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AN INTEGRATED DESIGN PROCESS FOR DURABLE CONCRETE STRUCTURES AT THE MINIMUM ENVIRONMENTAL COST – APPLICATION WITH THE INCORPORATION OF RICE HUSK ASH

PhD Dissertation

by

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Foreword

This PhD Dissertation is the result of an extensive research work and the end of a challenging trip that lasted three and half years, from January of 2011 until June of 2014. The main reason that urged me to start dealing with the specific subject was the fact that I felt we are all responsible for protecting the environment in which we are living. As a civil engineer I also thought that I have an additional responsibility towards both the social and scientific community, so I could not stay away from all the processes taken place at a global level aiming at the establishment of a sustainable way of building.

Nowadays there is a great concern about the environmental footprint of constructions while the principles of sustainable development have prevailed worldwide. Cement industry is responsible for a considerable amount of CO_2 emissions and unsatisfactory durability is a common case in reinforced concrete structures. In particular, corrosion of steel reinforcement is the most serious durability problem, caused by either carbonation or chloride diffusion. Concrete is considered to be the most popular building material and it is estimated that its consumption will increase considerably in the next years. Therefore, new strategies and techniques should be used to make cement and construction industry a more environmentally friendly sector.

A great challenge nowadays is the construction of durable concrete structures which are friendly to the environment and last longer. Towards achieving this target each involved party could play its own role and therefore should undertake its own responsibilities. Governments should provide incentives to engineers and manufactures to adopt new "green' methods and products. During the past decades scientists are investigating innovative ways for reducing the environmental cost of constructions, such as the utilisation of Supplementary Cementing Materials (SCM) in the concrete mix. By realizing the high importance of all these crucial issues and the necessity to develop initiatives aiming at the sustainable development of building sector, I decided to begin the elaboration of the present thesis, after discussions with Assoc. Prof. Vagelis G. Papadakis.

The study focuses on the enhancement of the structure and potential of an existing software tool, EUCON®, developed by Papadakis *et al* which is based on proven mathematical models, in full compliance with the *European Standards for cement: EN 197 and concrete: EN 206.* The environmental aspects of designing the concrete mix are highlighted and introduced in this software offering this way an Integrated Design Process (IDP) tool for reinforced concrete structures. The

valorisation of biomass ash and particularly rice husk ash (RHA) in the construction sector is thoroughly analysed in the study and new types of concrete incorporating these types of agro-industrial by-products are suggested, in order to achieve a balance between durability and sustainability. In general, this work is addressed to Construction and Environmental Engineers in addition to Building Material Manufacturers towards providing them a structured framework of methodologies for designing durable reinforced concrete constructions at the minimum environmental and economical cost and also an industrial ecology scheme for the sustainable development of the cement and construction industry.

Julia G. Tapali

June 2014

Julia G. Tapali holds a diploma in Civil Engineering (2007) from the Aristotle University of Thessaloniki, Greece, and a MSc. on Design, Organization and Management of Transport Systems from the same Institution (2009). The Diploma Thesis of MSc. was elaborated at the University of Piraeus on Funding for Greek and Greek-owned Shipping Companies. She is a Ph.D. candidate in the Department of Environmental and Natural Resources Management, University of Patras on the subject of Sustainable Development of the Building Sector - Estimation and Reduction Practices of the Environmental Cost of Constructions, under the supevision of Assoc. Prof. V.G. Papadakis. She has participated in a number of conferences and authored several papers. She worked on structural analysis and design of steel structures at the construction company "EKTE ATEVE" (2007-2008). She also worked as a consultant engineer on issues of renewable energy, at the company "Project Epsilon", in Thessaloniki (2012). At the present, she is a member of TSRG/AUTh (Transport Research Group of Aristotle University of Thessaloniki) and participates as a Researcher in the SEE project "ADB Multiplatform" (Adriatic-Danube-Black Sea Multimodal platform) which aims to develop and promote environmentally friendly, multimodal transport solutions.

Contents

Abstract

The construction industry is the largest consumer of materials in our society. Approximately 40% of all materials used are related to this section of the industry. Equivalent is the impact of the sector's activities to the environment in terms of non-renewable energy sources (grey energy), gas emissions (mainly CO_2), solid waste, etc. With concrete being the most widely used construction material (second only to water in total volumes consumed annually by society) and cement being the essential "glue" in concrete, emphasis should be placed on investigating and enforcing ways, methodologies and policies, to make cement manufacturing and the construction industry in general a more environmental friendly sector. At the same time, by considering, at one hand the significant amount of research and breakthroughs achieved on structural materials and design, as well as the level of sophistication of the modern European Standards and structural codes, and on the other hand, the increasing cases of premature deterioration of concrete structures, particular emphasis should also be placed on safeguarding the service life of reinforced concrete structures (in addition to tackling their environmental burden).

That is why it is very important to introduce the sustainable way of thinking and the concept of industrial ecology on the preliminary design stages of a structure, on the material selection process and on the service life estimation stage, in achieving a robust durable reinforced concrete (RC) structure (for a given service life) with the minimum environmental burden.

