $CaSO_4$ [9], and that $MgSO_4$ is even more damaging [19]. This would suggest that a gypsum contamination is less damaging than other types of sulfate attack that have been researched. However, these are external sources. The rapid availability of an internal $CaSO_4$ contamination could make this difference smaller.

Coarser gypsum particles are hypothesized to not feed early ettringite formation, but react later in an already rigid cement matrix. To keep the risk on sulfate attack at a reasonable level, the current water soluble sulfate limit in coarse recycled aggregates is established at 0.2% by EN 206 [20], with no mention of FRA. At these quantities, sulfates are considered the limiting reagent in the ettringite formation reaction so any augmentation would hypothetically lead to more swelling. The conclusions of recent durability studies indicate a level of 0.3% should be made possible [21].

Thaumasite formation Next to ettringite, sulfates can also contribute to the formation of the expansive mineral thaumasite. While damage caused by thaumasite is more severe than that caused by ettringite, thaumasite formation does not occur as often [22]. Only at temperatures lower than 10 °C and in the presence of a carbonate source, is thaumasite favored over ettringite [23].

1.3. Objectives

In this study, contaminated FRA were used in mortars to research the damaging effects of sulfates. Each parameter of interest was varied while others were kept constant, to identify the factors that can worsen or mitigate the sulfate attack results. Knowing which parameters to manipulate in a mix design with highly contaminated FRA will ultimately promote the use of these recycled aggregates. The results of this study could also contribute to the ongoing discussion about the sulfate attack reaction mechanism [24].

2. Materials and methods

2.1. Used materials

FRA were made in the laboratory by fabricating a concrete and subsequently crushing it. The composition of this original concrete is given in Table 1, and was designed to obtain a consistency class S3 and strength class C30/37. After 90 days of curing, this concrete was crushed by a jaw crusher and the resulting 0/4 mm fraction was used as FRA in all described tests. The use of this ‘model’ FRA gave exact control of the chemical composition of the materials and removed any possible variability or contamination at the level of the aggregates by chlorides, organics, etc. This FRA was then manually contaminated with gypsum to obtain a ‘clean’ material where only sulfates could contribute to a deteriorating reaction.

Fig. 1 and Table 2 summarize the properties of the resulting FRA. Water absorption and particle density of the FRA were determined via the method described by Zhao et al. [25]. Characterization techniques for natural aggregates, described in EN 1097-6 [26], consistently underestimate the water absorption of FRA because of the fineness and agglomeration issues between the particles. The method – designed in response to this difficulty – by IFSTTAR [27] seems to overestimate the water absorption of FRA but works well for particles in the 0.5/4 mm range. Thanks to an very good correlation between the hardened cement paste content or mass loss at 475 °C and the water absorption, the water absorption of the fines can then be extrapolated. Using the water absorption of each size fraction (either measured for the coarser particles or calculated for the fines) is more accurate than using either of the two mentioned experimental methods for the whole 0/4 mm bulk [28]. Even though no gypsum was added to the model concrete, 0.18% of water soluble sulfates were measured via ion chromatography, originating from the used cement.

The gypsum used to contaminate this FRA was a $CaSO_4.2H_2O$ powder (D50 13 μm) obtained from VWR Chemicals. The sulfates from this gypsum contamination are added to the 0.18% of water soluble sulfates already in this FRA, originating from cement particles. A CEM I 52.5 N cement from HOLCIM was used as the default cement, in one test replaced by a High Sulfate Resisting (HSR) CEM I from the same manufacturer. The chemical composition of these cements is shown in Table 3.

2.2. Mortar fabrication

All mortars were prepared with the FRA described in Section 2.1, and were contaminated with 5% (by weight of the granular fraction) of gypsum. This gyspum, together with the residual sulfates in the model FRA, brings the total sulfate content of this mix to 3.08%. 7 days before mixing, the FRA was presaturated with its absorbed water and 10% of the mixing water. The standard procedure described in EN 196-1 [29] for mortar fabrication was followed, where normalized sand was replaced volumetrically by

Table 1
Composition, in kg, of the original concrete.

CEM I 52.5 N	Water	Limestone aggregates (mm)				Superplasticizer
		0/4	2/7	7/14	14/20	
350	175	216	658	436	612	0.4%

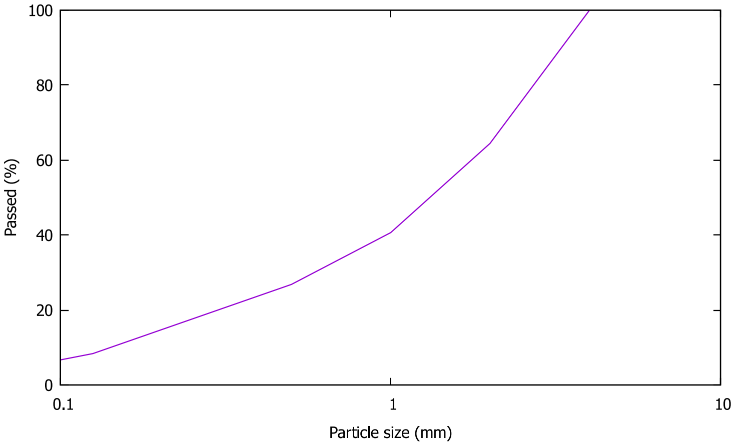


Fig. 1. Size distribution 0–4 mm of the used FRA.

Table 2
Characterization of the used FRA.

Water absorption	Particle density	SO_4^{2-} content
9.78%	1.95 g/cm^3	0.18%

Table 3
Chemical composition (mass%) of the used cement types.

Chemical	CEM I 52.5 N	CEM I HSR
CaO	64.3	64.6
SiO_2	18.3	21.4
Al_2O_3	5.2	3.7
Fe_2O_3	4.0	4.6
MgO	1.4	0.8
Na_2O	0.32	0.27
K_2O	0.43	0.40
SO_3	3.5	2.5
Cl^-	0.06	0.06
LOI	2.3	1.3
C_3A	6.6	2.4
C_4AF	12	14
C_3S	61.9	68.8
C_2S	11.2	9.4

Table 4
Summary of how the mortar composition was changed to obtain the levels of the different parameters.

Factor	Level	
Alkalinity (A)	−1	0.61% Na_2O Eq.
	+1	1.2% Na_2O Eq.
C_3A content (C)	−1	2.4% (CEM I HSR)
	+1	6.6% (CEM I)
Gypsum grain size (G)	−1	Powder (D50 13 μm)
	+1	2/4 mm distribution
Porosity (P)	−1	W/C 0.35
	0	W/C 0.5
	+1	W/C 0.65
Sulfate content (S)	−1	0.47% of water soluble sulfates
	+1	3.08% of water soluble sulfates
Temperature (T)	−1	5 °C and a carbonate addition
	+1	21 °C

FRA: using a particle density of 2.6 g/cm^3 for normalized sand and 1.95 g/cm^3 for the FRA, the aggregate envelope volume was kept constant. After a cure of 24 h, the mortars were kept in water at 21 °C. These described compositions or conditions were then varied accordingly, depending on the parameter that was tested.

2.3. Tested parameters

The following parameters were hypothesized to have an effect on the internal sulfate attack reaction. The influence of each one was tested with an exaggerated high (+1) and a low (−1) level, and in one case also an intermediate (0) level. Table 4 summarizes these levels and how each of them was obtained by adapting the standard mortar composition. Table 5 shows the compositions in more detail. To isolate the response of only one parameter, each series of replicates is kept in its own container, so as not to be influenced by the leaching water of another [30]. While one factor is being researched, all other parameters are kept as described in Section 2.2.

Alkalinity The lower level of this parameter is the normal alkalinity present in the used cement. The higher level is double this amount, achieved by adding NaOH to the mixing water.

Cement type To test the influence of the available C_3A, a HSR cement was used. A small difference in alkalinity between the HSR cement and the CEM I was mitigated by adding NaOH to the mixing water, bringing the Na_2O Eq. of both cements on the same level.

Gypsum grain size The same fine gypsum powder used in the other samples, was hardened and subsequently crushed to obtain particles in the 2/4 mm range. These two size distributions – the powder or the coarser particles – are used to contaminate the FRA.

Porosity To research the influence of the available porosity, the water to cement ratio (W/C) was varied.

Sulfate content A sulfate amount, one order of magnitude smaller than in the other mortars, was used to demonstrate the importance of this parameter.

Table 5
The compositions, in kg, of the different mortar samples. The changes between a mix and its reference composition is placed in bold. For the C-1 samples, the difference is in the *type* of cement, for the G+1 samples the *size* of the gypsum particles. Since the gypsum contamination is expressed as a mass% of the aggregate part, a lower gypsum content in S-1 means more FRA and thus also more absorbed water.

Name	Cement	FRA	Absorbed water	Mixing water	Gypsum	Extra
A-1, C+1, G-1, P0, S+1, T+1	1.35	0.96	0.094	0.675	0.05	
A+1	1.35	0.96	0.094	0.675	0.05	**10.30 g NaOH**
C-1	1.35	0.96	0.094	0.675	0.05	**1.2 g NaOH**
G+1	1.35	0.96	0.094	0.675	0.05	
P-1	1.35	0.96	0.094	**0.473**	0.05	
P+1	1.35	0.96	0.094	**0.878**	0.05	
S-1	1.35	**1.005**	**0.098**	0.675	**0.005**	
T-1	**1.08**	0.96	0.094	0.675	0.05	**270 g limestone filler,** **2.1 g NaOH**

Thaumasite formation These mortars were kept in water at 5°C to promote thaumasite formation over ettringite. For thaumasite formation, a source of carbonates is necessary besides C_3A, sulfates and water. 20% by mass of CEM I was therefore replaced with a limestone filler. Here again, NaOH was added so the alkalinity of the mix resembled the others.

2.4. Monitoring of the reaction

To follow the development of the internal sulfate attack reaction, the mortar specimens were subjected to different tests. On a macroscopic level, the mass, length and ultrasonic wavespeed were recorded weekly to observe features of sulfate attack such as swelling and possible internal cracking. At 7, 28, 90 and 180 days the mortars were characterized mechanically for their compressive strength [29] and porosity by Mercury Intrusion Porosimetry. Every described test was done for 3 replicate mortars. A microstructural analysis for the samples at 90 days was carried out to examine the pore structure and ettringite deposits, to complement the swelling results and provide grounds for their interpretation. The samples were prepared according to routine procedures of embedding and polishing [31] using a 2020 resin from Huntsman and MD System from Struers with water-free diamond pastes and lubricants. Images in scanning electron microscopy were obtained on a Hitachi S-4300/SE-N and coupled with EDS analyses.

3. Results and discussion

In Fig. 2, the length change of the mortars is shown. Standard deviations are not shown on these figures to improve their readability, but are taken into account when performing an unpaired t-test to check whether the swelling results differ from each other statistically.

According to Table 6, C-1, G+1 and P+1 are similar to the standard mix where all parameters have their normal value. Four other samples deviate from this trend: P-1 and T-1 had a larger expansion, A+1 and S-1 had a lower expansion. Next to their length, the mechanical properties that were monitored are presented in Fig. 3. The compressive strength of all samples kept steadily increasing over time but did not seem to have any correlation to the corresponding swelling amounts. The samples that showed a high or low swelling did not have a low or high compressive strength, respectively. There was a large variation of the measured strengths between 25 and 40 MPa, the parameters that did not influence the swelling amount did influence the compressive strength. There was less variation between the samples in terms of porosity, only the sample with a limited W/C ratio had a distinct lower porosity. The macroscopic differences between the parameters are interpreted together with microstructural observations.

3.1. General case

The four curves on Fig. 2 that stay together between the 0.06% and 0.08% marks, show that increasing the porosity, using larger

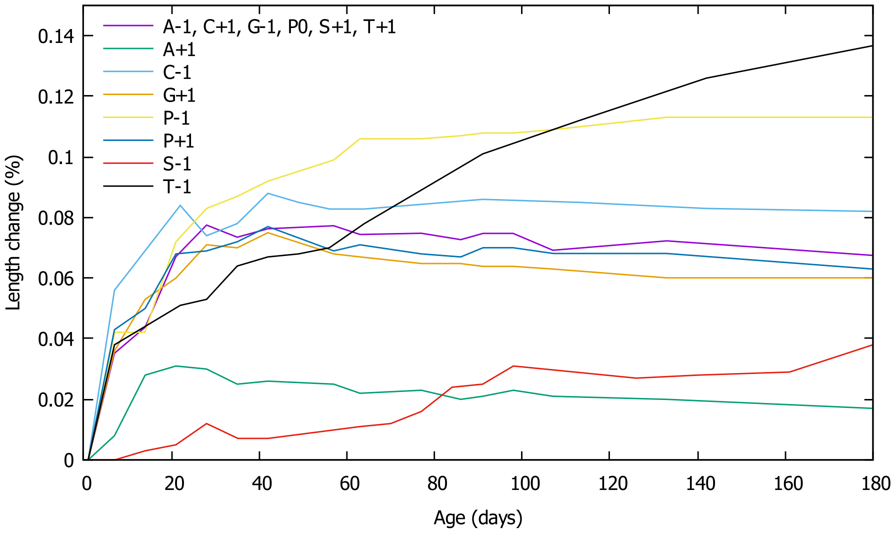


Fig. 2. 6 month swelling behavior of the mortar samples in function of the tested parameters.

Table 6
Unpaired t-test to evaluate if there is a significant difference between the samples and their reference mix, shows that 3 parameters did not change the swelling results (C-1, P+1 and G+1), and 4 did (T-1, P-1, S-1, A+1).

Name	Length (180 days)	Stdev (180 days)	Sample size	Difference for $p > 0.05$
A-1, C+1, G-1, P0, S+1, T+1	0.0675	0.007	3	
A+1	0.017	0.002	3	yes
C-1	0.081	0.005	3	no
G+1	0.060	0.002	3	no
P-1	0.113	0.004	3	yes
P+1	0.063	0.004	3	no
S-1	0.037	0.010	3	yes
T-1	0.137	0.004	3	yes

gypsum grains, or limiting the available C_3A did not influence the amount of swelling. SEM results confirmed that the morphology of these samples was very similar. Fig. 4 is a typical image found with recycled materials: the recycled aggregate is a cluster of natural aggregates in the original cement paste. The new cement paste, surrounding the recycled aggregates, had a notably higher air content, which has been observed before by Bouarroudj et al. [32] for the same material. This air content can be explained by the surface roughness of the recycled aggregates [33], which captures more air into the mixture than a round (natural) aggregate. Next to that, the difference in surface free energy between the new cement paste and the recycled aggregates could also have played a role in this elevated air content [34]. Fig. 5 illustrates how ettringite deposits in these samples were mainly found in pores or air bubbles, which sometimes also resulted in cracks in the surrounding paste.

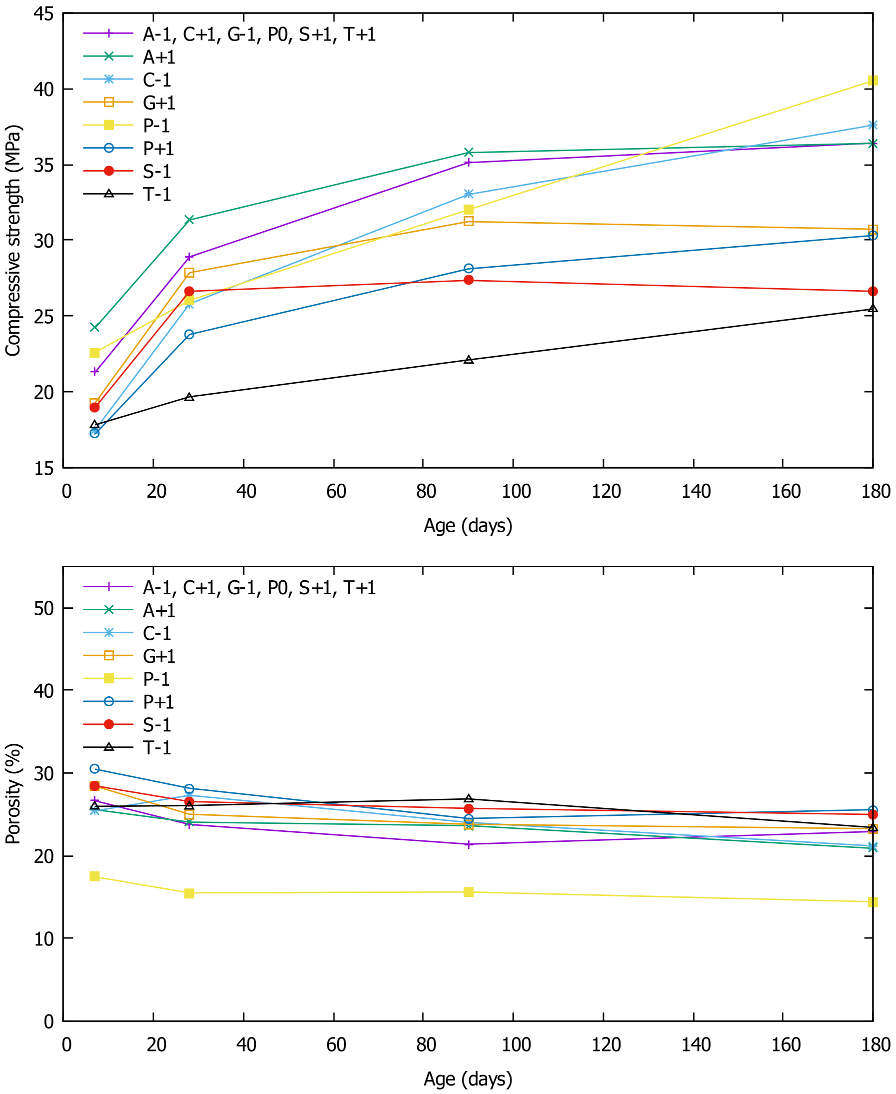


Fig. 3. Compressive strength and porosity of the samples at 7, 28, 90 and 180 days.

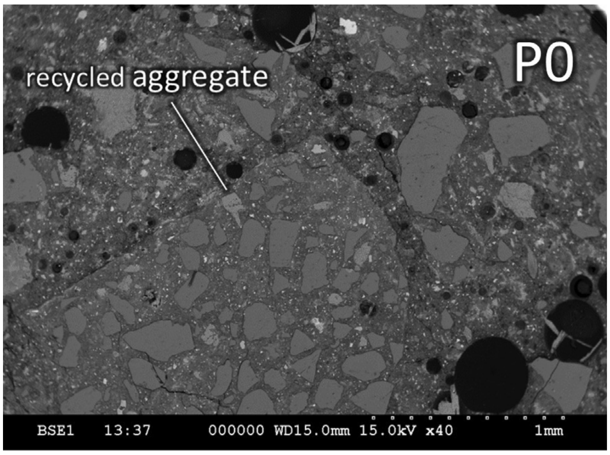


Fig. 4. Contrast between a recycled aggregate and the new cement paste with a high air content.