► **Thus, the main objective of the present Thesis is to focus on identifying and quantifying a structured framework of the appropriate methodologies in formulating an Integrated Design Process (IDP) for the design of durable and sustainable structures at the minimum environmental and economical cost (without compromising issues of structural safety) and also in identifying and demonstrating ways of industrial ecology for the sustainable development of the cement and construction industry.**

A significant step forward for a thorough durability design process of reinforced concrete structures is the development of software packages, based on predictive models, for the estimation of concrete strength and service life. Such an attempt, in full compliance with the European Standards for cement

and concrete, is presented in **Chapter 2**. Upon defining the concrete mix design, the software calculates the main chemical and volumetric characteristics, as well as the compressive strength, of concrete. By taking into account the environmental conditions where the structure will be exposed, concrete service life is predicted, using fundamental mathematical models (based on reaction engineering principles) that simulate the reinforced concrete deterioration mechanisms leading to corrosion of the embedded reinforcement (caused by either carbonation or chloride ingress). A validation process of the yielded results is also presented, and the effectiveness of the simulation tool in designing for durability is illustrated. The goal of this study is to promote wider acceptance in achieving feasible and durable solutions to structural concrete design problems.

Considering the well known environmental issues of cement manufacturing (direct and indirect levels of CO_2 emissions), clinker replacement by supplementary cementing materials (SCM) can be a very promising first step in reducing considerably the associated emissions. However, such a reduction is possible up to a particular level of SCM utilization, influenced by the rate of its pozzolanic reaction. In **Chapter 3**, a (4-step) structured methodology is proposed in order to be able to further adjust the concrete mix design of a particular SCM, in achieving additional reduction of the associated levels of CO_2 emissions and being at the same time accepted from a derived concrete strength and service life point of view. On this note, the aim of this study is twofold. To evaluate the environmental contribution of each concrete component and to provide the best possible mix design configuration, balanced between the principles of sustainability (low environmental cost) and durability (accepted concrete strength and service life). It was proved that such a balance can be achieved by utilising SCM by-products in the concrete mix, reducing in this way the fixed environmental emissions without compromising the long-term safety and durability of the structure.

Utilization of biomass ash from agro-industrial by-products (containing large amounts of silica in amorphous form) in cement manufacturing and/or concrete production can be an alternative solution to the incorporation of the traditionally used supplementary cementing materials (SCM). An evaluation of biomass ashes, identified in the literature, with varying SiO_2 contents in terms of concrete strength and performance in chloride exposure is the focus of **Chapter 4**. Results indicate that these materials are effective on concrete strength development and extremely efficient in reducing the concrete permeability. The dependency of this behavior on the level of SiO_2 of the ash content was examined in depth and was concluded that it is affected by the composition of other components of the biomass ash.

Main objective of **Chapter 5** is to identify the detailed economical outcome for rice hush ash (RHA) valorization technique as a pozzolanic material and main biomass ash. A techno-economical analysis of producing advanced and high-added value material from RHA is presented. The study was

elaborated in the framework of pilot production in a Greek rice industry. The importance of the issues examined is further enhanced by the emphasis given nowadays on adaptation of energy and emissions reducing solutions by the construction industry. Utilization of supplementary cementing materials (SCM) in concrete design, such as RHA, should be a very promising first step in reducing considerably the associated materials environmental footprint.

In contrast to common approach – that often involves extensive pre-grinding – the utilization potential of RHA as an SCM, in its untreated form was further examined. This is to meet industry's increasing awareness for lower embodied energy cement and concrete. Given the availability of current raw materials in cement manufacturing, what is needed is to be able to achieve an optimum approach, between sustainability and durability when designing concrete structures. Under this frame, as-produced RHAs (D50 of approx. 70 microns) were examined with respect to their inherent characteristics and their impact on the performance of cement-based mortars. Strength, hydration and durability properties were considered. Untreated RHA exhibits moderate pozzolanicity and a low efficiency factor of approximately 0.5-0.6. Its very high chemical reactivity (active silica ratio of approx. 90%) cannot be exploited since the lack of adequate specific surface slows down its engagement in hydration reactions. Taking into consideration their untreated nature, it can be supported that they exhibit an acceptable strength potential after 28 days, complying – even marginally – with the strength class (42.5) of the used cement. Durability results revealed that there is no need to pre-treat RHA in order to achieve equal or even better performance than mortar with plain cement in terms of sorptivity (50% increase for 15% RHA usage) and resistivity. Untreated RHA however fails – as most SCMs do – to improve carbonation resistance since for a 15% cement replacement, carbonation depth was almost doubled. Overall, results indicate that usage of untreated RHA in cement-based systems is an alternative to decrease their carbon profile, as long as cement replacement is kept relatively low (below 15%).

The internationally acclaimed efforts to reduce man-made CO_2 emissions require a more rigorous approach to be adopted by the construction industry. Given the need to provide a durable solution that guarantees a minimum service life, on a common reinforced concrete structure, the issue of sustainable durability design is of paramount importance. Bearing in mind that the major source of emission of gasses in concrete manufacturing arise from the clinker production process, during cement manufacturing several means of reducing the environmental footprint have been suggested, as incorporation of cement replacement materials. The present Thesis contributes to the evaluation of the environmental cost of each component of concrete and to provide the best possible mix design configuration (by means of a holistic analytical software tool) in terms of low environmental cost, as well as, to assess this proposed configuration in terms of strength and durability requirements. Overall, it has to be emphasized that through the present Thesis a **new indicator** is proposed for design

purposes: **the environmental cost**, which can be added to the existing strength, durability and economic cost indicators towards an integrated design optimization of concrete structures. Finally, the incorporation of new SCM, as biomass ashes and especially RHA, offers new perspectives for decreasing the environmental cost of constructions.