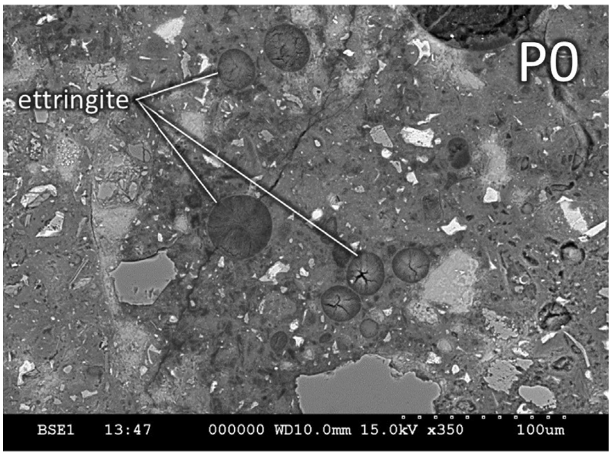


Fig. 5. Ettringite was found in pores and air bubbles, which exerted a pressure and cracked the surrounding cement paste.

3.2. Alkalinity

Sample A+1 with an increased alkalinity did not show any evidence of cracks. Air bubbles were often filled with ettringite, but not in a way that caused damage. Instead, a high percentage of them showed the presence of a piece of calcite or portlandite in their center, with ettringite crystals growing outwards of this center and not inwards from the cement paste. This is demonstrated in Fig. 6. Calcite has been described as a nucleation center for very fast ettringite growth at high alkalinity [35,36]. The kinetics of this reaction explain the lack of available sulfates to cause damage in a cured cement matrix. A higher alkalinity has also been observed by Juenger et al. [14] to increase the initial rate of hydration and cause a higher early compressive strength, which has been confirmed in Fig. 3. However, the swelling and compressive strength results obtained in these experiments contradicted the findings of numerous authors described in Section 1.2. This could be due to the chosen experimental setup: the high alkali values in this study were obtained by adding NaOH, which is immediately available. Alkali's coming from the adherent cement paste of FRA would take more time to leach into the interstitial solution. The rapid initial hydration in this sample prevented the higher swelling that is normally provoked by the alkalinity of FRA.

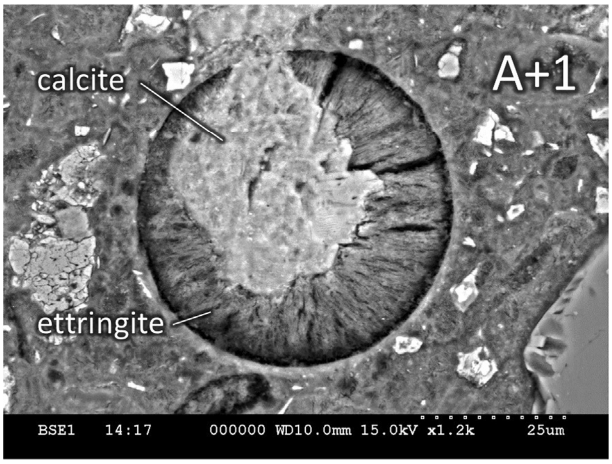


Fig. 6. A piece of calcite promoted the formation of ettringite at high alkalinity at an early age.

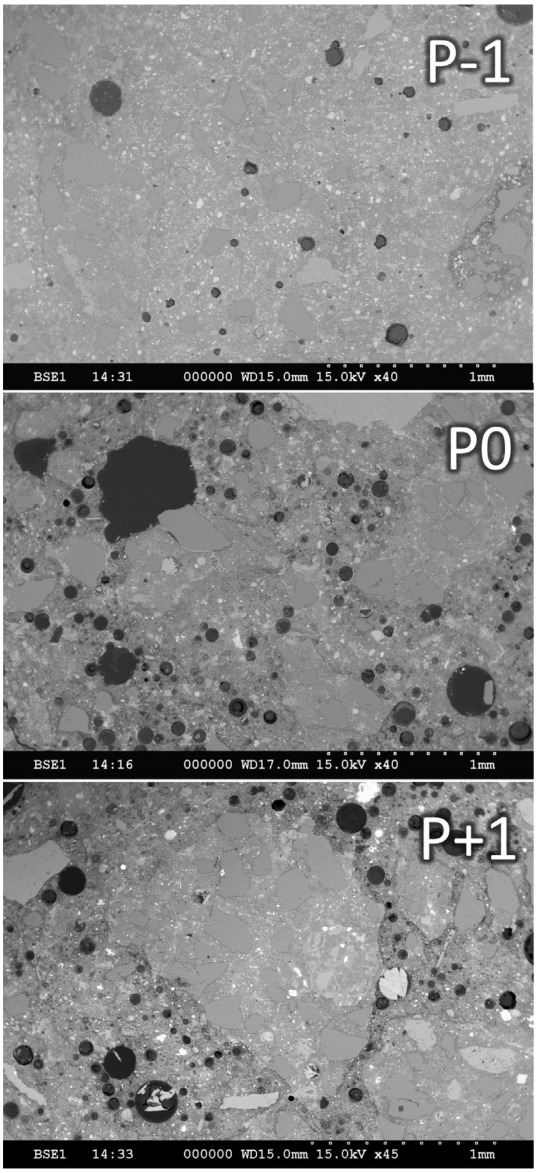


Fig. 7. Comparison of the cement paste density between P-1, P0, and P+1.

3.3. Porosity

While increasing the W/C ratio did not have an effect on the reaction, lowering it raised the swelling amount. Fig. 3 shows a distinctly lower porosity for sample P-1, but not an equally large difference between P0 and P+1. In Fig. 7, these findings are confirmed by showing a similar morphology for P0 and P+1, but a significantly denser matrix for P-1. No superplasticizer was added to counteract a loss in workability due to the lower W/C. The microstructure of P-1 also showed the presence of more unreacted cement particles. The P-1 samples displayed many cracks throughout which were filled with ettringite crystals, as illustrated in Fig. 8. A high swelling level would seemingly be a good indicator for internal damage.

3.4. Sulfates

The S-1 samples contained only 0.28% of water soluble sulfates, which is still well above the maximum allowable limit in recycled aggregates [20]. Still, no significant damage occured, as shown by its swelling behavior in Fig. 2 and microstructure in Fig. 9. The long term compressive strength of these samples, shown in Fig. 3, was lower than those with higher sulfate contaminations, but only because it did not increase after the first month of aging.

3.5. Temperature

The samples kept at lower temperatures showed an important amount of swelling compared to the other mixes, but the reaction seems slower and did not reach a stabilization point yet after 6 months. Compressive strength, shown in Fig. 3, was much lower compared to the other samples, which is due to the limited amount of cement in this mix. Fig. 10 shows the internal damage in these samples, while EDS confirmed that pores, air bubbles or cracks are filled with an ettringite/thaumasite mixture.

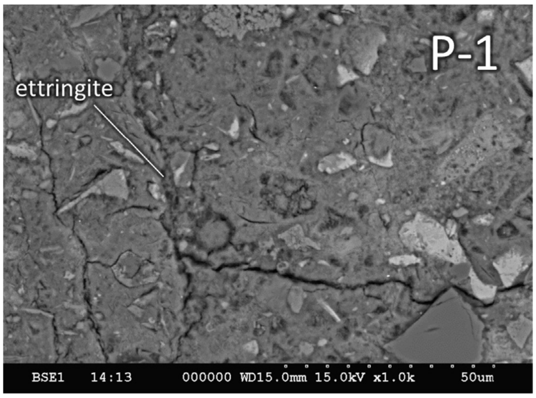


Fig. 8. Cracks filled with ettringite in a sample with lower porosity.

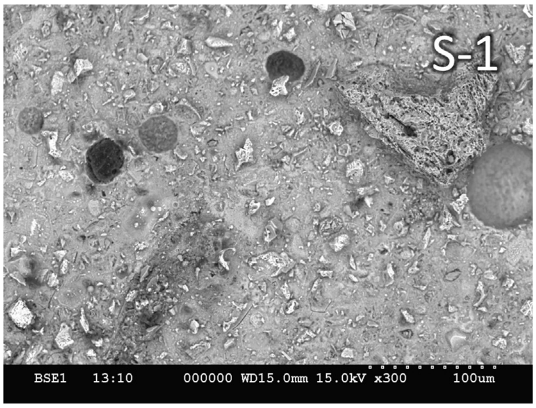


Fig. 9. Lowering the sulfate content resulted in an undamaged sample.

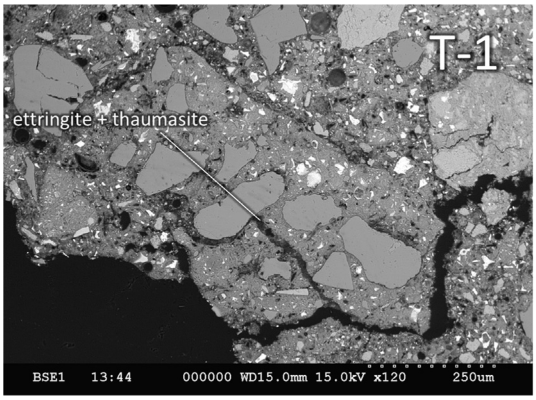


Fig. 10. The T-1 samples were damaged by a mixture of ettringite and thaumasite.

4. Conclusion

The water soluble sulfates in FRA are responsible for a deterioration when they react with C_3A and water in a new cementitious mix. These sulfates could originate from gypsum residues at the demolition site, but also from cement particles in otherwise ‘uncontaminated’ FRA. The severity of this deteriorating reaction is determined by other factors: some can limit the swelling potential, others enhance it. Six parameters were chosen to research and their influence on the sulfate attack reaction has been identified. The use of a model FRA manually contaminated with gypsum made it possible to isolate the responses of only one parameter at a time, without interference of other variabilities or contaminations.

Limiting the C_3A content, using coarse gypsum particles, or augmenting the W/C ratio did not significantly change the swelling results. The formation of thaumasite or limiting the available porosity lead to a larger expansion. On the other hand, increasing the alkalinity of the mix or using a lower sulfate content seemed to limit the swelling results. This indicates that the maximum sulfate content established in EN206 may be too strict, which is in line with the findings of the PN RecyBéton [21] and their subsequent proposal to set this limit at 0.3%. Unrelated to their influence on the swelling amount, the variation of these parameters also changed the compressive strength of the mortars.

In general, the use of FRA in mortars led to a high air content, which was responsible for a lower compressive strength when compared to the compressive strength of a standard mortar with natural aggregates. This air content was explained by the surface roughness of recycled aggregates.

These results provide industrials with helpful information for mix designs with high sulfate contents. This could in turn help promote the use of contaminated FRA, which are up to now not valorized.

Future work should focus on upscaling these tests to concrete, and/or research a possible interaction between the parameters.

CRediT authorship contribution statement

C. Colman: Investigation, Writing - original draft, Visualization. **D. Bulteel:** Supervision, Writing - review & editing. **V. Thiery:** Writing - review & editing. **S. Rémond:** Investigation, Writing -

review & editing. **F. Michel:** Writing - review & editing. **L. Courard:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was conducted in the framework of the Interreg project VALDEM ‘Solutions intégrées de valorisation des flux “matériaux” issus de la démolition des bâtiments: approche transfrontalière vers une économie circulaire’ (Convention n°1.1.57 of Interreg France–Wallonie–Vlaanderen 2014–2020).

References

[1] N. Oikonomou, Recycled concrete aggregates, Cement & Concrete Composites 27 (2005) 315–318, https://doi.org/10.1016/j.cemconcomp.2004.02.020.

[2] S. Delvoie, Z. Zhao, F. Michel, L. Courard, Market analysis of recycled sands and aggregates in northwest europe: drivers and barriers, in: IOP Conference series: Earth and Environmental Science, 2019, pp. 1–8. doi:10.1088/1755-1315/225/1/012055..

[3] M. Collepardi, A state-of-the-art review on delayed ettringite attack on concrete, Cement & Concrete Composites 25 (2003) 401–407, https://doi.org/10.1016/S0958-9465(02)00080-X.

[4] H. Asakura, Y. Watanabe, Y. Ono, M. Yamada, Y. Inoue, A.M. Alfaro, Characteristics of fine processed construction and demolition waste in japan and method to obtain fines having low gypsum component and wood contents, Waste Management & Research 28 (2010) 634–646, https://doi.org/10.1177/0734242X09339951.

[5] W. Ambrós, C. Sampaio, B. Cazacliu, G. Miltzarek, L. R. Miranda, Separation in air jigs of mixed construction and demolition waste, in: Advances in recycling and management of construction and demolition waste, 2017, pp. 25–28..

[6] F. Agrela, M.S. de Juan, J. Ayuso, V. Geraldes, J. Jiménez, Limiting properties in the characterisation of mixed recycled aggregates for use in the manufacture of concrete, Construction and Building Materials 25 (2011) 3950–3955, https://doi.org/10.1016/j.conbuildmat.2011.04.027.

[7] S. Diamond, Delayed ettringite formation – processes and problems, Cement & Concrete Composites 18 (1996) 205–215.

[8] C. Yu, W. Sun, K. Scrivener, Mechanism of expansion of mortars immersed in sodium sulfate solutions, Cement and Concrete Research 43 (2013) 105–111, https://doi.org/10.1016/j.cemconres.2012.10.001.

[9] G. Escadeillas, J. Aubert, M. Segerer, W. Prince, Some factors affecting delayed ettringite formation in heat-cured mortars, Cement and Concrete Research 37 (2007) 1445–1452, https://doi.org/10.1016/j.cemconres.2007.07.004.

[10] A. Pavoine, X. Brunetaud, L. Divet, The impact of cement parameters on delayed ettringite formation, Cement & Concrete Composites 34 (2012) 521–528, https://doi.org/10.1016/j.cemconcomp.2011.11.012.

[11] M. Halaweh, Effect of alkalis and sulfates on portland cement systems, Ph.D. thesis, University of South Florida (2006)..

[12] N. Leklou, Contribution à la connaissance de la réaction sulfatique interne, Ph. D. thesis, Université Paul Sabatier III (2008)..

[13] V. Nguyen, N. Leklou, J. Aubert, P. Mounanga, The effect of natural pozzolan on delayed ettringite formation of the heat-cured mortars, Construction and Building Materials 48 (2013) 479–484, https://doi.org/10.1016/j.conbuildmat.2013.07.016.

[14] M. Juenger, H. Jennings, Effects of high alkalinity on cement pastes, ACI Materials Journal 98a (2001) 251–255.

[15] F. Agrela, M. Cabrera, A. Galvín, A. Barbudo, A. Ramirez, Influence of the sulphate content of recycled aggregates on the properties of cement-treated granular materials using sulphate-resistant portland cement, Construction and Building Materials 68 (2014) 127–134, https://doi.org/10.1016/j.conbuildmat.2014.06.045.

[16] O. Batic, C. Milanesia, P. Maizab, S. Marfilb, Secondary ettringite formation in concrete subjected to different curing conditions, Cement and Concrete Research 30 (2000) 1407–1412, https://doi.org/10.1016/0003-4916(63)90068-X.

[17] D. Breysse, Deterioration processes in reinforced concrete: an overview, in: C. Maierhofer, H. Reinhardt, G. Dobmann (Eds.), Non-Destructive Evaluation of Reinforced Concrete Structures, Ch. 3, Woodhead Publishing, 2010, pp. 28–56.

[18] M. Zhang, J. Chen, Y. Lv, D. Wang, J. Ye, Study on the expansion of concrete under attack of sulfate and sulfate–chloride ions, Construction and Building Materials 39 (2013) 26–32, https://doi.org/10.1016/j.conbuildmat.2012.05.003.

[19] J. De Souza, M. Medeiros, J. Hoppe Filho, Evaluation of external sulfate attack (na2so4 and mgso4): Portland cement mortars containing fillers, Revista IBRACON de Estruturas e Materiais 13 (2020) 644–655, https://doi.org/10.1590/s1983-41952020000300013.

[20] E. C. for Standardization, EN 206:2014 ’Concrete: Specification, performance, production and conformity: Annex E.3 on Recycled Aggregates’ (2014)..

[21] P. Rougeau, L. Schmitt, J. Nai-Nhu, A. Djerbi, M. Saillio, E. Ghorbel, J.-M. Mechling, D. Bulteel, M. Cyr, A. Lecomte, N. Leklou, R. Trauchessec, I. Moulin, T. Lenormand, O. Amiri, Propriétés liées à la durabilité, in: F. D. Larrard, H. Colina (Eds.), Le béton recyclé, Iffstar, 2018..

[22] E. Irassar, Sulfate attack on cementitious materials containing limestone filler — a review, Cement and Concrete Research 39 (2009) 241–254, https://doi.org/10.1016/j.cemconres.2008.11.007.

[23] M. Rahman, M. Bassuoni, Thaumasite sulfate attack on concrete: Mechanisms, influential factors and mitigation, Construction and Building Materials 73 (2014) 652–662, https://doi.org/10.1016/j.conbuildmat.2014.09.034.

[24] A. Neville, The confused world of sulfate attack on concrete, Cement and Concrete Research 34 (2004) 1275–1296, https://doi.org/10.1016/j.cemconres.2004.04.004.

[25] Z. Zhao, S. Rémond, D. Damidot, W. Xu, Influence of hardened cement paste content on the water absorption of fine recycled concrete aggregates, Journal of Sustainable Cement-Based Materials 2 (2013) 186–203, https://doi.org/10.1080/21650373.2013.812942.

[26] E. C. for Standardization, EN 1097-6 ’Tests for mechanical and physical properties of aggregates. Part 6: Determination of particle density and water absorption’ (2001)..

[27] IFSTTAR, Test method no. 78:2011. Tests on aggregates for concrete: measurement of total water absorption by a crushed sand (2011)..

[28] T. Le, S. Rémond, G. Le Saout, E. Garcia-Diaz, Fresh behavior of mortar based on recycled sand: Influence of moisture condition, Construction and Building Materials 106 (2016) 35–42, https://doi.org/10.1016/j.conbuildmat.2015.12.071.

[29] E. C. for Standardization, EN 196-1 ’Methods of testing cement. Part 1: Determination of strength’ (2016)..

[30] H. Taylor, C. Famy, K. Scrivener, Delayed ettringite formation, Cement and Concrete Research 31 (2001) 683–693.

[31] K. Kjellsen, A. Monsoy, K. Isachsen, R. Detwiler, Preparation of flat-polished specimens for sem-backscattered electron imaging and x-ray microanalysis – importance of epoxy impregnation, Cement and Concrete Research 33 (2003) 611–616, https://doi.org/10.1016/S0008-8846(02)01029-3.

[32] M. Bouarroudj, S. Remond, F. Michel, Z. Zhao, D. Bulteel, L. Courard, Use of a reference limestone fine aggregate to study the fresh and hard behavior of mortar made with recycled fine aggregate, Materials and Structures 52 (2019) 1–14, https://doi.org/10.1617/s11527-019-1325-1.

[33] I. Mehdipour, K. Khayat, Understanding the role of particle packing characteristics in rheophysical properties of cementitious suspensions: A literature review, Construction and Building Materials 161 (2018) 340–353, https://doi.org/10.1016/j.conbuildmat.2017.11.147.