Περίληψη

Η κατασκευαστική βιομηχανία αποτελεί τον μεγαλύτερο καταναλωτή υλικών στην κοινωνία μας. Περίπου το 40% όλων των υλικών που χρησιμοποιούνται σχετίζονται με αυτόν τον τομέα της βιομηχανίας. Αντίστοιχο αντίκτυπο έχουν και οι δραστηριότητες του τομέα στο περιβάλλον σε ότι αφορά τις μη ανανεώσιμες πηγές ενέργειας («γκρίζα» ενέργεια), αέριες εκπομπές (κυρίως CO_2), στερεά απόβλητα, κλπ. Δεδομένου ότι το σκυρόδεμα αποτελεί το πιο ευρέως χρησιμοποιούμενο δομικό υλικό (δεύτερο μετά το νερό σε συνολικούς όγκους που καταναλώνονται ετησίως από την κοινωνία) και ότι το τσιμέντο είναι η απαραίτητη «κόλλα» στο σκυρόδεμα, έμφαση πρέπει να δοθεί στη διερεύνηση και επιβολή τρόπων, μεθοδολογιών και πολιτικών για τη μετατροπή της τσιμεντοβιομηχανίας και της κατασκευαστικής βιομηχανίας σε έναν γενικά περισσότερο περιβαλλοντικά φιλικό τομέα. Ταυτόχρονα, λαμβάνοντας υπόψη από τη μια μεριά τη σημαντική ποσότητα έρευνας και τα επιτεύγματα σχετικά με τα δομικά υλικά και τον σχεδιασμό, και επιπλέον το επίπεδο της επιτήδευσης των σύγχρονων Ευρωπαϊκών Προτύπων και κατασκευαστικών κανονισμών, και από την άλλη μεριά τις αυξανόμενες περιπτώσεις της πρώιμης φθοράς των κατασκευών από σκυρόδεμα, ιδιαίτερη έμφαση θα πρέπει να δοθεί στη διασφάλιση της διάρκειας ζωής των κατασκευών οπλισμένου σκυροδέματος (σε συνδυασμό με την αντιμετώπιση της περιβαλλοντικής τους επιβάρυνσης).

Για το λόγο αυτό είναι ιδιαίτερα σημαντική η εισαγωγή του βιώσιμου τρόπου σκέψης και της έννοιας της βιομηχανικής οικολογίας στα προκαταρκτικά στάδια σχεδιασμού μιας κατασκευής, κατά την διαδικασία επιλογής υλικών και κατά το στάδιο εκτίμησης της διάρκειας ζωής, ώστε να επιτευχθεί μια εύρωστη, ανθεκτική κατασκευή οπλισμένου σκυροδέματος (για δεδομένη διάρκεια ζωής) με την ελάχιστη περιβαλλοντική επιβάρυνση.

► Συνεπώς, ο κύριος στόχος της παρούσας Διατριβής είναι να επικεντρωθεί στον εντοπισμό και ποσοτικοποίηση ενός δομημένου προτύπου κατάλληλων μεθοδολογιών για τον σχηματισμό μιας Ενοποιημένης Διαδικασίας Σχεδιασμού για τον σχεδιασμό ανθεκτικών και βιώσιμων κατασκευών με το ελάχιστο περιβαλλοντικό και οικονομικό κόστος (χωρίς συμβιβασμούς σε θέματα που άπτονται της κατασκευαστικής ασφάλειας) και επίσης για την αναγνώριση και επίδειξη τρόπων βιομηχανικής οικολογίας για την βιώσιμη ανάπτυξη της βιομηχανίας τσιμέντου και σκυροδέματος.

Ένα σημαντικό βήμα προς μια ολοκληρωμένη διαδικασία σχεδιασμού των κατασκευών οπλισμένου σκυροδέματος, είναι η ανάπτυξη πακέτων λογισμικού, βασισμένα σε μοντέλα πρόβλεψης, για την εκτίμηση της αντοχής και της διάρκειας ζωής σκυροδέματος. Μια τέτοια προσπάθεια, σε πλήρη συμφωνία με τα Ευρωπαϊκά Πρότυπα για το τσιμέντο και το σκυρόδεμα, παρουσιάζεται στο **Κεφάλαιο 2.** Για τον καθορισμό του σχεδιασμού της σύνθεσης σκυροδέματος, το λογισμικό υπολογίζει τα κύρια χημικά και ογκομετρικά χαρακτηριστικά, καθώς και τη θλιπτική αντοχή σκυροδέματος. Λαμβάνοντας υπόψη τις περιβαλλοντικές συνθήκες όπου θα εκτίθεται η κατασκευή, γίνεται πρόβλεψη της διάρκειας ζωής σκυροδέματος, με τη χρήση μαθηματικών μοντέλων (βασισμένα σε αρχές χημικής μηχανικής) τα οποία προσομοιώνουν τους μηχανισμούς φθοράς του οπλισμένου σκυροδέματος (που προκαλείται λόγω ενανθράκωσης ή επίθεσης χλωριόντων). Επίσης, παρουσιάζεται μια διαδικασία επικύρωσης των αποτελεσμάτων καθώς και η αποτελεσματικότητα του εργαλείου προσομοίωσης στο σχεδιασμό της ανθεκτικότητας. Στόχος της μελέτης αυτής είναι να προωθήσει την ευρύτερη αποδοχή της επίτευξης αποτελεσματικών και ανθεκτικών λύσεων για τα προβλήματα σχεδιασμού σκυροδέματος των κατασκευών.

Λαμβάνοντας υπόψη τα γνωστά περιβαλλοντικά ζητήματα της βιομηχανίας τσιμέντου (άμεσες και έμμεσες εκπομπές CO_2), η αντικατάσταση κλίνκερ από συμπληρωματικά υδραυλικά υλικά (SCM) μπορεί να αποτελέσει ένα πολλά υποσχόμενο πρώτο βήμα για την σημαντική μείωση των σχετιζόμενων εκπομπών. Παρόλα αυτά, μια τέτοια μείωση είναι δυνατή έως ένα συγκεκριμένο επίπεδο χρήσης SCM, επηρεαζόμενο από το βαθμό της ποζολανικής του αντίδρασης. Στο **Κεφάλαιο 3**, προτείνεται μια (4-βημάτων) δομημένη μεθοδολογία ούτως ώστε να είναι δυνατή η περαιτέρω προσαρμογή της σύνθεσης μίγματος σκυροδέματος ενός συγκεκριμένου SCM, ώστε να επιτευχθεί επιπλέον μείωση των σχετιζόμενων εκπομπών CO_2 που ταυτόχρονα θα είναι αποδεκτή από άποψη προκύπτουσας αντοχής σκυροδέματος και διάρκειας ζωής. Κατ' επέκταση, ο στόχος της εργασίας αυτής είναι διττός. Να αξιολογήσει τη περιβαλλοντική συνεισφορά κάθε συστατικού του σκυροδέματος και να παράσχει τη καλύτερη δυνατή σύνθεση μίγματος σκυροδέματος, ισορροπημένη μεταξύ των αρχών της βιωσιμότητας (χαμηλό περιβαλλοντικό κόστος) και ανθεκτικότητας (αποδεκτή αντοχή σκυροδέματος και διάρκεια ζωής). Αποδείχτηκε πως μια τέτοιου είδους ισορροπία είναι δυνατό να επιτευχθεί με την αξιοποίηση προϊόντων SCM στο μίγμα σκυροδέματος, μειώνοντας κατ' αυτόν τον τρόπο τις πάγιες περιβαλλοντικές εκπομπές χωρίς συμβιβασμούς για τη μακροπρόθεσμη ασφάλεια και την ανθεκτικότητα της κατασκευής.

Η αξιοποίηση της τέφρας βιομάζας από αγρό-βιομηχανικά παραπροϊόντα (τα οποία περιέχουν μεγάλες ποσότητες άμορφου πυριτίου) στη παραγωγή τσιμέντου ή/και στη παραγωγή σκυροδέματος μπορεί να αποτελέσει μια εναλλακτική λύση της ενσωμάτωσης των παραδοσιακά χρησιμοποιούμενων συμπληρωματικών υδραυλικών υλικών (SCM). Μια αξιολόγηση των τεφρών βιομάζας, οι οποίες εντοπίζονται στη βιβλιογραφία, με διαφορετικό περιεχόμενο SiO_2, σε ότι αφορά την αντοχή

σκυροδέματος και τη συμπεριφορά στην έκθεση χλωριόντων αποτελεί το επίκεντρο του **Κεφαλαίου 4**. Τα αποτελέσματα δείχνουν ότι τα υλικά αυτά είναι αποτελεσματικά ως προς την ανάπτυξη αντοχής σκυροδέματος και εξαιρετικά αποδοτικά στη μείωση της διαπερατότητας σκυροδέματος. Η εξάρτηση της συμπεριφοράς αυτής από το επίπεδο της περιεκτικότητας της τέφρας σε SiO_2 εξετάστηκε σε βάθος και εξήχθη το συμπέρασμα ότι αυτή επηρεάζεται από τη σύνθεση των άλλων συστατικών της τέφρας βιομάζας.

Κύριος στόχος του **Κεφαλαίου 5** είναι ο εντοπισμός του λεπτομερούς οικονομικού αποτελέσματος για την τεχνική αξιοποίησης της τέφρας φλοιού ρυζιού (RHA) ως ποζολανικού υλικού και κύριας τέφρας βιομάζας. Παρουσιάζεται μια τεχνοοικονομική ανάλυση της παραγωγής αναβαθμισμένου και υψηλής προστιθέμενης αξίας υλικού από RHA. Η μελέτη έγινε στο πλαίσιο της πιλοτικής παραγωγής σε μια Ελληνική βιομηχανία ρυζιού. Η σημασία των θεμάτων που εξετάστηκαν ενισχύεται περαιτέρω από την έμφαση η οποία δίνεται σήμερα στην υιοθέτηση λύσεων εξοικονόμησης ενέργειας και μείωσης των εκπομπών από την κατασκευαστική βιομηχανία. Η αξιοποίηση των συμπληρωματικών υδραυλικών υλικών (SCM) στο σχεδιασμό σκυροδέματος, όπως η RHA, μπορεί να αποτελέσει ένα πολλά υποσχόμενο πρώτο βήμα για τη σημαντική μείωση του περιβαλλοντικού αποτυπώματος που σχετίζεται με τα υλικά.