[34] L. Courard, F. Michel, M. Martin, The evaluation of the surface free energy of liquids and solids in concrete technology, Construction and Building Materials 25 (2011) 260–266, https://doi.org/10.1016/j.conbuildmat.2010.06.030.

[35] R. Komatsu, N. Mizukoshi, K. Makida, K. Tsukamoto, In-situ observation of ettringite crystals, Journal of Crystal Growth 311 (2009) 1005–1008, https://doi.org/10.1016/j.jcrysgro.2008.09.124.

[36] C. Hargis, A. Telesca, P. Monteiro, Calcium sulfoaluminate (ye’elimite) hydration in the presence of gypsum, calcite, and vaterite, Cement and Concrete Research 65 (2014) 15–20, https://doi.org/10.1016/j.cemconres.2014.07.004.

Annex

The fresh mortars showed a similar slump and density right after mixing (Table 8.1), except for the mix with a limited W/C ratio ('P-1'): its slump was notably lower because no superplastifier was used.

	Slump (mm)	Fresh density (g/cm^3)
A-1, C+1, G-1, P0, S+1, T+1	20.6	1.95
A+1	18.2	2.03
C-1	30.3	1.93
G+1	28.3	1.91
P-1	3.0	1.95
P+1	31.4	1.90
S-1	29.3	1.82
T-1	29.2	2.03

Table 8.1: Fresh properties of the mortar mixes.

Next to the length change, the mass and wavespeed was recorded weekly too. These results are shown in Figure 8.1 and 8.2. No important drops or peaks could be distinguished here, and the mass or wavespeed of a sample did not seem to correlate with its swelling potential (Figure 2 in the publication).

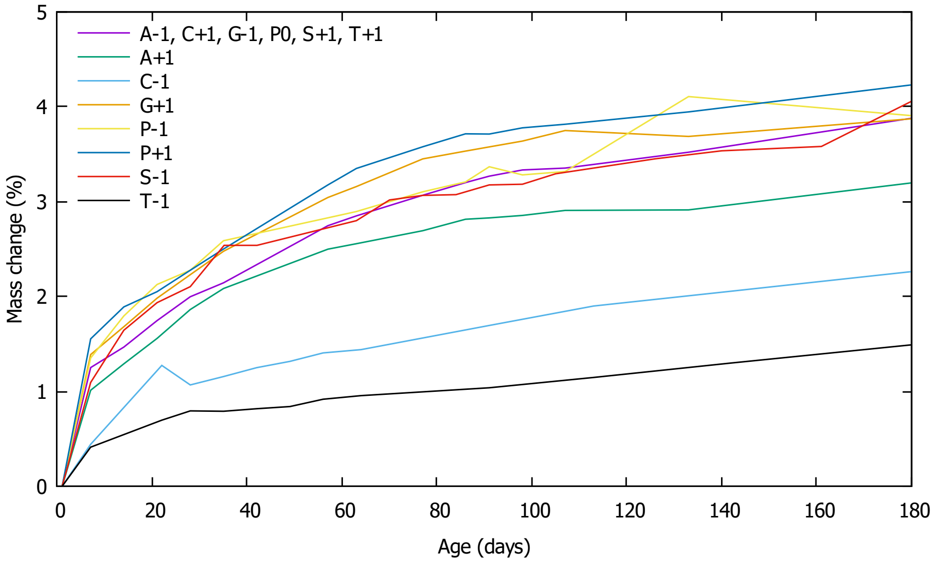


Figure 8.1: Mass change of the mortar samples.

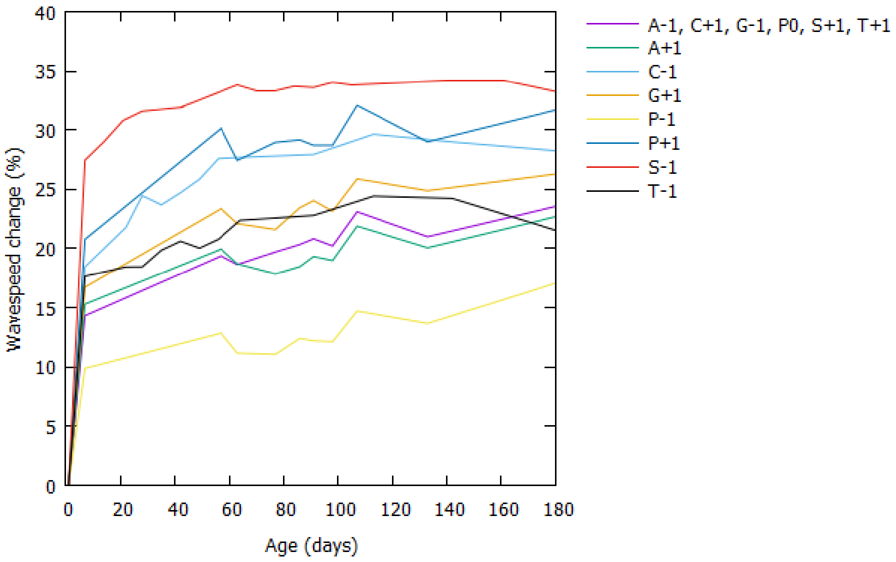


Figure 8.2: Wavespeed change of the mortar samples.

The tensile strength of the mortars was recorded at the same ages as their compressive strength or porosity, and is shown in Figure 8.3. This tensile strength is measured by attaching the samples with an epoxy glue to an apparatus that is subsequently pulled apart by the press. At 180 days of age (and for 'G+1' and 'P-1' at 90 days also), this glue was not strong enough and the samples broke off at this glue interface. As a consequence, these results will not represent the actual tensile strength of the sample and aren't shown. In general, the results from 7, 28 and 90 days were similar as the trends seen for their compressive strength.

Some more microstructure observations are presented below. In Figure 8.4, a general photo series is shown of the transition between the new and old paste and a close-up of those two. The new paste, which contained gypsum from the start of mixing, is significantly more rich in ettringite and has a different morphology. Sulfur mapping shows that ettringite is spread somewhat evenly throughout the new paste, so massive deposits are harder to detect analytically.

The phenomenon where a piece of calcite acted as a nucleation center for ettringite growth at high alkalinities was found throughout the 'A+1' sample. More examples are shown in Figure 8.5.

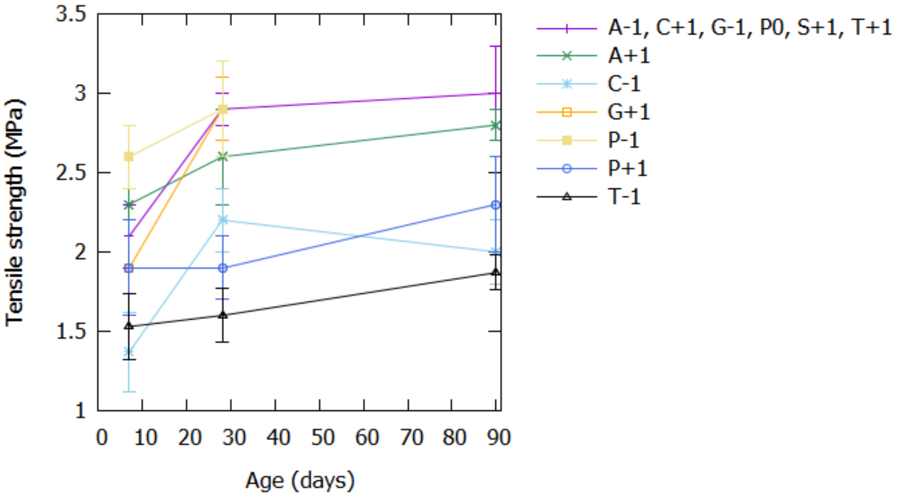


Figure 8.3: Tensile strength of the mortars at 7, 28, 90 and 180 days.

The SEM images in Figure 8.6 show how cracks were not always filled with ettringite. In these cases, the pressure of the cement paste (which was uniformly filled with ettringite as shown before) caused the fissurations, sometimes around or through existing air bubbles.

The question could be posed if the ettringite found inside cracks (Figure 8.7) was the *cause* of the fissuration, or rather a consequence. If ettringite would have formed in pre-existing cracks, the unrestricted formation would create needle-like crystals perpendicular to the crack surface. The crystals in these images were however too small to make out their orientation. The most probable situation would be a mix of both, as (yet) unfilled cracks were observed together with filled ones - which are a classic example of sulfate attack pathology.

Next to a reduced porosity, the limited W/C ratio in the 'P-1' sample had the consequence that more unhydrated cement particles could be found (Figure 8.8).

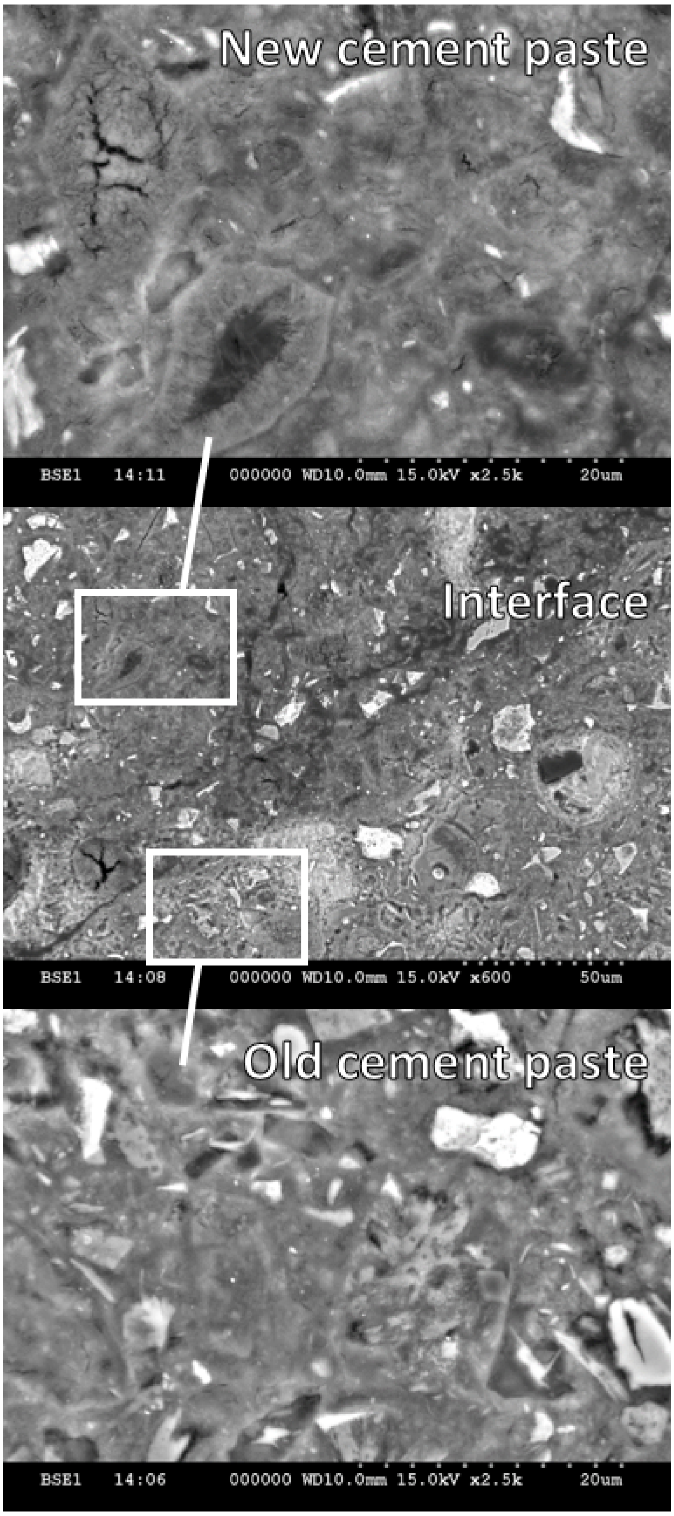


Figure 8.4: The transition between the new and old cement paste.

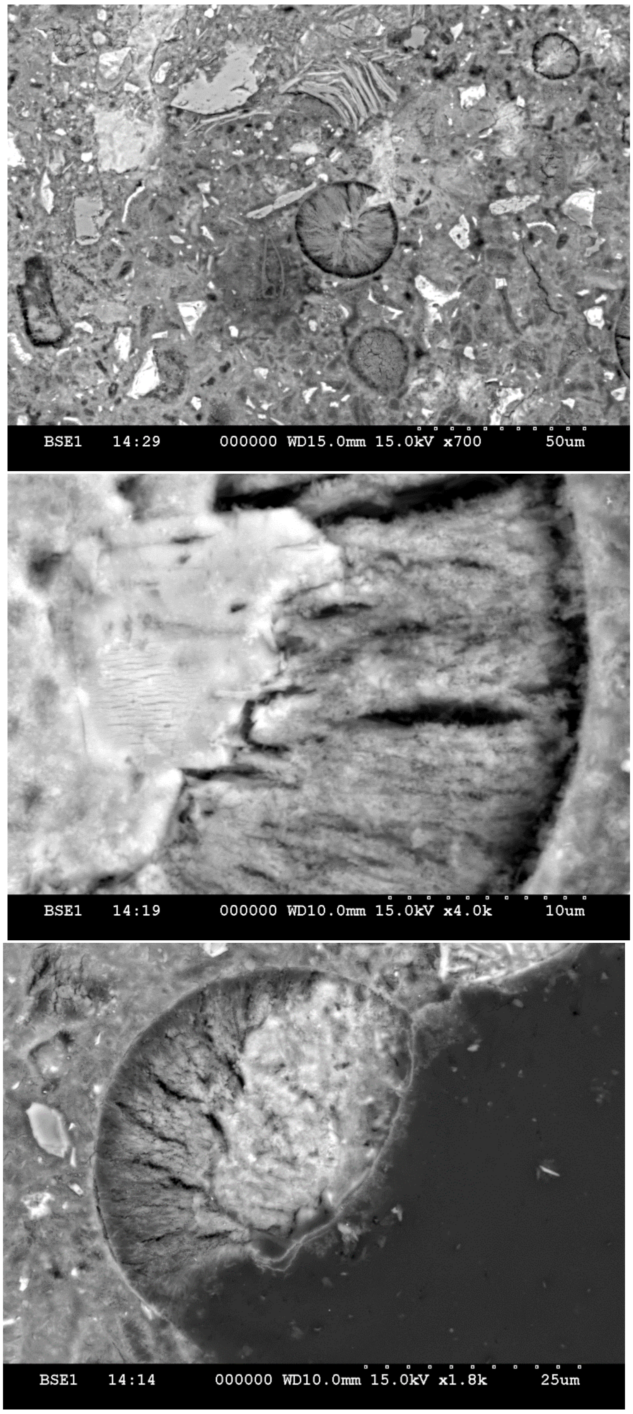


Figure 8.5: More examples of a pore with calcite piece in the center of the ettringite crystals, from the 'A+1' sample.

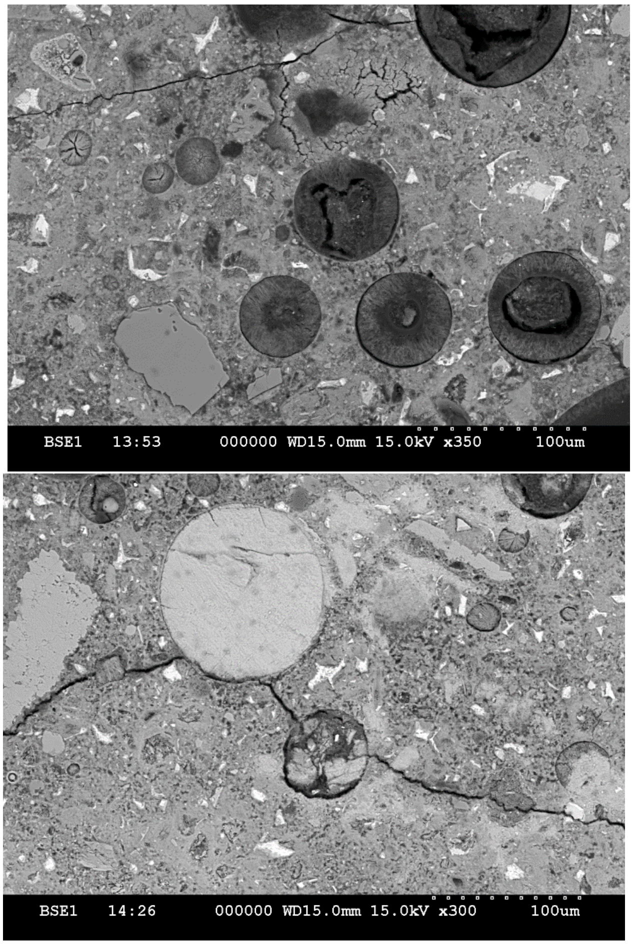


Figure 8.6: Examples of cracks in the 'P+1' sample that were caused by pressure from the cement paste, not by ettringite deposits in pores or air bubbles.

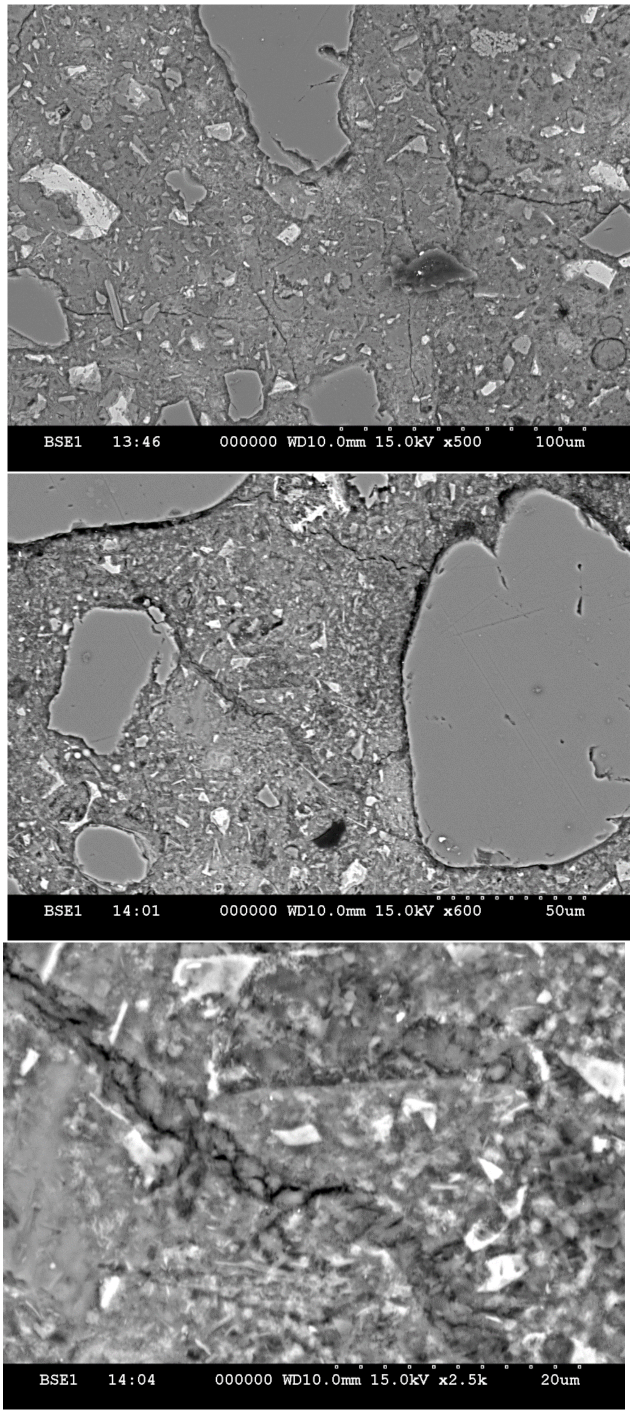


Figure 8.7: Examples of cracks filled with ettringite found in the 'P-1' sample.