Σε αντίθεση με την κοινή προσέγγιση - η οποία συχνά περιλαμβάνει εκτεταμένη άλεση - το δυναμικό αξιοποίησης της RHA ως SCM, εξετάστηκε περαιτέρω στην ανεπεξέργαστη μορφή της. Αυτό γίνεται ώστε να ικανοποιηθεί η αυξανόμενη ευαισθητοποίηση της βιομηχανίας για χαμηλότερη ενσωματωμένη ενέργεια τσιμέντου και σκυροδέματος. Δεδομένης της διαθεσιμότητας των υφιστάμενων πρώτων υλών στη παραγωγή τσιμέντου, αυτό που χρειάζεται είναι η επίτευξη μιας βέλτιστης προσέγγισης, μεταξύ βιωσιμότητας και ανθεκτικότητας, κατά τον σχεδιασμό κατασκευών σκυροδέματος. Σε αυτό το πλαίσιο, τέφρες φλοιού ρυζιού με την μορφή που παρήχθησαν, (μέση διάμετρος περίπου 70 μm) εξετάστηκαν ως προς τα εγγενή χαρακτηριστικά τους και την επίδραση τους στην απόδοση των κονιαμάτων με βάση το τσιμέντο. Ελήφθησαν υπόψη ιδιότητες αντοχής, ενυδάτωσης και ποζολανικότητας. Η ανεπεξέργαστη RHA έχει μέτρια ποζολανικότητα και ένα χαμηλό δείκτη αποδοτικότητας, περίπου 0.5-0.6. Η πολύ υψηλή της χημική αντιδραστικότητα (αναλογία ενεργού πυριτίου περίπου 90%) δεν μπορεί να αξιοποιηθεί δεδομένου ότι η έλλειψη επαρκούς ειδικής επιφάνειας επιβραδύνει την εμπλοκή της σε αντιδράσεις ενυδάτωσης. Λαμβάνοντας υπόψη την ανεπεξέργαστη φύση της, μπορεί να υποστηριχθεί πως επιδεικνύει ένα αποδεκτό δυναμικό αντοχής μετά από 28 ημέρες, οπότε συμμορφώνεται - έστω και οριακά - με την κατηγορία αντοχής του χρησιμοποιούμενου τσιμέντου. Τα αποτελέσματα ανθεκτικότητας αποκάλυψαν ότι δεν υπάρχει ανάγκη για προεπεξεργασία της RHA ώστε να επιτευχθεί ίση ή ακόμα καλύτερη συμπεριφορά από τα κονιάματα με απλό τσιμέντο σε ότι αφορά την απορροφητικότητα (50% αύξηση για 15% χρήση της RHA) και την αντίσταση. Η ανεπεξέργαστη RHA όμως αποτυγχάνει - όπως τα περισσότερα SCMs -

να βελτιώσει την αντίσταση σε ενανθράκωση δεδομένου ότι για 15% αντικατάσταση του τσιμέντου, το βάθος εναθράκωσης σχεδόν διπλασιάστηκε. Γενικά, τα αποτελέσματα υποδεικνύουν ότι η αξιοποίηση της ανεπεξέργαστης RHA σε συστήματα με βάση το τσιμέντο αποτελεί μια εναλλακτική λύση για την μείωση του βάθους εναθράκωσης, με τη προϋπόθεση ότι η αντικατάσταση τσιμέντου διατηρείται σχετικά χαμηλά (κάτω από 15%).

Οι διεθνούς διάστασης προσπάθειες για τη μείωση των ανθρωπογενών εκπομπών CO_2 απαιτούν την υιοθέτηση μιας πιο αυστηρής προσέγγισης από την κατασκευαστική βιομηχανία. Με δεδομένη την ανάγκη για την εξεύρεση βιώσιμης λύσης που θα εγγυάται μια ελάχιστη διάρκεια ζωής, σε μια κοινή κατασκευή οπλισμένου σκυροδέματος, το θέμα σχεδιασμού της βιώσιμης ανθεκτικότητας είναι υψίστης σημασίας. Λαμβάνοντας υπόψη πως η κύρια πηγή αέριων εκπομπών κατά τη παραγωγή σκυροδέματος προκύπτει από τη διαδικασία παραγωγής κλίνκερ, έχουν προταθεί αρκετοί τρόποι μείωσης του περιβαλλοντικού αποτυπώματος κατά τη παραγωγή τσιμέντου, όπως η ενσωμάτωση υλικών αντικατάστασης τσιμέντου. Η παρούσα Διατριβή συνεισφέρει στην αξιολόγηση του περιβαλλοντικού κόστους κάθε συστατικού του σκυροδέματος αλλά και στην παροχή ενός καλύτερου δυνατού σχεδιασμού σύνθεσης σκυροδέματος (μέσω ενός ολιστικού αναλυτικού λογισμικού) υπό όρους χαμηλού περιβαλλοντικού κόστους, καθώς και στο να αξιολογήσει την προτεινόμενη σύνθεση υπό όρους αντοχής και απαιτήσεων ανθεκτικότητας. Συνολικά, πρέπει να τονισθεί ότι στη παρούσα Διατριβή προτείνεται για πρώτη φορά ένας **νέος δείκτης** για σκοπούς σχεδιασμού: **το περιβαλλοντικό κόστος**, το οποίο μπορεί να προστεθεί στους υπάρχοντες δείκτες αντοχής, ανθεκτικότητας και οικονομικού κόστους προς μια ολοκληρωμένη αριστοποίηση σχεδιασμού κατασκευών από σκυρόδεμα. Τέλος, η ενσωμάτωση νέων SCM, όπως οι τέφρες βιομάζας και ειδικά η RHA, προσφέρει νέες προοπτικές για τη μείωση του περιβαλλοντικού κόστους σκυροδέματος.

Λέξεις κλειδιά: ανθεκτικότητα, αριστοποίηση, βιωσιμότητα, μοντέλα πρόβλεψης, περιβαλλοντικό κόστος, σκυρόδεμα, συμπληρωματικά υδραυλικά υλικά, τέφρα βιομάζας, τέφρα φλοιών ρυζιού, τσιμέντο, χρήσιμη ζωή κατασκευής.

Chapter 1. **Introduction**

1.1 Brief description of the building sector

The **building sector** stands worldwide a prior position in generic industrial/technological activities. It is considered to be the largest industry in European grounds, with an annual turnover of 1.5 trillion € that corresponds to 11% of total European income and employs almost 20% of total work force of EU (European Commission 2013). Equivalent is the impact of the sector's activities to the environment in terms of non-renewable energy sources (grey energy), gas emissions (mainly CO_2), solid waste etc. The leading position in the building sector is held by cement/concrete industry (65% work force, 80% gas emissions, European Commission 2013). The following three subjects are matters of great significance for the construction industry:

✓ The immense need for structure for rapid urbanization of our current civilization.

✓ The necessity for balance among industrial development and environment.

✓ The crisis in the space of durability of constructions and especially concrete.

Construction in Europe (construction market forecasting network EUROCONSTRUCT 2013) performs still unfavourable in 2013. The decline of total construction output results from various factors:

- dislocations because of the public debt crises,

- the pressure to save on public households and

- uncertainty about the future economic development.

The pressure on European construction will lead to a lower output in 2013 which is expected to decrease by 2.8% compared to the previous year. This is the result of the leading construction market forecasting network EUROCONSTRUCT, which includes 19 European countries, see Fig. 1.1. Austerity measures are mainly dampening civil engineering, while the weak overall economy along

with high unemployment and a lack of consumer confidence dampens the prospects for housing and non-residential construction.
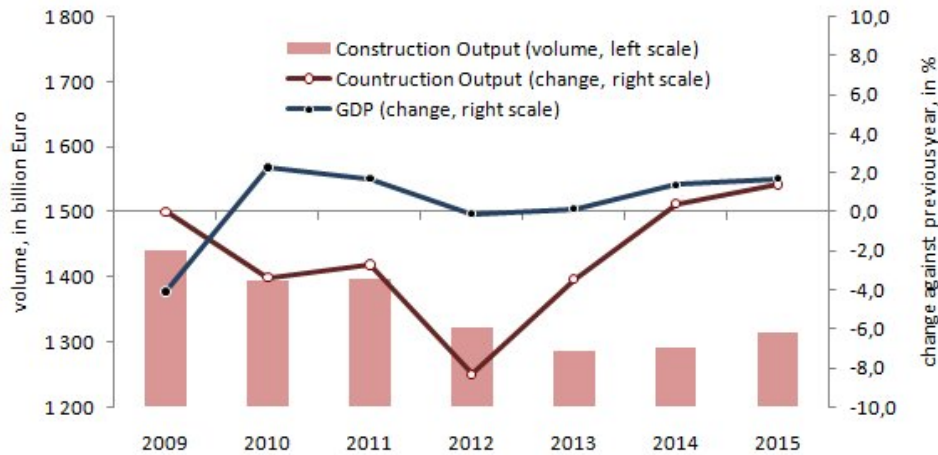
Figure 1.1 Construction activity and economic growth in Europe (EC-19) at 2012 prices (source: 75th EUROCONSTRUCT Conference - Copenhagen, 2013).

The European public debt crisis dampens the outlook mainly in **civil engineering**. This sector has been shrinking continuously for four years. It declined by one fifth compared to 2009 (when it was supported by budgetary stimulus measures). Extensions and renovation of infrastructure projects were delayed which led to overloads in some areas. Public bodies especially in northern and central Europe are aware of this and are planning to react - therefore increasing investments and growth in civil engineering are expected in 2014.

The European economic recovery is being delayed despite the improving international framework and increasing economic activity in the United States and the emerging countries. The outlook for private consumption, labor and income are therefore dampened. Unemployment is expected to reach its maximum in 2013. These factors are influencing **building construction** negatively. Non-residential construction, especially commercial building and office construction are especially under pressure. All in all construction output in building is expected to shrink by -3.3%. The declines in Greece, Spain and Portugal are most severe.

European **housing market** was also negatively affected by the poor economic performance. In 2013 about 1.3 million housing units will be completed within the 19 Euroconstruct countries – about 125,000 units less than in 2012. Banks tightened their credit volume but also the demand for loans is

decreasing, despite the low interest rate. However, since the beginning of 2013 there are some signs of improvement. In UK for instance due to appropriate governmental policies, the housing industry is moving up with more new buyers around and house – loans available from the banks.