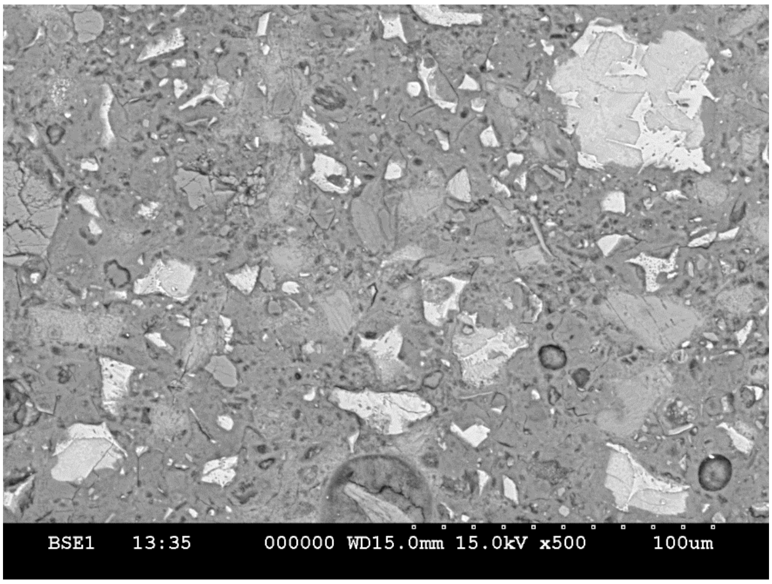


Figure 8.8: Unhydrated cement particles in the 'P-1' sample.

9 | Evaluation of the sulfate limit on concrete

While the study on the incorporation of FRA and the influence of mix parameters was done on mortars, the question could now be posed if the conclusions taken in Chapter 7 and 8 remain true on concrete. Is the expansion in function of certain contamination levels the same on mortars as on concrete? If not, how does this translate to the sulfate limit?

As a fine aggregates in all these mixes, the reference FRA was used. Coarse recycled aggregates, obtained from the same source concrete as the reference FRA, were used in one series but all other experiments were done with coarse natural aggregates. This choice was made because after all, the goal was to valorize contaminated *fine* recycled aggregates, and not research the incorporation of coarse recycled aggregates. In the same mindset, the sulfate contents were always expressed as a mass% of the FRA and not the total aggregate mass.

In the line of Chapter 7 and the valorization of FRA, different sulfate contents were researched to evaluate the sulfate limit from EN206 (0.2 %) and the one proposed in the national project RecyBeton (0.3 %). Following the identification of the parameters in Chapter 8, a limited porosity was used to see if an acceptable contamination could still surpass a swelling limit. An increased alkalinity was tested to see if the expansion caused by unacceptable sulfate contents could be mitigated.

The results showed, just like with mortars, that a mix with FRA either did or didn't swell: there was no middle ground proportional to sulfate concentrations. The level at which the swelling reaction started was however slightly different. For a concrete made with fine as well as coarse recycled aggregates, this was between 0.3 and 0.8 mass% of FRA. A concrete with coarse natural aggregates could handle more sulfates: between 0.8 and 3.1 %. The explanation for this difference was found in the pore size distribution. It seemed that a lower W/C ratio could only affect the expansion of materials that were already undergoing a swelling reaction (cfr Chapter 8):

the concrete with 0.2 % of sulfates did not swell more because of a limited porosity. An increased alkalinity caused an important increase in compressive strength, more than seen on mortars in Chapter 8.

Expansion of concrete by secondary ettringite formation, caused by fine recycled aggregates contaminated with gypsum

Colman, C.[a,b,*], Bulteel, D.[a], Rémond, S.[c], Bouarroudj, M.[a,b], Courard, L.[b]

[a] *Univ. Lille, IMT Lille Douai, ULR 4515 - LGCgE, Laboratoire de Génie Civil et géo-Environnement, F-59000 Lille, France*
[b] *University of Liège, Urban and Environmental Engineering, GeMMe Building Materials, 4000 Liège, Belgium*
[c] *Univ Orléans, Univ Tours, INSA CVL, LaMé, EA 7494, France*

Abstract

Recycled aggregates, and especially the fine (0/4 mm) fraction, are often contaminated with sulfates coming from gypsum residues on the demolition site. When these aggregates are used in concrete, the sulfates can induce internal sulfate attack which causes the expansion of concrete. Standard EN206 sets the water soluble sulfate limit at 0.2 % by weight of the aggregate but other studies suggest this limit could be safely increased. In addition to the sulfate content, other parameters like the porosity and alkalinity of a mix have been seen to influence the swelling results. In this study, the different proposed sulfate limits are evaluated on concrete made with 100 % fine recycled aggregates. It is also researched whether mixing parameters could change the swelling amount regardless of sulfate content. The results showed that the incorporation of fine recycled aggregates with sulfate contents up to 0.8 mass% is safe when combined with coarse natural aggregates. If coarse recycled aggregates are used, the sulfate content of fine recycled aggregates could reach up to 0.3 %. The swelling caused by these sulfate levels was not high enough to be influenced by porosity or alkalinity.

Keywords: Recycled aggregates, sulfate attack, waste management, secondary

---

[*] Corresponding author
Email address: `charlotte.colman@uliege.be` (Colman, C.)

ettringite formation, expansion, contaminated aggregates

---

1. Introduction

The construction industry is one of the most energy and resource consuming sectors in the world and produces an enormous amount of construction and demolition waste (C&DW) [1]. This C&DW consists mostly of crushed concrete [2] and the challenge exists in valorizing this waste stream. C&DW can be reprocessed into recycled aggregates, that can be used inside a new concrete structure as a replacement for natural aggregates [3, 4]. Using recycled aggregates is a practice that decreases the environmental impact of the construction sector by reducing the need for landfills, aggregate extraction and transport [5]. 1.7 tonnes of these recycled aggregates are produced per person per year in Europe, waiting to be valorized [6].

While coarse recycled aggregates (CRA) are already used in various applications without important losses in properties [7, 8, 9, 10, 11, 12], the incorporation of fine recycled aggregates (FRA) faces some problems.

FRA are variably defined by different authors as particles below 4, 4.8 or 5 mm. Typically, they are seen as the less valorizable fraction of the processed C&DW [13]. FRA are a byproduct of the crushing and not made on purpose [14], but nevertheless make up 50 % of the C&DW weight [15]. The negative properties of RA become worse with a smaller particle size: more adherent mortar, higher water absorption [16, 17], more contaminations [18]. Properties like water absorption become more difficult to measure with fineness, which makes special techniques necessary. Where coarse RA can be processed to remove some adherent mortar or impurities, this is not possible for FRA. FRA vary even more in their characteristics - due to heterogeneity - than seen for coarse particles [19]. These characteristics are cited among the reasons why FRA are up to now not valorized [20, 21].

While some authors measure a decline in compressive strength after the incorporation of FRA (like with coarse RA) [22], others note an increase. In those cases, it is assumed that the high fines content acts as a filler, increasing the compacity of the mix and its mechanical performance [23]. The high cement content in FRA could also ensure a better bond [18]. Another reason why some authors find an increase in compressive strength, is because they failed to compensate for the extra water demand of the aggregates, thereby effectively lowering the W/C ratio of their mix.

Gypsum ($CaSO_4.2H_2O$) is often found as a contamination in recycled aggregates, which could have originated from different sources. The demolition of a building will cause gypsum residues - coming from plaster and drywall - to end up in FRA. Gypsum is also used as an addition to Portland cement, to regulate its setting time and prevent a flash set [24]. These gypsum residues are more problematic for the finer size fractions of recycled aggregates, because larger concrete and gypsum particles can still be separated from each other based on a difference in color [25] or density [26], and because the FRA contain a high residual cement content [27, 28, 29]. There is a clear variability between different recycling centers: in industrial FRA samples, values of 0.03-0.25% [30], 0.15-0.8% [31] and up to 1.52% [32] of sulfates have been found in different studies. The valorization of FRA is strongly limited by contaminations with water soluble sulfates [33], because they can induce internal sulfate attack.

Sulfate attack is a deteriorating process for concrete where sulfates react with water and aluminates from cement to form ettringite [34, 35]. Primary ettringite is a normal hydration product in the cement paste: it is only secondary ettringite, formed in an already rigid cement matrix, that risks deteriorating the concrete [36]. Ettringite is an expansive mineral, and will exert a pressure on its surrounding cement paste [37, 38, 39]. The volumetric deformation caused by this reaction can in its turn induce (micro)cracking [24] and a general loss in mechanical performances. Macroscopically, the swelling of concrete can be measured as an indication of internal sulfate attack.

A distinction can be made between different types of sulfate attack. External sulfate attack happens when the sulfates diffuse into the concrete from an aggressive environment [39]. Another reaction called Delayed Ettringite Formation

(DEF) occurs when primary ettringite is destroyed by high curing temperatures, and formed anew in a hardened cement paste. The sulfates in this case come from cement, an internal source.

While external sulfate attack and Delayed Ettringite Formation are known reations, but the context where swelling is caused by the presence of gypsum in FRA is not well researched. The gypsum residues contaminating FRA are another internal source of sulfates and unlike with the DEF reaction, high curing temperatures are not needed to observe the swelling effect of ettringite formation. The term 'secondary ettringite formation' will be used to distinguish this reaction from DEF.

To keep the risk for secondary ettringite formation at a reasonable level, the current water soluble sulfate limit in coarse recycled aggregates is established at 0.2% by EN206 [40], with no specific mention of FRA. The conclusions of recent durability studies indicate a higher level should be made possible [41], specifically up to contents of 0.3% [42].

Research on mortar samples made with FRA and an elevated sulfate concentration of 3% showed that several mixing parameters could influence the swelling results without changing the contamination level itself. Two notable parameters were discovered: a limited porosity enhanced the total expansion, and an increased alkalinity inhibited it [43]. The most commonly accepted theory about the cause of expansion is the heterogeneous crystal pressure exerted by the growing ettringite crystals. In this sense, a lower porosity means more confinement and a higher internal pressure. The alkalinity of the interstitial solution interferes with the equilibrium between the different sulfate phases. A higher alkalinity favors the existence of monosulfate and the absorption of sulfur on the C-S-H gel instead of the formation of ettringite [44], so ettringite formation will trigger as pH lowers. Next to a decrease in swelling results, a higher mechanical performance was found too: alkalinity speeds up hydration and increases early compressive strength [45].

In this study, the effect of sulfate concentration of FRA on the swelling reaction has been analyzed to evaluate different (proposed) sulfate limits. Next, the relevant parameters that could influence the swelling results are studied: can an allowed sulfate content still cause swelling because of a limited porosity, and can an increased alkalinity mitigate the swelling caused by an otherwise rejected sulfate content?

2. Materials and methods

2.1. Used materials

Recycled aggregates were produced in the laboratory by fabricating a standard concrete and subsequently crushing it. The use of 'model' recycled aggregates gave exact control of the chemical composition of the materials and removed any possible variability or contamination at the level of the aggregates by chlorides, organics, etc. The composition of this original concrete is given in Table 1: it was designed to obtain a consistency class S3 and strength class C30/37.

After 90 days of curing at 100 % humidity, this concrete was crushed by a jaw crusher with a jaw opening of 8 cm and divided in two groups: fine recycled aggregates (FRA) of 0/4 mm, and coarse recycled aggregates (CRA) of 4/16 mm. Their size distributions are shown in Figure 1.

While all concrete formulations contained *fine* recycled aggregates, the used *coarse* aggregates were either the CRA or natural limestone aggregates (CNA). These CNA were recomposed to have the same size distribution as CRA, so they resemble the model material. The properties of these 3 aggregate types - FRA, CRA and CNA - are shown in Table 2. The water soluble sulfate content was determined via leaching and analysis with ion chromatography [46]. The water

CEM I 52.5 N	Water	Limestone aggregates (mm)				Superplasticizer
		0/4	2/7	7/14	14/20	
350	175	216	658	436	612	0.4%

Table 1: Composition, in kg, of the original concrete

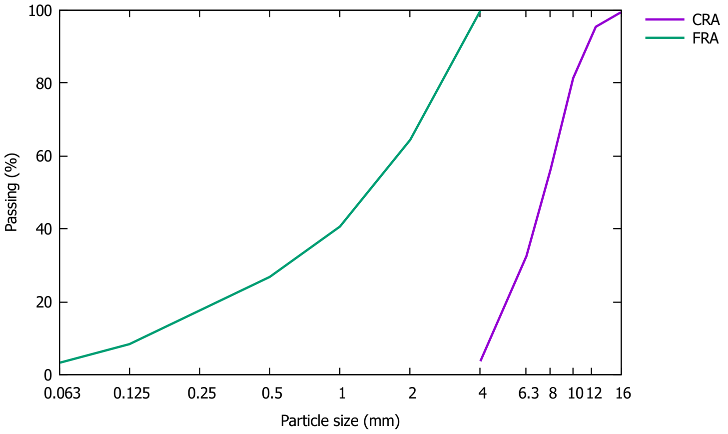


Figure 1: Size distribution of the used recycled aggregates.

	Water absorption (%)	Particle density g/cm^3	SO$_4$$^{2-}$ content (%)
FRA (0/4 mm)	9.78	1.95	0.18
CRA (4/16 mm)	3.12	2.38	0.05
CNA (4/16 mm)	1.4	2.77	0

Table 2: Properties of the used aggregates.

absorption and density of recycled materials was measured with the method described by Zhao et al. [16].

Depending on the concrete formulation, the 0/4 mm fraction of the recycled aggregates was manually contaminated with gypsum - a $CaSO_4.2H_2O$ powder (D50 13 μm) obtained from VWR Chemicals. This gypsum was added and mixed through the aggregates right before the concrete mixing. A CEM I 52.5 N cement from HOLCIM was used; its chemical composition is shown in Table 3. To reach the desired slump, the ViskoCrete superplastifier from Sika was added to the concrete during mixing.

Chemical	CEM I 52.5 N
CaO	64.3
SiO_2	18.3
Al_2O_3	5.2
Fe_2O_3	4.0
MgO	1.4
Na_2O	0.32
K_2O	0.43
SO_3	3.5
Cl^-	0.06
LOI	2.3
C_3A	6.6
C_4AF	12
C_3S	61.9
C_2S	11.2

Table 3: Chemical composition (mass%) of the cement.

2.2. Concrete fabrication

Following previous research, 4 series of experiments were envisaged:

- The sulfate limit was evaluated on concrete with FRA and CRA. Different amounts of gypsum contaminations in the FRA were used.
- These same gypsum contaminations were tested on concrete with FRA and CNA.
- A limited porosity, which was found to be an aggravating parameter, was tested on a concrete that contained the maximum sulfate limit according to EN206.
- An increased alkalinity, which was found to limit the swelling amount, was tested on a concrete with a sulfate content that is normally not accepted.

The nomenclature of the mixes is as follows: [natural or recycled coarse aggregate] - [W/C ratio] - [sulfate content as a mass% of FRA] (-[added alkalinity]).

The design of the concretes was done with the Dreux-Gorisse method: the resulting compositions are given in Table 4. This method specifies the volume fraction of aggregates in the mix. Because this aggregate envelope volume was kept constant, the weights of CRA and CNA depended on their density. To compensate for the elevated water absorption of recycled aggregates, they were presaturated with their absorbed water and 15% of the mixing water, one week before mixing. Presaturating recycled aggregates has been shown to improve the maniability of a mix [47].

The mixing protocol is given in Table 5. The presaturated aggregates were placed in the mixer with gypsum after which the water, cement and superplastifier were added. The superplastifier was added progressively and the slump of the concrete was checked with the help of an Abrams cone according to EN 12350-8, until a value of 10 to 15 cm was obtained. The fresh properties of the concrete mixes are shown in Table 6. 7x7x28 cm bars with measuring pins were cast for weekly swelling tests, and 15x15x15 cm cubes for the periodic mechanical measurements.

Name	FRA	CRA	CNA	Cement	Water	Superplast.	Gypsum	NaOH
R-0.5-3.1	15.2	28.2	0	10.5	7.62	0.0355	0.785	
R-0.5-0.8	15.8	28.2	0	10.5	7.68	0.0317	0.148	
R-0.5-0.3	16.0	28.2	0	10.5	7.69	0.0207	0.033	
R-0.5-0.2	16.0	28.2	0	10.5	7.69	0.0216	0.005	
N-0.5-3.1	15.2	0	32.8	10.5	7.20	0.0355	0.806	
N-0.5-0.8	15.8	0	32.8	10.5	7.26	0.0236	0.171	
N-0.5-0.3	16.0	0	32.8	10.5	7.27	0.0456	0.033	
N-0.5-0.2	16.0	0	32.8	10.5	7.27	0.0121	0.005	
N-0.35-0.2	16.0	0	32.8	10.5	5.70	0.1104	0.005	
N-0.5-0.3-A	16.0	0	32.8	10.5	7.27	0.0431	0.033	0.0224

Table 4: Compositions, in kg, of the concrete mixes.

Action	Time	Total time
Add aggregates (0/16 mm), mix	30”	30”
Add half of the mixing water, mix	2’	2’30”
Rest	2’	4’30”
Add cement, mix	30”	5’
Add second half of mixing water and superplastifier, mix	1’30	6’30”

Table 5: Concrete mixing procedure in function of mixer speed.

Name	Slump (cm)	Density (g/cm^3)
R-0.5-3.1	12	1.894
R-0.5-0.8	14.5	2.066
R-0.5-0.3	10.5	1.958
R-0.5-0.2	14.5	1.726
N-0.5-3.1	11	2.335
N-0.5-0.8	11	2.007
N-0.5-0.3	11.5	1.918
N-0.5-0.2	11.5	1.948
N-0.35-0.2	15	2.079
N-0.5-0.3-A	15	2.075

Table 6: Fresh properties of the concrete mixes.

2.3. Monitoring of the reaction

To follow the development of the internal sulfate attack reaction, the concrete specimens were subjected to different tests. The length change of the concrete bars was recorded weekly with a digital length comparator, in reference to an Invar bar. At 7, 28, 90 and 180 days the concrete samples were characterized mechanically for their compressive strength according to EN 12390-3 [48] with an INSTRON press. Every described test was done for 3 replicates.

3. Results and discussion

In a first series of experiments, the sulfate limits were evaluated. Standard EN206 sets this limit at 0.2 %, while the French national project RecyBéton proposes to increase this to 0.3 %. Two other high sulfate contents, 0.8 % and 3.1 % were tested too.

In Figure 2 the swelling results of the concretes made with FRA and CRA can be seen, and in Figure 3 the results for concrete made with FRA and CNA. For the "R" series made with recycled aggregates, two groups of results can be noticed: those with elevated sulfate contents indeed showed an important swelling, but the mixes with 0.2 and 0.3 % of sulfates did not swell significantly. This indicates that the proposed increase to 0.3 % is feasible. While no difference in swelling results could be seen between 0.2 and 0.3 % of sulfates, the compressive strength did show a difference. The concretes with the lowest and highest amount of sulfates performed worse than those with intermediate levels. It seemed that adding a little gypsum improved the compressive strength, but that 3.1 % was already too much to have a beneficial effect on compressive strength. The fresh density of these concretes was lower which could also have played a role in their diminished compressive strength.

For the "N" concretes which contained CNA in addition to FRA, the mix with 0.8 % of sulfates also showed an acceptable expansion together with the two lower contamination levels. This means that depending on the concrete formulation, even higher amounts than 0.3 % must be possible. The use of CNA

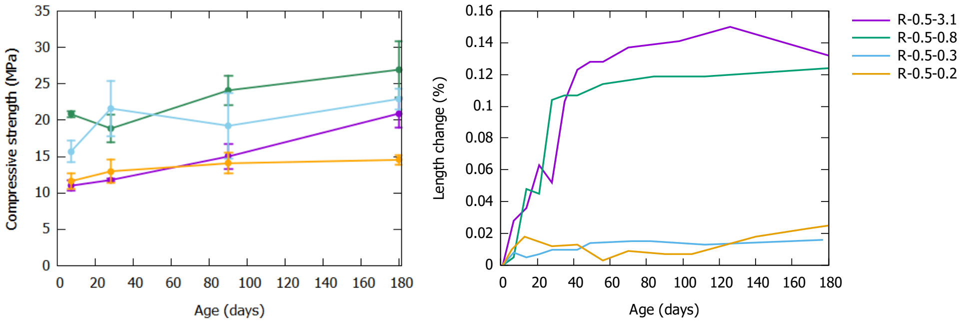


Figure 2: Compressive strength and swelling results for the concrete series with FRA and CRA and varying sulfate contaminations.

lowered the differences between the samples in compressive strength, mostly due to the fact that it was possible to keep their fresh properties such as slump and density very similar.

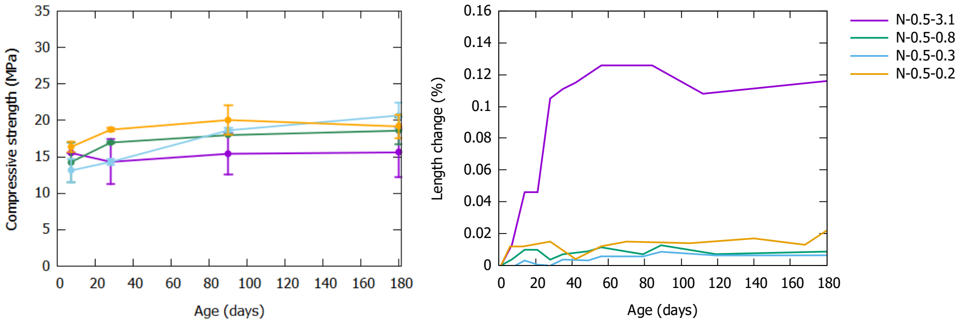


Figure 3: Compressive strength and swelling results for the concrete series with FRA and CNA and varying sulfate contaminations.

The absolute expansion of the concretes that showed a swelling response seemed to be on the same level with the results of other researchers working on sulfate contaminated aggregates: expansions between 0 and 0.12 % are often obtained for roughly the same range of sulfate concentrations [49, 50, 51, 52].

The expansions of ”R-0.5-0.8”, ”R-0.5-3.1” and ”N-0.5-3.1” were 0.124 ± 0.004, 0.132 ± 0.010 and 0.116 ± 0.029 respectively, which is not significantly different for $p>0.05$. It seemed that as soon as swelling occurred, the absolute amount was always the same, unrelated to the sulfate content or the type of coarse aggregate. What *Collepardi et al.* [24] suggested about the necessity of microcracks could explain why there was almost no difference in swelling results between "R-0.5-3.1", "R-0.5-0.8" and "N-0.5-3.1", or all other concrete bars with lower sulfate levels. As soon as the swelling process starts it maintains and accelerates itself regardless of actual sulfate contents. There seemed to be a certain treshold of sulfates for when a concrete started swelling, and the use of CNA increased this treshold: the sulfate content needed to kickstart the expansion was between 0.3 and 0.8 for the "R" series and between 0.8 and 3.1 for the "N" series.

An explanation for this difference in swelling between "R-0.5-0.8" and "N-0.5-0.8" could lie in the pore size distribution. Figure 4 shows the volume of mercury intrusion for different pore sizes of these samples at 90 days. Concretes made with CNA showed two distinct groups of pores at 0.01-0.1 μm and 1-10 μm, while mixes with CRA only exhibited the smaller pore sizes at 0.01-0.1 μm. Ettringite crystals as a hydration product are in the 1-5 μm size range [53], and SEM images of massive ettringite deposits in deteriorated concrete show sizes from a few to 15 μm [43, 54, 55]. It would make sense that these larger pore sizes get 'filled up' first and the "N-0.5-0.8" has enough reserve of these pore sizes to accommodate this. On the other hand, "R-0.5-0.8" does not have these micrometric pores and the formation of ettringite lead to a degradation of the concrete.

The porosity of a mix, influenced by its W/C ratio, has been shown to be an enhancing factor for the expansion due to internal sulfate attack. For an acceptable sulfate content of 0.2 %, this means that the expansion could still be significant with low W/C ratios. Figure 5 shows this was not the case. A sulfate contamination of 0.2 % was not enough to provoke a significant swelling reaction even in these aggravating circumstances. As expected, "N-0.35-0.2" did show a higher compressive strength. This is clearly caused by its low W/C ratio and subsequently lower porosity, as the fresh densities were very similar. The actual porosity of these mixes, measured by Mercury Intrusion, is presented in Figure

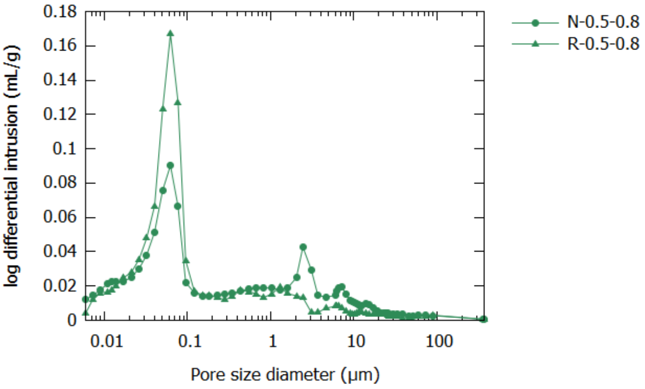


Figure 4: The pore size distribution at 90 days of R-0.5-0.8 and N-0.5-0.8.

6.

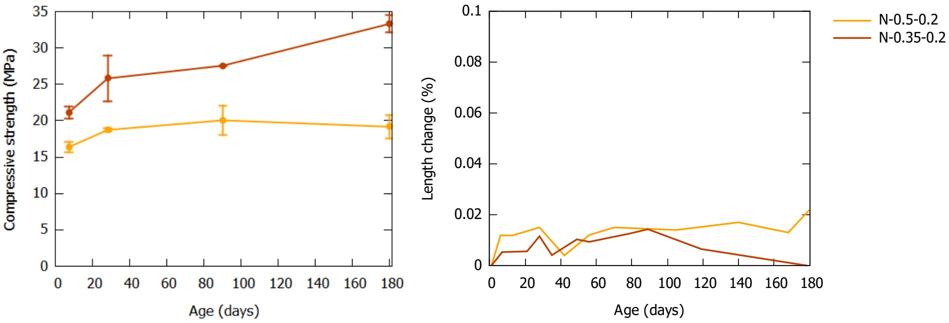


Figure 5: Compressive strength and swelling results for the concrete series with the maximum allowable sulfate content and a varying porosity.

As seen in a previous study, increasing the alkalinity of a mix will inhibit the swelling effect caused by a sulfate contamination. A sulfate level of 0.3 %, which was proposed as a safe contamination by recent research but not yet accepted by international standards, was chosen as a reference. Although the expansion with 0.3 % of sulfates is not significant, an increased alkalinity still lowered this amount. The compressive strength of this mix was very high compared to the other concretes in these experiments, and again not correlated to any fresh properties. The increased performance caused by alkalinity was already

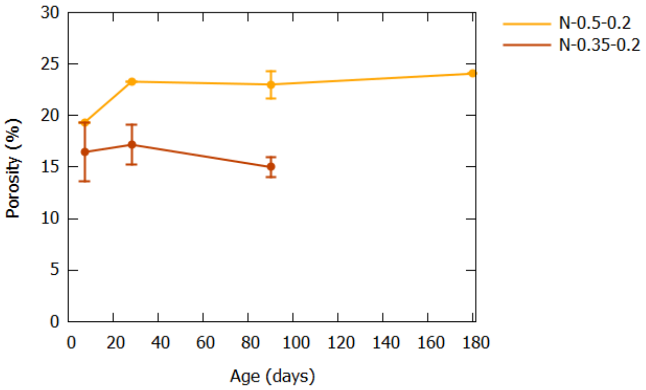


Figure 6: Porosity of the concrete series with the maximum allowable sulfate content and a varying porosity.

described by other authors.

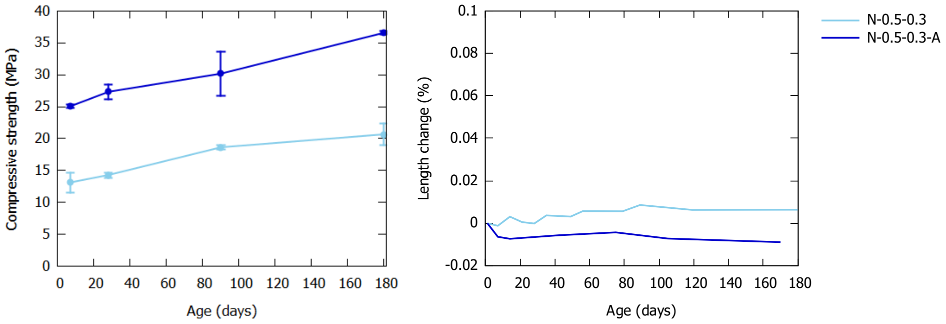


Figure 7: Compressive strength and swelling results for the concrete series with a higher sulfate content, and a varying alkalinity.

4. Conclusion

The sulfate limit was evaluated on concretes with fine recycled aggregates. Both the limit of 0.2 % from EN206 and the proposed one of 0.3 % proved to be safe and did not provoke any significant swelling. Depending on the nature of the coarse aggregates (natural or recycled), the contamination level at which swelling starts may differ. For CRA, this sulfate concentration was between

0.3 and 0.8 mass% of FRA, and for CNA this was between 0.8 and 3.1 mass% of FRA. This difference in limits could be due to the pore size distribution: a lack of pores in the 1-10 μm range means less resistance to swelling. The amount of expansion did not correlate with the amount of sulfates: as soon as swelling started, the absolute length changes stayed the same regardless of sulfate contents.

These results showed that the sulfate limit of 0.2 % could be seen as too strict, and that an increase to *at least* 0.3 % should be possible. Unless a high contamination level is present, a limited porosity will not worsen the swelling, and an increased alkalinity would not be necessary to limit it.

Some perspectives were gained from this study that could inspire future research. More sulfate contents, in smaller increments, could be tested to narrow down the limit where the reaction starts. While significant swelling has been recorded for 3.1 % of sulfates, the other deterioration symptoms (like cracking, sudden mechanical performance loss) that are associated with sulfate attack were not seen. Extreme sulfate contents could be tested to assess what kind of damage they can provoke. The effect of pore size distribution on sensitivity to expansion could be very interesting to research. Porosity measurements on the nano scale, and microstructure observations can be useful here.

Acknowledgements

This research was conducted in the framework of the Interreg project VALDEM ‘Solutions intégrées de valorisation des flux ”matériaux” issus de la démolition des bâtiments: approche transfrontalière vers une économie circulaire’ (Convention n°1.1.57 of Interreg France–Wallonie-Vlaanderen 2014-2020). We thank the Centre Terre et Pierre in Tournai, Belgium for the crushing of concrete which provided the reference materials for this study.

References

[1] United Nations Environment Programme, Sustainable buildings and climate initiative (2016).

[2] M. Behera, S. Bhattacharyya, A. Minocha, R. Deoliya, S. Maiti, Recycled aggregate from C&D waste and its use in concrete, a breakthrough towards sustainability in the construction sector: A review, Construction and Building Materials 68 (2014) 501–516. `doi:10.1016/j.conbuildmat.2014.07.003`.

[3] C. Thormark, Conservation of energy and natural resources by recycling building waste, Resources, Conservation and Recycling 33 (2001) 113–130. `doi:10.1016/S0921-3449(01)00078-7`.

[4] N. Oikonomou, Recycled concrete aggregates, Cement & Concrete Composites 27 (2005) 315–318. `doi:10.1016/j.cemconcomp.2004.02.020`.

[5] N. Serres, S. Braymand, F. Feugeas, Environmental evaluation of concrete made from recycled concrete aggregate implementing life cycle assessment, Journal of Building Engineering 5 (2016) 24–33. `doi:10.1016/j.jobe.2015.11.004`.

[6] S. Delvoie, Z. Zhao, F. Michel, L. Courard, Market analysis of recycled sands and aggregates in NorthWest Europe: drivers and barriers, in: IOP Conference series: Earth and Environmental Science, 2019, pp. 1–8. `doi:10.1088/1755-1315/225/1/012055`.

[7] J. De Brito, J. Ferreira, J. Pacheco, D. Soares, M. Guerreiro, Structural, material, mechanical and durability properties and behaviour of recycled aggregates concrete, Journal of Building Engineering 6 (2016) 1–16. `doi:10.1016/j.jobe.2016.02.003`.

[8] M. Bravo, J. De Brito, J. Pontes, L. Evangelista, Mechanical performance of concrete with recycled aggregates from construction and demolition waste

recycling plants, Journal of Cleaner Production 99 (2015) 59–74. `doi:10.1016/j.jclepro.2015.03.012`.

[9] P. Gutierrez, M. Sanchez de Juan, Utilization of recycled concrete aggregate for structural concrete, in: Service Life Design for Infrastructures, Delft, 2018.

[10] A. Rao, K. Jha, S. Misra, Use of aggregates from recycled construction and demolition waste in concrete, Resources, Conservation and Recycling 50 (2007) 71–81. `doi:10.1016/j.resconrec.2006.05.010`.

[11] Z. Zhao, L. Courard, S. Groslambert, T. Jehin, A. Léonard, J. Xiao, Use of recycled concrete aggregates from precast block for the production of new building blocks: An industrial scale study, Resources, Conservation and Recycling 157 (2020). `doi:10.1016/j.resconrec.2020.104786`.

[12] J. Thomas, N. Thaickavil, P. Wilson, Strength and durability of concrete containing recycled concrete aggregates, Journal of Building Engineering 19 (2018) 349–365. `doi:10.1016/j.jobe.2018.05.007`.

[13] B. Mignon, H. Bréquel, Comparative case study of the construction and demolition waste practical treatment induced by different legislations in France and Belgium (Wallonia and Flanders), in: International HISER Conference on Advances in Recycling and Management of Construction and Demolition Waste, 2017.

[14] C. Ulsen, H. Kahn, G. Hawlitschek, E. Masini, S. Angulo, V. John, Production of recycled sand from construction and demolition waste, Construction and Building Materials 40 (2013) 1168–1173. `doi:10.1016/j.conbuildmat.2012.02.004`.

[15] S. Angulo, C. Ulsen, V. John, H. Kahn, M. Cincotto, Chemical–mineralogical characterization of C&D waste recycled aggregates from São Paulo, Brazil, Waste Management 29 (2009) 721–730. `doi:10.1016/j.wasman.2008.07.009`.

[16] Z. Zhao, S. Rémond, D. Damidot, W. Xu, Influence of hardened cement paste content on the water absorption of fine recycled concrete aggregates, Journal of Sustainable Cement-Based Materials 2 (2013) 186–203. `doi:10.1080/21650373.2013.812942`.

[17] V. Tam, C. Tam, K. Le, Removal of cement mortar remains from recycled aggregate using pre-soaking approaches, Resources, Conservation and Recycling 50 (2007) 82–101. `doi:10.1016/j.resconrec.2006.05.012`.

[18] L. Evangelista, J. De Brito, Concrete with fine recycled aggregates: a review, European Journal of Environmental and Civil Engineering 18 (2014) 129–172. `doi:10.1080/19648189.2013.851038`.

[19] E. Robinet, Utilisation des fines de recyclage dans la formulation de bétons autocompactants, Master's thesis, Université de Liège (2017).

[20] M. Bravo, J. De Brito, J. Pontes, L. Evangelista, Durability performance of concrete with recycled aggregates from construction and demolition waste plants, Construction and Building Materials 77 (2015) 357–369. `doi:10.1016/j.conbuildmat.2014.12.103`.

[21] S. Braymand, S. Roux, K. Deodonne, C. Mihalcea, F. Feugeas, C. Fond, Les granulats recyclés de bétons: un matériau à fort potentiel de valorisation dans les bétons, in: Matériaux, Montpellier, 2014.

[22] J. Khatib, Properties of concrete incorporating fine recycled aggregate, Cement and Concrete Research 35 (2005) 763–769. `doi:10.1016/j.cemconres.2004.06.017`.

[23] M. Braga, J. De Brito, R. Veiga, Incorporation of fine concrete aggregates in mortars, Construction and Building Materials 36 (2012) 960–968. `doi:10.1016/j.conbuildmat.2012.06.031`.

[24] M. Collepardi, A state-of-the-art review on delayed ettringite attack on concrete, Cement & Concrete Composites 25 (2003) 401–407. `doi:10.1016/S0958-9465(02)00080-X`.

[25] H. Asakura, Y. Watanabe, Y. Ono, M. Yamada, Y. Inoue, A. M. Alfaro, Characteristics of fine processed construction and demolition waste in japan and method to obtain fines having low gypsum component and wood contents, Waste Management & Research 28 (2010) 634–646. `doi:10.1177/0734242X09339951`.

[26] W. Ambrós, C. Sampaio, B. Cazacliu, G. Miltzarek, L. R. Miranda, Separation in air jigs of mixed construction and demolition waste, in: Advances in recycling and management of construction and demolition waste, 2017, pp. 25–28.