On the other hand, the **renovation market** is performing more stable. On the one hand side investment volumes in renovation are lower so the project risks are smaller than in new construction on the other hand many European countries provide public funds which help stimulating the sector.
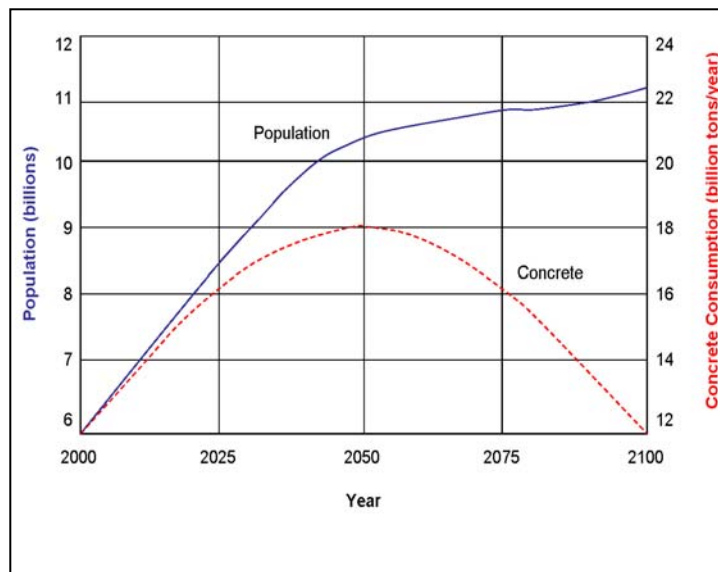
Figure 1.2 Forecast for concrete consumption up to 2100 (WBCSD 2009).

Consumption of cement is closely linked to both the state of economic development in any given country or region and to the economic cycle. In mature markets, such as in Europe, where cement consumption per capita still varies considerably from one country to another, cement sales are dependent on evolution and habits in the construction sector, a sector that is itself following very closely (usually after a brief delay) the evolution of the economy in general. Even though the global economic recession which began in 2008 led to a notable slowdown in construction activity, signs of stabilisation in the EU construction industry after a two-year drop are already appearing and an increase in construction spending and cement sales is expected. It is predicted that global demand for cement is expected to rise 4.1% yearly through 2013, to 3.5 billion metric tons in 2013, valued at $246 billion. Overall at the rate of cement consumption before the effects of the economical crisis and based on the early signs of improvement, the demand for concrete (hence of cement) is expected (Fig. 1.2) to rise to about 18 billion tonnes a year by 2050 (WBCSD 2009).

In 2010, the economic recession in Greece had a negative impact on both private and public construction activity. In terms of production, the increase in prices of solid and liquid fuels, as well as the higher cost of electricity, was added to the cost of cement production. This trend was counterbalanced in part by the use of alternative fuels, such as the combustion of dried sludge from biological sewage processing, tires, and other materials. Almost all capital expenditure from Greek Cement manufacturers in 2010 was related to investments in emissions reduction, such as use of alternative fuels.

1.2 Environmental impacts of the building sector

The construction sector and cement industry, in particular, plays a major role in meeting society's needs for housing and infrastructure that are expected to increase considerably in the developing world. The challenge we face is to develop processes and practices that will curb the intensity of CO_2 emissions produced in order to strike a balance between climate change risk and global growth.

From a production point of view almost every type of structural material used has a considerable impact on the local and global environment. In general, any set of construction materials entails certain aspects of **environmental cost (in the form of carbon dioxide and other gasses emissions and grey energy consumed)** from its manufacturing stage to its end-use (**<u>fixed environmental cost</u>**), or during-use of the structure (**<u>operational environmental cost</u>**) according to the particular type of construction.

In concrete production for example (CEMBUREAU 2009), the main emissions to air are associated with the cement-making process, where during the stage of clinker formation, CO_2 gasses and other greenhouse emissions are emitted to the atmosphere (0.873 tonnes of CO_2 gases are emitted per 1 ton of cement produced (WBCSD 2005, 2009). Bearing in mind that, cement manufacturing is a mature industry applying the same chemical process (in principle) for more than a hundred years (thus any revolutionary breakthroughs are rendered at a slow pace) and by considering that facts that, the construction sector accounts for a considerable share of the total EU final energy consumption (more than 42%) and produces more than 35% of all the greenhouse emissions (WBCSD 2009, Zampini 2009), with cement manufacturing contributing 5% of the global man made CO_2 emissions, increasing emphasis should be placed on investigating and enforcing ways, methodologies and policies, to make cement manufacturing and the construction industry in general a more environmental friendly sector.

The construction activity is a major contributor to environmental pollution and especially to greenhouse gases emissions (GHG). At world level, civil works and building construction consumes

60% of the raw materials extracted from the lithosphere (Bribian *et al.* 2011). According to data from the Worldwatch Institute, the construction of buildings annually consumes 40% of the stone, sand and gravel, 25% of the timber and 16% of the water in the world (Arena and Rosa 2003). Buildings through their construction, use and demolition, consume approximately 50% of the final energy consumption in the members states of the European Union and contribute almost 50% of the CO_2 emissions released in the atmosphere (Dimoudi and Tombra 2008). As referred, the Portland cement manufacturing industry represents 5-7% of the total CO_2 anthropogenic emissions (Hendricks *et al.* 2004, Humphreys and Mahasenan 2002). The manufacture, transport and installation in a building made of materials such as steel, concrete and glass require a large quantity of energy, despite them representing a minimal part of the ultimate cost in the building as a whole. This contradiction is known as the "Rule of the Notary" (Bribian *et al.* 2011).

Concrete is second only to water in total volume produced and consumed annually by society. The fact that concrete has very good mechanical and durability properties explains why it has become the most important building material. Nevertheless, concrete has an enormous environmental footprint (Meyer 2008). First of all production of concrete each year creates a major need for natural resources. The production of Portland cement is energy intensive and is also responsible for CO_2 emissions. The cement subsector consumes approximately 12–15% of the total industrial energy use. Therefore, this subsector releases CO_2 emissions to the atmosphere as a result of burning fossil fuels to produce energy needed for the cement manufacturing process. Moreover, the concrete industry requires large water consumption. Construction and demolition waste have a high environmental impact as well.