[27] T. Hansen, H. Narud, Strength of recycled concrete made from crushed concrete coarse aggregate, Concrete International 5 (1983) 79–83.

[28] R. Nassar, P. Soroushian, Strength and durability of recycled aggregate concrete containing milled glass as partial replacement for cement, Construction and Building Materials 29 (2012) 368–377. `doi:10.1016/j.conbuildmat.2011.10.061`.

[29] C. Poon, Z. Shui, L. Lam, Effect of microstructure of itz on compressive strength of concrete prepared with recycled aggregates, Construction and Building Materials 18 (2004) 461–468. `doi:10.1016/j.conbuildmat.2004.03.005`.

[30] F. Rodrigues, M. Carvalho, L. Evangelista, J. De Brito, Physical–chemical and mineralogical characterization of fine aggregates from construction and demolition waste recycling plants, Journal of Cleaner Production 52 (2013) 438–445. `doi:10.1016/j.jclepro.2013.02.023`.

[31] C. Colman, D. Bulteel, S. Rémond, Z. Zhao, L. Courard, Valorization of fine recycled aggregates contaminated with gypsum residues: characterization and evaluation of the risk for secondary ettringite formation, Materials 13 (2020). `doi:10.3390/ma13214866`.

[32] M. Martín-Morales, M. Zamorano, A. Ruiz-Moyano, I. Valverde-Espinosa, Characterization of recycled aggregates construction and demolition waste for concrete production following the spanish structural concrete code ehe-08, Construction and Building Materials 25 (2011) 742–748. `doi:10.1016/j.conbuildmat.2010.07.012`.

[33] F. Agrela, M. S. de Juan, J. Ayuso, V. Geraldes, J. Jiménez, Limiting properties in the characterisation of mixed recycled aggregates for use in the manufacture of concrete, Construction and Building Materials 25 (2011) 3950–3955. `doi:10.1016/j.conbuildmat.2011.04.027`.

[34] K. Mehta, P. Monteiro, Concrete: Microstructure, Properties, and Materials, McGraw-Hill, 2006.

[35] A. Le Roux, S. Orsetti, Les réactions sulfatiques: conditions de formation, structure et expansion des minéraux secondaires sulfatés, Bulletin des laboratoires des ponts et chaussées 225 (2000) 41–50.

[36] X. Brunetaud, Etude de l'influence de différents paramètres et de leurs interactions sur la cinétique et l'amplitude de la réaction sulfatique interne au béton, Ph.D. thesis, École Centrale Paris (2005).

[37] S. Diamond, Delayed ettringite formation - processes and problems, Cement & Concrete Composites 18 (1996) 205–215.

[38] H. Taylor, C. Famy, K. Scrivener, Delayed ettringite formation, Cement and Concrete Research 31 (2001) 683–693.

[39] D. Breysse, Deterioration processes in reinforced concrete: an overview, in: C. Maierhofer, H. Reinhardt, G. Dobmann (Eds.), Non-Destructive Evaluation of Reinforced Concrete Structures, Woodhead Publishing, 2010, Ch. 3, pp. 28–56.

[40] European Committee for Standardization, EN 206 'Concrete: Specification, performance, production and conformity: Annex E.3 on Recycled Aggregates' (2014).

[41] A. Yammine, L. Nordine, M. Choinska, F. Bignonnet, J. Mechling, DEF damage in heat cured mortars made of recycled concrete sand aggregate, Construction and Building Materials 252 (2020). `doi:10.1016/j.conbuildmat.2020.119059`.

[42] P. Rougeau, L. Schmitt, J. Nai-Nhu, A. Djerbi, M. Saillio, E. Ghorbel, J.-M. Mechling, A. Lecomte, R. Trauchessec, D. Bulteel, M. Cyr, N. Leklou, O. Amiri, I. Moulin, T. Lenormand, Durability-related properties, in: F. De Larrard, H. Colina (Eds.), Concrete Recycling : Research and Practice, CRC Press, 2019.

[43] C. Colman, D. Bulteel, V. Thiery, S. Rémond, F. Michel, L. Courard, Internal sulfate attack in mortars containing contaminated fine recycled concrete aggregates, Construction and Building Materials 272 (2020). `doi:10.1016/j.conbuildmat.2020.121851`.

[44] G. Escadeillas, J. Aubert, M. Segerer, W. Prince, Some factors affecting delayed ettringite formation in heat-cured mortars, Cement and Concrete Research 37 (2007) 1445–1452. `doi:10.1016/j.cemconres.2007.07.004`.

[45] M. Juenger, H. Jennings, Effects of high alkalinity on cement pastes, ACI Materials Journal 98a (2001) 251–255.

[46] C. Colman, Z. Zhao, F. Michel, S. Rémond, D. Bulteel, L. Courard, Gypsum residues in recycled materials: Characterization of fine recycled aggregates, in: Service Life Design for Infrastructures, Delft, 2018.

[47] T. Le, S. Rémond, G. Le Saout, E. Garcia-Diaz, Fresh behavior of mortar based on recycled sand: Influence of moisture condition, Construction and Building Materials 106 (2016) 35–42. `doi:10.1016/j.conbuildmat.2015.12.071`.

[48] European Committee for Standardization, EN 12390 'Testing hardened concrete. Part 3: Compressive strength of tests specimens' (2001).

[49] S. Abid, A. Nahhab, H. Al-aayedi, A. Nuhair, Expansion and strength properties of concrete containing contaminated recycled concrete aggregate, Case studies in Construction Materials 9 (2018). `doi:10.1016/j.cscm.2018.e00201`.

[50] S. Orsetti, Influence des sulfates sur l'apparition et le développement de pathologies dans les matériaux de génie civil traités ou non aux liants hydrauliques: cas du plâtre dans les granulats issus de produits de démolition, Ph.D. thesis, Université Pierre et Marie Curie (1997).

[51] G. Tovar-Rodrígues, M. Barra, S. Pialarissi, D. Aponte, E. Vázquez, Expansion of mortars with gypsum contaminated fine recycled aggregates, Construction and Building Materials 38 (2013) 1211–1220. `doi:10.1016/j.conbuildmat.2012.09.059`.

[52] J. Gallias, Action of gypsum on recycled aggregate concrete, in: Proceedings CIB World Building Congress, Gaevle, Sweden, 1998.

[53] P. C. Hewlett, M. Liska (Eds.), Lea's Chemistry of Cement and Concrete, fifth edition Edition, Butterworth-Heinemann, London, 2019. `doi:https://doi.org/10.1016/B978-0-08-100773-0.09991-3`.

[54] A. Campos, C. López, A. Blanco, A. Aguado, Effects of an internal sulfate attack and an alkali-aggregate reactionin a concrete dam, Construction and Building Materials 166 (2018) 668–683. `doi:10.1016/j.conbuildmat.2018.01.180`.

[55] M. Thomas, K. Folliard, T. Drimalas, T. Ramlochan, Diagnosing delayed ettringite formation in concrete structures, Cement and Concrete Research 38 (2008) 841–847. `doi:10.1016/j.cemconres.2008.01.003`.

Annex

Next to the length change, the resonance frequency of the samples was recorded. For the 'R'-series (Figure 9.1) it was higher for the most contaminated sample but did not show any sudden changes to indicate internal damage. The porosity of these samples, shown in Figure 9.2, correlated well with their compressive strength (Figure 2 in the publication): lower porosities performed better mechanically.

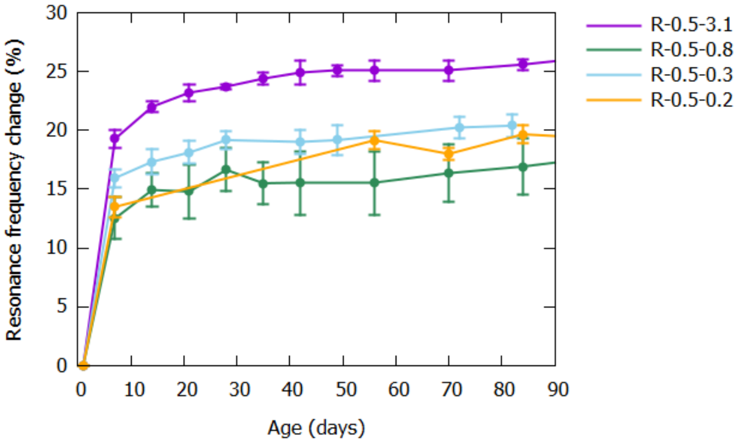


Figure 9.1: Resonance frequency change for the concrete series with FRA and CRA and varying sulfate contaminations.

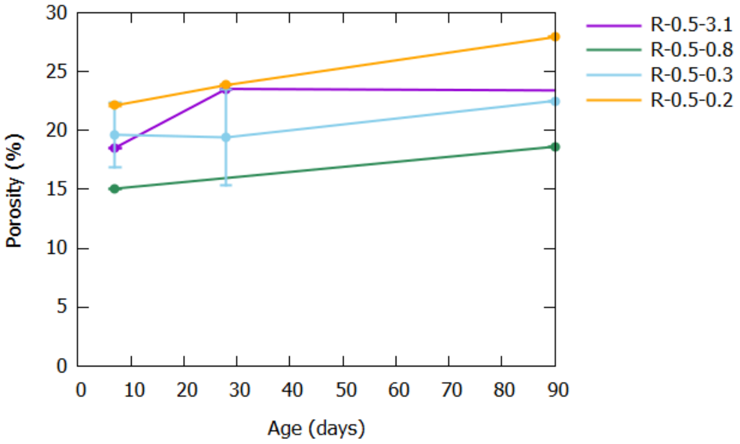


Figure 9.2: Porosity by mercury intrusion of the concrete series with FRA and CRA and varying sulfate contaminations.

For the 'N'-series the resonance frequency (Figure 9.3) continues to rise, contrary to the samples with full recycled aggregates. This has been seen in the preliminary studies in Chapter 5.3 too, where mixes with recycled aggregates reach their 'final' point much faster. The differences between the samples in porosity (Figure 9.4) are smaller, just as with their compressive strength (Figure 3 in the publication). No link can be seen between their porosity and expansion.

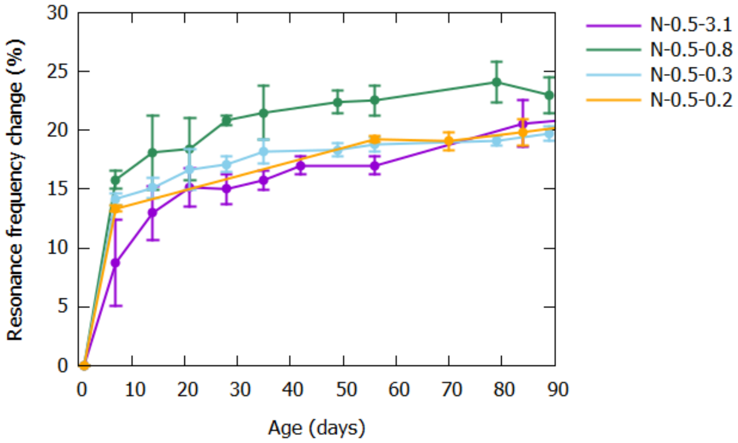


Figure 9.3: Resonance frequency change for the concrete series with FRA and CNA and varying sulfate contaminations.

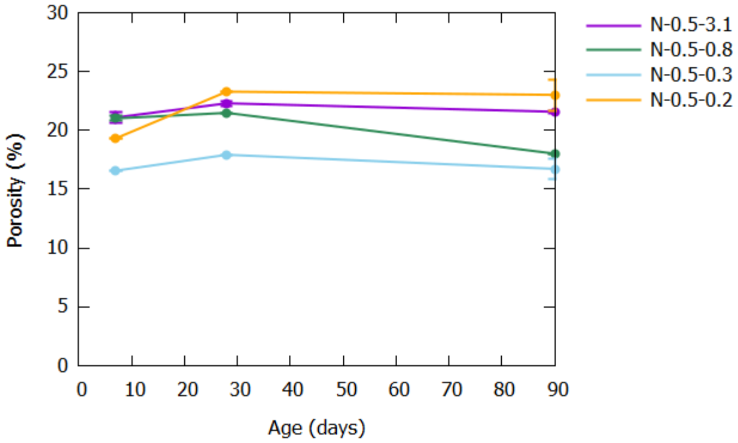


Figure 9.4: Porosity by mercury intrusion of the concrete series with FRA and CNA and varying sulfate contaminations.

The porosity of 'N-0.35-0.2' and 'N-0.5-0.2' has already been shown in the publication (Figure 6). Following the same trend as their swelling, porosity and compressive strength, there is a clear difference in resonance frequency (Figure 9.5).

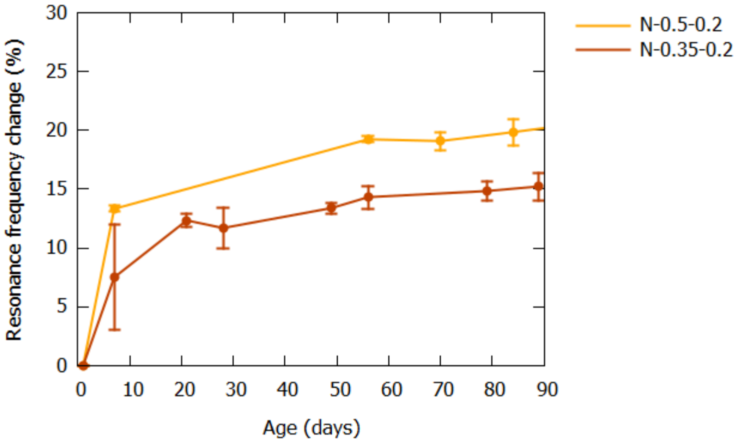


Figure 9.5: Resonance frequency change for the concrete series with the maximum allowable sulfate content and a varying porosity.

While a slight difference in swelling and a large difference in compressive strength was recorded for the concretes with varying alkalinity, their resonance frequency is nearly the same. As with the other concretes made with coarse natural aggregates, it also continues to rise. The differences in porosity between the two samples are not as high as would be expected looking at their compressive strength. Following these two observations, the increase in mechanical performance for 'N-0.5-0.3-A' is the chemical consequence of the alkalinity, and not of differences in cement paste compacity/porosity.

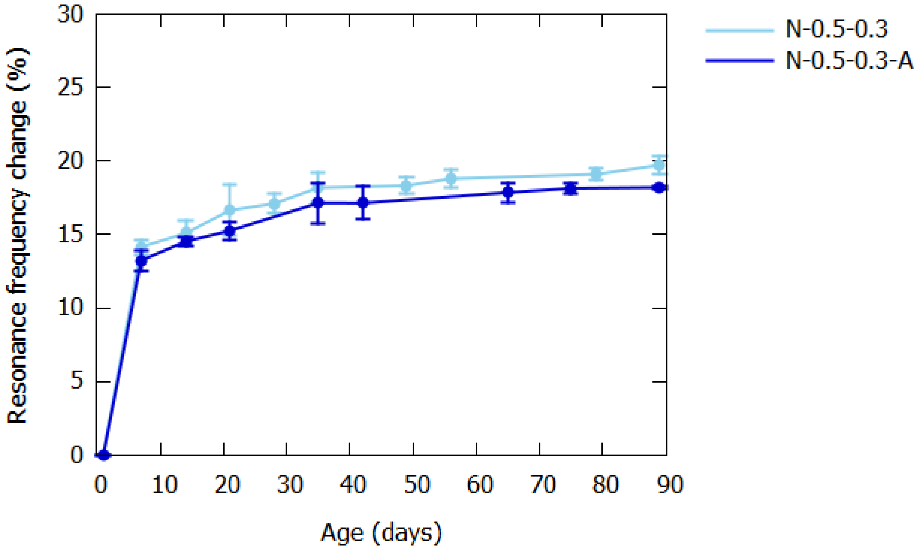


Figure 9.6: Resonance frequency change for the concrete series with a higher sulfate content, and a varying alkalinity.

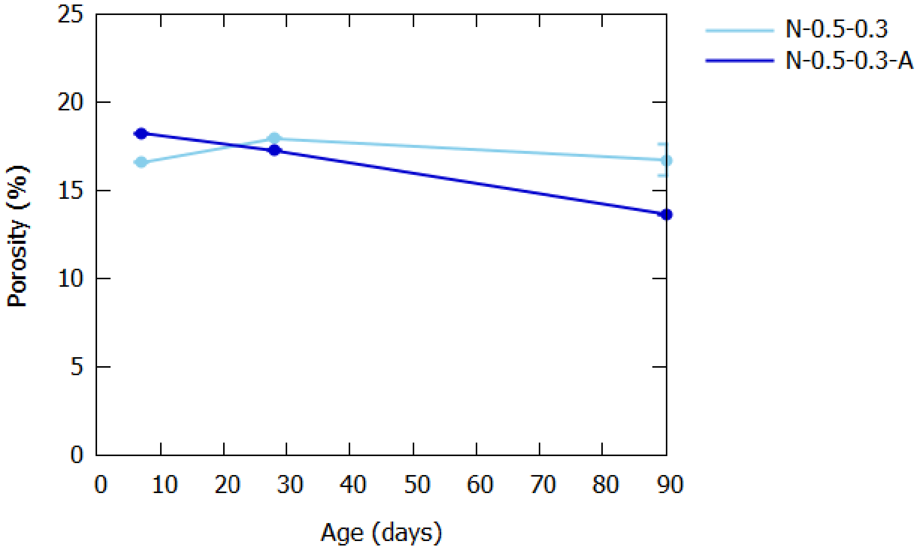


Figure 9.7: Porosity by mercury intrusion of the concrete series with a higher sulfate content, and a varying alkalinity.

Conclusion

Industrial FRA samples showed the typical characteristics of recycled aggregates that were also laid out in Chapter 1, such as a high water absorption, low density and high fines content. They were indeed contaminated with important amounts of sulfates - much more than allowed according to EN206 - confirming the hesitation of industrials to valorize them. Nevertheless, the mortars that incorporated these FRA did not show any significant swelling reaction or other signs of damage. The properties of the mortars with these aggregates were also better than with the reference FRA. These results were very positive towards a valorization of contaminated FRA, provided the mix design takes into account their water absorption and density.

For a recycled aggregate with an elevated sulfate contamination, several parameters were found to be important with regards to its swelling potential, while others did not influence it. An increase in alkalinity was shown to decrease the total expansion of a mortar. Factors such as a low W/C ratio and the possibility for thaumasite formation in a mix proved to be important in the other sense: it should be taken into account that they can significantly worsen the swelling reaction. Microstructure analyses showed that ettringite was concentrated in pores and air bubbles, from which cracks can propagate. Other observations were the other way around: ettringite in the cement paste was exerting pressure on pores. It was also discovered how calcite favors a rapid ettringite growth at high alkalinities, explaining its effect on the swelling amount. These results indicate that a sulfate content of at least 3.1 % could be mitigated in mortars, which promotes the valorization of even very highly contaminated aggregates.

These conclusions were then evaluated on a concrete scale. For different sulfate contents in FRA, two types of swelling were observed: negligible ($<$ 0.02 %) or significant (0.10-0.12 %) expansions. A certain sulfate content seemed to 'kickstart' the reaction, but the resulting swelling amount stayed the same regardless of actual sulfate concentration. This sulfate limit was different depending on the type of material: between 0.3-0.8 % for concrete with coarse recycled aggregates, and between 0.8-3.1 % for coarse natural aggregates. The explanation was found in the pore size distribution on the concretes, where the absence of pores in the 1-10 μm range made the sample susceptible to swelling. Both an aggravating and a limiting parameter have been tested on concretes with 0.2 and 0.3 % of sulfates. This level contamination was not enough to provoke any swelling and the porosity/alkalinity of the mix did not change that. This means that, for reasonable sulfate contents, those parameters do not need to be as accurately tuned as for very contaminated samples - in contrast with the mixes from Chapter 8. These results are positive towards a slight increase of the allowable sulfate limit in FRA.

General conclusion and perspectives

Fine recycled aggregates - and especially those contaminated with sulfate residues - are not valorized on a high enough scale, resulting in a very voluminous material stream going to waste. Internal sulfate attack as a deteriorating reaction caused by FRA is not well researched and leads to the hesitation of industrials to incorporate FRA. This is further perpetuated by strict standards and legislations. The goal of this research was consequently to study the risk for internal sulfate attack with these types of materials. Within the framework of the Interreg VALDEM project, this objective will also inform industrials of possible applications for FRA.

This research was performed on the one hand with a laboratory-made material, to research certain characteristics of the sulfate attack mechanism without interference from variabilities other than sulfates. On the other hand, samples of FRA were collected from industrial sources to relate conclusions from 'model' materials to 'real' samples. Results ranged from theoretical aspects of internal sulfate attack on a microstructural level, to industrially applicable information about the recycling of contaminated FRA.

In reference to the research objectives that resulted from the literature review in Part I, the following questions can now be answered:

How much sulfates are contaminating industrial FRA? FRA samples from different recycling centers have been characterized and their water soluble sulfate content ranged from 0.15 to 0.8 % which surpasses the maximum allowed concentration according to EN206 (0.2 %). In the same line with other negative characteristics (higher water absorption, higher cement paste content, lower density) the sulfate content was highest in the smallest size fractions. This is likely due to the fragility of gypsum particles during the crushing process. Sulfates were also found in a 'model' material which was not contaminated. A certain percentage of sulfates can thus be expected from the residual cement paste content, unrelated to plaster drywall from demolished buildings. It was interesting to note the variability in characteristics between the different industrial sources, but especially between different batches of FRA from the same recycling center. This confirms that a thorough characterization of FRA is necessary before utilization, as a generalisation can't be easily made.

Do these sulfate amounts cause a swelling reaction? The swelling results obtained in the different chapters of this thesis make it clear that high sulfate contents were necessary to provoke an expansion. It should be said that, while those samples did surpass a swelling limit, serious degradations like visible cracking, sudden drops in ultrasonic wavespeed, or important losses in mechanical performances were never recorded. There was no significant distinction between the swelling amounts of different samples: they either did or didn't swell and the absolute amount was not visibly proportional to the sulfate content. There seemed to be a certain sulfate content that was the 'starting point' for the swelling reaction, but this limit varied depending on the mortar or concrete composition. In any case, the sulfate content routinely present in industrial FRA did not cause a degradation - in fact, these FRA performed very well when incorporated into mortars. Up to a certain point, gypsum residues even had positive effects on the hydration reaction and compressive strengths.

With a given sulfate concentration, can other factors be varied to change the swelling outcome? For mortar samples with the exact same sulfate content, swelling tests showed different responses depending on certain parameters. The possibility of thaumasite formation - when a carbonate source is present and the sample is kept at low temperatures - was the most damaging circumstance. These conditions are however not common. The aspect that requires the most attention is a limited porosity, attained by a low W/C ratio: this factor made the swelling response increase and is probably a common occurrence seeing as the water absorption of recycled aggregates is difficult to quantify and often underestimated. Next to a necessary characterization of the water absorption, using the aggregates in a presaturated state can also help control the effective W/C. In the other sense, large sulfate contents could be mitigated by increasing the alkalinity of a mix. This has the added benefit of improving compressive strength. The alkalinity influences the equilibrium between different sulfate phases: ettringite formation is less favorable at higher pH. Due to the risk on alkali aggregate reactivity, this solution is very dependant on the composition and application of the concrete. Another parameter that can reduce the action of sulfates is to have a reserve of pore sizes in the 1-10 μm range. In these experiments those pore sizes became available by using coarse natural aggregates instead of recycled ones. In general, only the swelling results of samples already undergoing expansion could be influenced. Even with these important parameters varied, no significant change in results was seen for samples with sulfate contents under the proposed sulfate limit of 0.3 %, as they did not swell.

These conclusions in mind, some general recommendations about the reuse of contaminated FRA can be formed. In general, a characterization of the material is necessary to properly adapt the mix composition for their higher water absorption and lower density. Sulfate contents of up to 0.3 mass% of FRA have not posed any problems with regards to swelling or mechanical properties. Higher concentrations should also not be dismissed automatically, because several parameters can be varied accordingly to counterbalance the action of the sulfates: the W/C ratio, the alkalinity, and micrometric porosity.

Nevertheless, the obtained results also made room for new questions that could inspire future research:

- More sulfate contents, in smaller increments, could be tested to narrow down the limit where the reaction starts. While significant swelling has been recorded for 3.1 % of sulfates, the other deterioration symptoms (like cracking, sudden mechanical performance loss) that are associated with sulfate attack were not seen. Extreme sulfate contents could be tested to assess what kind of damage they can provoke.

- The effect of pore size distribution on sensitivity to expansion came to light at the end of the experimental part, and could use more research. Microstructure observations can be interesting here. Finding a way to obtain pore sizes in the 1-10 μm range by adapting certain mixing parameters or using adjuvants could further be used to valorize FRA.

- Different parameters have been identified that did or did not have an influence on the swelling reaction. A full factorial design where interactions between them are studied could be interesting. For example, in a mix where both a limited porosity and an increased alkalinity are present, which effect will prevail?

The results of this study demonstrate that for a large part of the mixed C&DW currently landfilled, it is actually very feasible to be incorporated into cementitious composites. Recycling FRA would bring the construction sector a step closer towards a circular economy of aggregates.

Bibliography

[1] United Nations Environment Programme, Sustainable buildings and climate initiative (2016).

[2] P. Aïtcin, Cements of yesterday and today, concrete of tomorrow, Cement and Concrete Research 30 (2000) 1349–1359.

[3] J. Crow, The concrete conundrum, Chemistry World (2008) 62–66.

[4] C. Chen, G. Habert, Y. Bouzidi, A. Jullien, Environmental impact of cement production: detail of the different processes and cement plant variability evaluation, Journal of Cleaner Production 18 (2010) 478–485. `doi:10.1016/j.jclepro.2009.12.014`.

[5] L. Buruberri, M. Seabra, J. Labrincha, Preparation of clinker from paper pulp industry wastes, Journal of Hazardous Materials 286 (2015) 252–260. `doi:10.1016/j.jhazmat.2014.12.053`.

[6] M. De Schepper, K. De Buysser, I. Van Driessche, N. De Belie, The regeneration of cement out of completely recyclable concrete: clinker production evaluation, Construction and Building Materials 38 (2013) 1001–1009. `doi:10.1016/j.conbuildmat.2012.09.061`.

[7] C. Shi, A. Jiménez, A. Palomo, New cements for the 21st century: The pursuit of an alternative to portland cement, Cement and Concrete Research 41 (2011) 750–763. `doi:10.1016/j.cemconres.2011.03.016`.

[8] J. Damtoft, M. Glavind, C. Munch-Petersen, Sustainable development of cement and concrete, in: Third CANMET/ACI International Conference, Danish Centre for Green Concrete, 2001, pp. 401–418.

[9] J. Damtoft, J. Lukasik, D. Herfort, D. Sorrentino, E. Gartner, Sustainable development and climate change initiatives, Cement and Concrete Research 38 (2008) 115–127. `doi:10.1016/j.cemconres.2007.09.008`.

[10] S. Kosmatka, B. Kerkhoff, W. Panarese, Design and Control of Concrete Mixtures, Portland Cement Association, 2002.

[11] A. Coelho, J. De Brito, Influence of construction and demolition waste management on the environmental impact of buildings, Waste Management 32 (2012) 532–541. `doi:10.1016/j.wasman.2011.11.011`.

[12] European Aggregates Association, Annual review (2017).

[13] D. Wilburn, T. Goonan, Aggregates from natural and recycled sources: Economic assessments for construction applications, a materials flow analysis, Tech. rep., U.S. Department of the Interior (1998).

[14] N. Müller, J. Harnisch, A blueprint for a climate friendly cement industry, Tech. rep., WWF - Lafarge (2008).

[15] European Commission, on resource efficiency opportunities in the building sector, COM/2014/0445final (2014).

[16] Deloitte, Study on resource efficient use of mixed wastes, improving management of construction and demolition waste: Final report. prepared for the european commission (2017).

[17] Council Directive 2008/98/EC of the European Parliament, on waste and repealing certain directives, Official Journal of the European Union L312 (2008).

[18] European Commission, Eu construction & demolition waste management protocol (2016).

[19] L. Mongeard, D. Collonge, F. Jezequel, Disponibilité et variabilité des granulats recyclés en France, in: F. D. Larrard, H. Colina (Eds.), Le béton recyclé, IFSTTAR, 2018.

[20] C. Sampaio, B. Cazacliu, W. Ambros, The use of air jigging to recycle construction and demolition waste, Journal of Mining and Mechanical Engineering 1 (2019).

[21] X. Wei-hong, A. Fraaij, H. Pietersen, P. Rem, K. Dijk, The quality improvement of stony construction and demolition waste (CDW), Journal of Wuhan University of Technology-Mater. 19 (2004) 78–80. `doi:10.1007/BF02835068`.

[22] C. Ulsen, H. Kahn, G. Hawlitschek, E. Masini, S. Angulo, Separability studies of construction and demolition waste recycled sand, Waste Management 33 (2013) 656–662. `doi:10.1016/j.wasman.2012.06.018`.

[23] W. Ambrós, C. Sampaio, B. Cazacliu, G. Miltzarek, L. R. Miranda, Separation in air jigs of mixed construction and demolition waste, in: Advances in recycling and management of construction and demolition waste, 2017, pp. 25–28.

[24] H. Asakura, Y. Watanabe, Y. Ono, M. Yamada, Y. Inoue, A. M. Alfaro, Characteristics of fine processed construction and demolition waste in japan and method to obtain fines having low gypsum component and wood contents, Waste Management & Research 28 (2010) 634–646. `doi:10.1177/0734242X09339951`.

[25] Tracimat, Kwaliteitszorgsysteem voor de werf, `http://www.tracimat.be/wp-content/uploads/2017/08/Kwaliteitszorgsysteem-voor-de-werf.pdf` (2018).

[26] Centraal College van Deskundigen Slopen, Beoordelingsrichtlijn veilig en milieukundig slopen, `https://www.veiligslopen.nl/site/media/upload/files/svms-007-17-01-definitief-14022017.pdf` (2017).

[27] Swedish Construction Federation, Resource and waste guidelines for constructions and demolition, `https://byggforetagen.se/appendix-resource-and-waste-guidelines-for-constructions-and-demolition-2019/` (2019).

[28] T. Hansen, H. Narud, Strength of recycled concrete made from crushed concrete coarse aggregate, Concrete International 5 (1983) 79–83.

[29] E. Khoury, Maîtrise de l'eau efficace dans les bétons de granulats recyclés, Ph.D. thesis, IMT Lille Douai (2018).

[30] Z. Ben Aouda, Mélange d'un sable naturel et d'un sable recyclé: détermination de leur proportion, Master's thesis, Université de Lorraine (2016).

[31] K. Paine, R. Dhir, Recycled aggregates in concrete: A performance-related approach, Magazine of Concrete Research 62 (2010) 519–530. `doi:10.1680/macr.2010.62.7.519`.

[32] European Committee for Standardization, EN12620 'Aggregates for concrete' (2008).

[33] R. Dhir, K. Paine, N. Ho, C. Poon, M. Etxeberria, J. De Brito, V. Tam, Use of recycled and secondary aggregates in concrete: An overview, in: UKIERI Concrete Congress: Concrete for 21st Century Construction, New Delhi, India, 2011.

[34] C. Medina, W. Zhu, T. Howind, M. Sánchez de Rojas, M. Frías, Influence of mixed recycled aggregate on the physical – mechanical properties of recycled concrete, Journal of Cleaner Production 68 (2014) 216–225. `doi:10.1016/j.jclepro.2014.01.002`.

[35] R. Nassar, P. Soroushian, Strength and durability of recycled aggregate concrete containing milled glass as partial replacement for cement, Construction and Building Materials 29 (2012) 368–377. `doi:10.1016/j.conbuildmat.2011.10.061`.

[36] C. Poon, Z. Shui, L. Lam, Effect of microstructure of ITZ on compressive strength of concrete prepared with recycled aggregates, Construction and Building Materials 18 (2004) 461–468. `doi:10.1016/j.conbuildmat.2004.03.005`.

[37] M. Behera, S. Bhattacharyya, A. Minocha, R. Deoliya, S. Maiti, Recycled aggregate from C&D waste and its use in concrete: A breakthrough towards sustainability in construction sector: A review, Construction and Building Materials 68 (2014) 501–516. `doi:10.1016/j.conbuildmat.2014.07.003`.

[38] T. Le, Influence de l'humidité des granulats de béton recyclé sur le comportement à l'état frais et durcissant des mortiers, Ph.D. thesis, IMT Lille Douai (2015).

[39] Z. Zhao, L. Courard, F. Michel, S. Rémond, D. Damidot, Influence of granular fraction and origin of recycled concrete aggregates on their properties, European Journal of Environmental and Civil Engineering (2017). `doi:10.1080/19648189.2017.1304281`.

[40] M. Limbachiya, A. Koulouris, J. Roberts, A. Fried, Performance of recycled aggregate concrete, in: RILEM International symposium on environment-conscious materials and system for sustainable development, 2004.

[41] F. Debieb, L. Courard, S. Kenai, R. Degeimbre, Mechanical and durability properties of concrete using contaminated recycled aggregates, Cement & Concrete Composites 21 (2010) 421–426. `doi:10.1016/j.cemconcomp.2010.03.004`.

[42] European Committee for Standardization, EN 1097-6 'Tests for mechanical and physical properties of aggregates. Part 6: Determination of particle density and water absorption' (2001).

[43] IFSTTAR, Test method no. 78:2011. Tests on aggregates for concrete: measurement of total water absorption by a crushed sand (2011).

[44] Z. Zhao, S. Rémond, D. Damidot, W. Xu, Influence of hardened cement paste content on the water absorption of fine recycled concrete aggregates, Journal of Sustainable Cement-Based Materials 2 (2013) 186–203. `doi:10.1080/21650373.2013.812942`.

[45] T. Le, S. Rémond, G. Le Saout, E. Garcia-Diaz, Fresh behavior of mortar based on recycled sand: Influence of moisture condition, Construction and Building Materials 106 (2016) 35–42. `doi:10.1016/j.conbuildmat.2015.12.071`.

[46] J.-M. Mechling, A. Lecomte, K. Merriaux, Mesure de l'absorption d'eau des additions minérales des bétons par évaporométrie, Materials and Structures 36 (2003) 32–39. `doi:10.1007/BF02481568`.

[47] S. Kou, C. Poon, Enhancing the durability properties of concrete prepared with coarse recycled aggregate, Construction and Building Materials 35 (2012) 69–76. `doi:10.1016/j.conbuildmat.2012.02.032`.

[48] D. Matias, J. De Brito, A. Rosa, D. Pedro, Mechanical properties of concrete produced with recycled coarse aggregates: Influence of the use of superplasticizers, Construction and Building Materials 44 (2013) 101–109. `doi:10.1016/j.conbuildmat.2013.03.011`.

[49] A. Padmini, K. Ramamurthy, M. Mathews, Influence of parent concrete on the properties of recycled aggregate concrete, Construction and Building Materials 23 (2009) 829–836. `doi:10.1016/j.conbuildmat.2008.03.006`.

[50] S. Tabsch, A. Abdelfatah, Influence of recycled concrete aggregates on strength properties of concrete, Construction and Building Materials 23 (2009) 1163–1167. `doi:10.1016/j.conbuildmat.2008.06.007`.

[51] C. Poon, Z. Shui, L. Lam, H. Fok, S. Kou, Influence of moisture states of natural and recycled aggregates on the slump and compressive strength of concrete, Cement and Concrete Research 34 (2004) 31–36. `doi:10.1016/S0008-8846(03)00186-8`.

[52] M. Etxeberria, E. Vázquez, A. Marí, M. Barra, Influence of amount of recycled coarse aggregates and production process on properties of recycled aggregate concrete, Cement and concrete research 37 (2007) 735–742. `doi:10.1016/j.cemconres.2007.02.002`.

[53] L. Evangelista, J. De Brito, Concrete with fine recycled aggregates: a review, European Journal of Environmental and Civil Engineering 18 (2014) 129–172. `doi:10.1080/19648189.2013.851038`.

[54] G. Lee, H. Choi, Study on interfacial transition zone properties of recycled aggregate by micro-hardness test, Construction and Building Materials 40 (2013) 455–460. `doi:10.1016/j.conbuildmat.2012.09.114`.

[55] M. Bouarroudj, Utilisation de matériaux naturels modèles pour la formulation de mortier contenant des sables et des fines de granulats recyclés, Ph.D. thesis, IMT Lille Douai, Université de Liège (2019).

[56] I. Mehdipour, K. Khayat, Understanding the role of particle packing characteristics in rheophysical properties of cementitious suspensions: A literature review, Construction and Building Materials 161 (2018) 340–353. `doi:10.1016/j.conbuildmat.2017.11.147`.

[57] N. Oikonomou, Recycled concrete aggregates, Cement & Concrete Composites 27 (2005) 315–318.

[58] F. Grondin, C. de Sa, T. Sedran, F. Cassagnabère, F. Benboudjema, A. Z. Bendimerad, M. Guo, A. Loukili, P. Nicot, E. Rozière, B. Fouré, Propriétés mécaniques différées, in: F. D. Larrard, H. Colina (Eds.), Le béton recyclé, IFSTTAR, 2018.

[59] J. De Brito, N. Saikia, Recycled Aggregate in Concrete, Springer, 2013.

[60] European Committee for Standardization, EN 206 'Concrete: Specification, performance, production and conformity: Annex E.3 on Recycled Aggregates' (2014).

[61] F. De Larrard, H. Colina (Eds.), Concrete Recycling : Research and Practice, CRC Press, 2019.

[62] A. Djerbi Tegguer, M. Saillo, J. Mai-Nhu, L. Schmitt, P. Rougeau, Propriétés des bétons de granulats recyclés, in: GC'2015, Paris, France, 2015.

[63] B. Mignon, H. Bréquel, Comparative case study of the construction and demolition waste practical treatment induced by different legislations in France and Belgium (Wallonia and Flanders), in: International HISER Conference on Advances in Recycling and Management of Construction and Demolition Waste, 2017.

[64] C. Ulsen, H. Kahn, G. Hawlitschek, E. Masini, S. Angulo, V. John, Production of recycled sand from construction and demolition waste, Construction and Building Materials 40 (2013) 1168–1173. `doi:10.1016/j.conbuildmat.2012.02.004`.

[65] S. Angulo, C. Ulsen, V. John, H. Kahn, M. Cincotto, Chemical–mineralogical characterization of C&D waste recycled aggregates from São Paulo, Brazil, Waste Management 29 (2009) 721–730. `doi:10.1016/j.wasman.2008.07.009`.

[66] E. Robinet, Utilisation des fines de recyclage dans la formulation de bétons autocompactants, Master's thesis, Université de Liège (2017).

[67] J. Khatib, Properties of concrete incorporating fine recycled aggregate, Cement and Concrete Research 35 (2005) 763–769. `doi:10.1016/j.cemconres.2004.06.017`.

[68] M. Braga, J. De Brito, R. Veiga, Incorporation of fine concrete aggregates in mortars, Construction and Building Materials 36 (2012) 960–968. `doi:10.1016/j.conbuildmat.2012.06.031`.

[69] D. Breysse, Deterioration processes in reinforced concrete: an overview, in: C. Maierhofer, H. Reinhardt, G. Dobmann (Eds.), Non-Destructive Evaluation of Reinforced Concrete Structures: Deterioration Processes and Standard Test Methods, Woodhead Publishing, 2010.

[70] K. Mehta, P. Monteiro, Concrete: Microstructure, Properties, and Materials, McGraw-Hill, 2006.

[71] A. Le Roux, S. Orsetti, Les réactions sulfatiques: conditions de formation, structure et expansion des minéraux secondaires sulfatés, Bulletin des laboratoires des ponts et chaussées 225 (2000) 41–50.

[72] M. Collepardi, A state of the art review on delayed ettringite attack on concrete, Cement & Concrete Composites 25 (2003) 401–407. `doi:10.1016/S0958-9465(02)00080-X`.

[73] X. Brunetaud, Etude de l'influence de différents paramètres et de leurs interactions sur la cinétique et l'amplitude de la réaction sulfatique interne au béton, Ph.D. thesis, École Centrale Paris (2005).

[74] M. Rahman, M. Bassuoni, Thaumasite sulfate attack on concrete: Mechanisms, influential factors and mitigation, Construction and Building Materials 73 (2014) 652–662. `doi:10.1016/j.conbuildmat.2014.09.034`.

[75] E. Irassar, Sulfate attack on cementitious materials containing limestone filler: A review, Cement and Concrete Research 39 (2009) 241–254. `doi:10.1016/j.cemconres.2008.11.007`.

[76] E. Irassar, V. Bonavetti, M. Trezza, M. González, Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20 °c, Construction & Concrete Composites 27 (2005) 77–84. `doi:10.1016/j.cemconcomp.2003.10.003`.

[77] X. Brunetaud, M. Khelifa, M. Al-Mukhtar, Size effect of concrete samples on the kinetics of external sulfate attack, Cement & Concrete Composites 34 (2012) 370–376. `doi:10.1016/j.cemconcomp.2011.08.014`.

[78] S. Diamond, Delayed ettringite formation: Processes and problems, Cement & Concrete Composites 18 (1996) 205–215.

[79] L. Divet, Les réactions sulfatiques internes au béton : contribution à l'étude des mécanismes de la formation de l'ettringite, Laboratoire central des ponts et chaussées, 2001.

[80] C. Yu, W. Sun, K. Scrivener, Mechanism of expansion of mortars immersed in sodium sulfate solutions, Cement and Concrete Research 43 (2013) 105–111. `doi:10.1016/j.cemconres.2012.10.001`.

[81] K. Scrivener, H. Taylor, Delayed ettringite formation: a microstructural and microanalytical study, Advances in cement research 5 (1993) 139–145.

[82] M. Salgues, Modélisation des effets structuraux des réactions sulfatiques internes: Application aux barrages en béton, Ph.D. thesis, Université de Toulouse (2013).

[83] W. Chen, B. Huang, Y. Yuan, M. Deng, Deterioration process of concrete exposed to internal sulfate attack, Materials 13 (2020). `doi:10.3390/ma13061336`.

[84] A. Neville, The confused world of sulfate attack on concrete, Cement and Concrete Research 34 (2004) 1275–1296. `doi:10.1016/j.cemconres.2004.04.004`.

[85] H. Taylor, C. Famy, K. Scrivener, Delayed ettringite formation, Cement and Concrete Research 31 (2001) 683–693.

[86] A. Campos, C. López, A. Blanco, A. Aguado, Effects of an internal sulfate attack and an alkali-aggregate reactionin a concrete dam, Construction and Building Materials 166 (2018) 668–683. `doi:10.1016/j.conbuildmat.2018.01.180`.

[87] Portland Cement Association, Ettringite formation and the performance of concrete (2001).

[88] L. Divet, R. Randriambololona, Delayed ettringite formation: The effect of temperature and basicity on the interaction of sulphate and C-S-H phase, Cement and Concrete Research 28 (1998) 357–363. `doi:10.1016/S0008-8846(98)00006-4`.

[89] R. Barbarulo, H. Peycelon, S. Leclercq, Chemical equilibria between CSH and ettringite, at 20 and 85 °c, Cement and Concrete Research 37 (2007) 1176–1181. `doi:10.1016/j.cemconres.2007.04.013`.

[90] M. Collepardi, Damage by delayed ettringite formation, Concrete International 21 (1999) 69–74.

[91] S. Kosmatka, B. Kerkhoff, W. Panarese, The Effect of Secondary Ettringite Formation on the Durability of Concrete: A Literature Analysis, Research and Development Bulletin RD108T, Portland Cement Association, 1992.

[92] S. Ekolu, G. Rakgosi, D. Hooton, Long-term mitigating effect of lithium nitrate on delayed ettringite formation and ASR in concrete: Microscopic analysis, Materials Characterization 133 (2017) 165–175. `doi:10.1016/j.matchar.2017.09.025`.

[93] N. Leklou, P. Mounanga, The effect of the partial cement substitution with fly ash on delayed ettringite formation in heat-cured mortars, KSCE Journal of Civil Engineering 21 (2017) 1359–1366. `doi:10.1007/s12205-016-0778-9`.

[94] B. Fournier, M. Bérubé, Alkali aggregate reaction in concrete: a review of basic concepts and engineering implications, Canadian Journal of Civil Engineering 27 (2000) 167–191.

[95] Portland Cement Association, Types and causes of concrete deterioration (2002).

[96] A. Pavoine, X. Brunetaud, L. Divet, The impact of cement parameters on delayed ettringite formation, Cement & Concrete Composites 34 (2012) 521–528. `doi:10.1016/j.cemconcomp.2011.11.012`.

[97] M. Thomas, K. Folliard, T. Drimalas, T. Ramlochan, Diagnosing delayed ettringite formation in concrete structures, Cement and Concrete Research 38 (2008) 841–847. `doi:10.1016/j.cemconres.2008.01.003`.

[98] G. Escadeillas, J. Aubert, M. Segerer, W. Prince, Some factors affecting delayed ettringite formation in heat-cured mortars, Cement and Concrete Research 37 (2007) 1445–1452. `doi:10.1016/j.cemconres.2007.07.004`.

[99] M. Halaweh, Effect of alkalis and sulfates on portland cement systems, Ph.D. thesis, University of South Florida (2006).

[100] N. Leklou, Contribution à la connaissance de la réaction sulfatique interne, Ph.D. thesis, Université Paul Sabatier III (2008).

[101] V. Nguyen, N. Leklou, J. Aubert, P. Mounanga, The effect of natural pozzolan on delayed ettringite formation of the heat-cured mortars, Construction and Building Materials 48 (2013) 479–484. `doi:10.1016/j.conbuildmat.2013.07.016`.

[102] M. Juenger, H. Jennings, Effects of high alkalinity on cement pastes, ACI Materials Journal 98a (2001) 251–255.

[103] F. Agrela, M. Cabrera, A. Galvín, A. Barbudo, A. Ramirez, Influence of the sulphate content of recycled aggregates on the properties of cement treated granular materials using sulphate resistant portland cement, Construction and Building Materials 68 (2014) 127–134. `doi:10.1016/j.conbuildmat.2014.06.045`.

[104] O. Batic, C. Milanesi, P. Maiza, S. Marfil, Secondary ettringite formation in concrete subjected to different curing conditions, Cement and Concrete Research 30 (2000) 1407–1412.

[105] M. Zhang, J. Chen, Y. Lv, D. Wang, J. Ye, Study on the expansion of concrete under attack of sulfate and sulfate–chloride ions, Construction and Building Materials 39 (2013) 26–32. `doi:10.1016/j.conbuildmat.2012.05.003`.

[106] T. Fukami, S. Tahara, K. Nakasone, C. Yasuda, Synthesis, crystal structure, and thermal properties of CaSO4·2H2O single crystals, International Journal of Chemistry 7 (2015) 12–20. `doi:10.5539/ijc.v7n2p12`.

[107] J. Shukla, V. Mohandas, A. Kumar, Effect of pH on the solubility of CaSO4·2H2O in aqueous NaCl solutions and physicochemical solution properties at 35 °C, Journal of Chemical and Engineering data 53 (2008) 2797–2800. `doi:10.1021/je800465f`.

[108] J. Colas, Etude de valorisation des déblais de chantiers de tunnels riches en sulfates en granulats à béton, Ph.D. thesis, Université Paris-Est (2012).

[109] L. . ENV/BE/001039, Gypsum to gypsum: From production to recycling a circular economy for the european gypsum industry with the demolition and recycling industry (2016).

[110] L. . ENV/BE/001039, European handbook on best practices in deconstruction techniques (2015).

[111] S. Pinheiro, G. Camarini, Characteristics of gypsum recycling in different cycles, International Journal of Engineering and Technology 7 (2015) 215–218. `doi:10.7763/IJET.2015.V7.794`.

[112] A. Rivero, R. Sarthre, J. Navarro, Life cycle energy and material flow implications of gypsum plasterboard recycling in the European Union, Resources, Conservation and Recycling 108 (2016) 171–181. `doi:10.1016/j.resconrec.2016.01.014`.

[113] J. Bergmans, P. Nielsen, R. Snellings, K. Broos, Recycling of autoclaved aerated concrete in floor screeds: sulfate leaching reduction by ettringite formation, Construction and Building Materials 111 (2016) 9–14. `doi:10.1016/j.conbuildmat.2016.02.075`.

[114] J. Geurts, J. Sarneel, B. Willers, J. Roelofs, J. Verhoeven, L. Lamers, Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation development in fens: a mesocosm experiment, Environmental Pollution 157 (2009) 2072–2081. `doi:10.1016/j.envpol.2009.02.024`.

[115] K. Scrivener, P. Juilland, P. Monteiro, Advances in understanding hydration of Portland cement, Cement and Concrete Research 78 (2015) 38–56. `doi:10.1016/j.cemconres.2015.05.025`.

[116] F. Agrela, M. S. de Juan, J. Ayuso, V. Geraldes, J. Jiménez, Limiting properties in the characterisation of mixed recycled aggregates for use in the manufacture of concrete, Construction and Building Materials 25 (2011) 3950–3955. `doi:10.1016/j.conbuildmat.2011.04.027`.

[117] F. Rodrigues, M. Carvalho, L. Evangelista, J. De Brito, Physical–chemical and mineralogical characterization of fine aggregates from construction and demolition waste recycling plants, Journal of Cleaner Production 52 (2013) 438–445. `doi:10.1016/j.jclepro.2013.02.023`.

[118] M. Martín-Morales, M. Zamorano, A. Ruiz-Moyano, I. Valverde-Espinosa, Characterization of recycled aggregates construction and demolition waste for concrete production following the Spanish Structural Concrete Code EHE-08, Construction and Building Materials 25 (2011) 742–748. `doi:10.1016/j.conbuildmat.2010.07.012`.

[119] S. Abid, A. Nahhab, H. Al-aayedi, A. Nuhair, Expansion and strength properties of concrete containing contaminated recycled concrete aggregate, Case studies in Construction Materials 9 (2018). `doi:10.1016/j.cscm.2018.e00201`.

[120] G. Tovar-Rodrígues, M. Barra, S. Pialarissi, D. Aponte, E. Vázquez, Expansion of mortars with gypsum contaminated fine recycled aggregates, Construction and Building Materials 38 (2013) 1211–1220. `doi:10.1016/j.conbuildmat.2012.09.059`.

[121] J. Gallias, Action of gypsum on recycled aggregate concrete, in: Proceedings CIB World Building Congress, Gaevle, Sweden, 1998.

[122] S. Orsetti, Influence des sulfates sur l'apparition et le développement de pathologies dans les matériaux de génie civil traités ou non aux

liants hydrauliques: cas du plâtre dans les granulats issus de produits de démolition, Ph.D. thesis, Université Pierre et Marie Curie (1997).

[123] P. Rougeau, L. Schmitt, J. Nai-Nhu, A. Djerbi, M. Saillio, E. Ghorbel, J.-M. Mechling, A. Lecomte, R. Trauchessec, D. Bulteel, M. Cyr, N. Leklou, O. Amiri, I. Moulin, T. Lenormand, Durability-related properties, in: F. De Larrard, H. Colina (Eds.), Concrete Recycling: Research and Practice, CRC Press, 2019.

[124] A. Pavoine, L. Divet, Réactivité d'un béton vis-a-vis d'une réaction sulfatique interne: essai de performance, Laboratoire central des ponts et chaussées, 2007.

[125] European Committee for Standardization, EN 933 'Tests for geometrical properties of aggregates. Part 1: Determination of particle size distribution' (2012).

[126] European Committee for Standardization, EN 1744-1 'Tests for chemical properties of aggregates. Part 1: Chemical analysis.' (2014).

[127] European Committee for Standardization, EN 196-1 'Methods of testing cement. Part 1: determination of strength.' (2014).

[128] J. Brozovsky, Ultrasonic pulse and resonance method–evaluation of the degree of damage to the internal structure of repair mortars caused by exposure to high temperatures, Russian Journal of Nondestructive Testing 53 (2017) 744–753.

[129] X. Chen, J. Kim, K. Kurtis, J. Qu, C. Shen, L. Jacobs, Characterization of progressive microcracking in portland cement mortar using nonlinear ultrasonics, NDT&E International 41 (2008) 112–118. `doi:10.1016/j.ndteint.2007.08.009`.

[130] Bureau voor Normalisatie, NBN B 15-211: 'Proeven op beton - Rechtstreekse trek' (1974).

[131] K. Kjellsen, A. Monsoy, K. Isachsen, R. Detwiler, Preparation of flat-polished specimens for sem-backscattered electron imaging and x-ray microanalysis - importance of epoxy impregnation, Cement and Concrete Research 33 (2003) 611–616. `doi:10.1016/S0008-8846(02)01029-3`.

Gypsum residues in fine recycled aggregates: effects on mechanical and microstructural properties of cementitious composites

Fine recycled aggregates are an important waste stream coming from the demolition of old concrete structures. They are up to now not valorized because of an increased water absorption, lower density and higher fines content compared to natural aggregates. Moreover, they often have a high sulfate concentration. These sulfates could have originated from plaster in a demolished building, or from the residual cement that is commonly present in these materials. The sulfate level of recycled aggregates is recommended to stay under 0.2 mass% by standard EN206, to limit the risk on sulfate attack: the reaction between cement components, water and sulfates results in the formation of expansive minerals such as ettringite. This expansion can eventually lead to cracking of the material and a general loss in mechanical performances. Fine recycled aggregates from recycling plants did contain 0.15 to 0.80 % of sulfates which is more than allowed, but these amounts did not cause any swelling or degradation when the aggregates were incorporated into mortars. A very elevated sulfate content of 3 % was needed to observe significant expansion, and even this level of contamination could be mitigated by increasing the alkalinity of a mix. Concretes made with varying sulfate levels either expanded or they didn't: the absolute swelling amount was not proportional to its sulfate content. The actual threshold concentration that started the swelling reaction was dependant on the type of coarse aggregate. The results of this study provide recommendations for the use of fine recycled aggregates contaminated with gypsum residues: a sulfate content of at least 0.3 % could be possible, and even more if certain parameters and mix compositions can be adjusted accordingly. The current limit of 0.2 % seems too strict and hinders the valorization of fine recycled aggregates in high quality construction applications.

Keywords: *Fine recycled aggregates; sulfate attack; construction and demolition waste; secondary ettringite formation; microstructure; expansion*

Résidus de plâtre dans les sables recyclés : effets sur les propriétés mécaniques et microstructurales des composites cimentaires

Les sables recyclés représentent un flux important de déchets provenant de la démolition d'anciennes structures en béton. Ils ne sont jusqu'à présent pas valorisés à cause d'une absorption d'eau élevée, d'une densité plus faible et d'une teneur en fines plus importante que dans les granulats naturels. De plus, ils sont souvent contaminés par des sulfates. Ces sulfates pourraient provenir du plâtre du bâtiment démoli ou du ciment résiduel qui est couramment présent dans ces matériaux. Le taux de sulfate recommandé pour les granulats recyclés est inférieur à 0,2 % en masse selon la norme EN206, afin de limiter le risque d'attaque sulfatique : la réaction entre les composants du ciment, l'eau et les sulfates entraîne la formation de minéraux expansifs comme l'ettringite. Cette expansion peut éventuellement conduire à une fissuration du matériau et à une perte générale des performances mécaniques. Une étude systématique a permis de mettre en évidence que les sables recyclés provenant des centres de recyclage contenaient de 0,15 à 0,80 % de sulfates ce qui est plus que ce qui est autorisé. Néanmoins, ces quantités n'ont pas engendré de gonflement ni de dégradation lorsque les granulats contaminés ont été incorporés dans des mortiers. Une teneur en sulfate très élevée de 3 % a été nécessaire pour observer une expansion significative ; toutefois, l’expansion a pu être contrôlée en augmentant l'alcalinité d'un mélange. Des bétons fabriqués avec différents niveaux de sulfates ont présenté des gonflements ou non : l’ampleur d’expansion n'était pas proportionnelle à la teneur en sulfate. Le seuil qui a déclenché la réaction de gonflement dépendait aussi du type de granulat. Les résultats de cette étude fournissent des recommandations pour l'utilisation de sables recyclés contaminés par des résidus de gypse : une teneur en sulfate jusque 0,3 % pourrait être possible, et même plus en fonction de certains paramètres et compositions de mélange. La limite actuelle de 0,2 % semble trop stricte et freine la valorisation de sables recyclés dans des bétons durables et résistants.

Mots clés : *Sable recyclé; attaque sulfatique; déchets de démolition; formation d'ettringite secondaire; microstructure; expansion*