However, many aspects of the environmental cost in construction have not been analyzed yet. The concrete industry faces a great challenge which is the sustainable design of buildings and structures by taking into account environmental and financial factors. The competition among constructors imposes the application of "green" technology in the production process and the marketing of new and more durable building materials. Therefore, since environmental issues have become really important, construction industry must adjust to the principles of sustainable development. The implementation of specific environmental policies and the adoption of proper methods by industries can result in the reduction of CO_2 emissions from reinforced concrete constructions.

1.2.1 Environmental cost components

The main environmental impacts of construction activity are: air pollution, waste pollution, noise pollution and water pollution. More specifically, the most harmful environmental effects of materials and energy consumption due to construction are:

- global warming

- acid rain

- resource depletion

- habitat destruction by fuel extraction

- environmental damage from processing and transportation photochemical smog

At the Kyoto Conference in December 1997, developed countries agreed to cut their emissions of greenhouse gases by an average of 5.2% in the period 2008 to 2012.The target for the European Union was an 8% reduction, shared out amongst Member States. According to the definition in the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC), GHG (Greenhouse Gas) includes six types of gas, namely carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydroflurocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6).
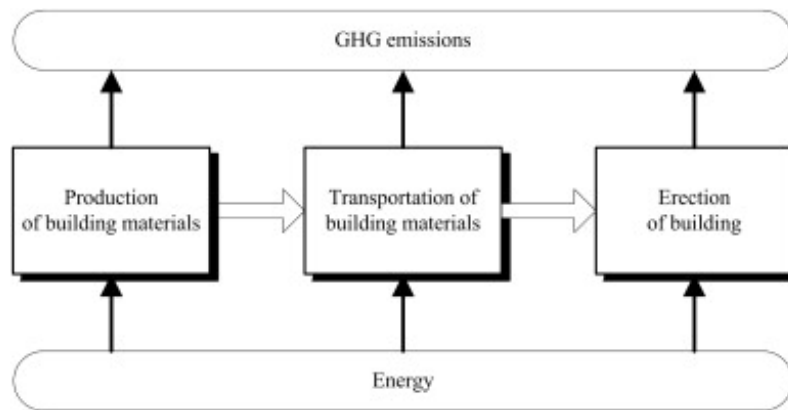
Figure 1.3   System boundary of GHG emissions in the construction of buildings (Yan et al. 2010).

Fig.1.3 defines the system boundary of greenhouse gas emissions in building. Processes embraced in construction of buildings are: production of building materials (including acquisition of raw materials and manufacture of building materials), transportation of building materials to construction sites and erection of buildings (including disposal of waste and auxiliary materials incurred in the construction work). Energy consumption in these processes accounts for GHG emissions (Yan *et al.* 2010).

The main sources of GHG emissions in building construction therefore are:

a) *Manufacture and transportation of building materials*

- embodied GHG emissions of building materials, which are GHG emissions due to energy consumption for manufacture of building materials before transporting to construction sites

- GHG emissions from transportation for building materials, which are GHG emissions due to fuel and energy consumption for transporting building materials to construction sites

b) *Energy consumption of construction equipment*
- GHG emissions from fuel combustion of construction equipment
- GHG emissions due to electricity used for construction equipment

c) *Energy consumption for processing resources*
- emissions due to electricity used for processing fresh water and sewage

d) *Disposal of construction waste*
- GHG emissions from fuel combustion of transportation for construction waste

The main way to estimate the environmental cost of construction is by measuring the emissions of CO_2 during the production, transport and use of materials in construction. In addition, the calculation of energy consumed by industries contributes to the estimation of environmental cost of construction. This energy (kWh) is responsible for CO_2 emissions to the environment. In addition, other factors like the consumption of raw materials, noise pollution, emissions of other gases or dust are counted in the total environmental cost.

There are many research studies about the environmental cost of buildings and constructions in general. The results of these studies are very interesting and must be taken into consideration, since they provide useful information. For example, it was found that all the life cycle phases cause serious environmental impacts, but operational phase has the highest percentage of energy consumption and emissions (80-85% of total energy consumption and emissions) in a building's life (Zampini 2009, Penttala 1997, Flower and Sanjayan 2007, Gerilla *et al.* 2007). Furthermore, commercial buildings were found to have a higher environmental footprint, compared to the residential buildings. All these issues need of course further investigation and analysis.

The construction industry must adopt the principles of sustainable development in order to reduce its environmental footprint. *Sustainability means meeting the needs of today without compromising the ability of future generations to meet their needs.* **Sustainable Construction aims to apply this principle to the construction industry by providing ways of buildings that use less virgin material and less energy, cause less pollution and less waste but still provide the benefits that construction projects have brought us throughout history.** A typical Sustainable Construction Project involves the following criteria in the phases of Design, Construction and Use (Table 1.1).

Table 1.1   Criteria for a sustainable construction project.

DESIGN	CONSTRUCTION	USE
Integrated Design	Environmental Policy	Extended Design life
Sustainable Materials Insulation	Waste Reduction Targets Utility Conservation	Building Log Books Commission Systems
Fitting Specifications	Materials Purchase Audits	Native plant species
HVAC Systems (Heating, Ventilating, and Air Conditioning)	Materials Waste Audits	Recycling facilities
White Goods	Site Recycling	HVAC Services
Water Systems	Ecological Conservation	Modular Maintenance
Lighting	Performance reporting	Internal Environment

1.2.2   Environmental impact of building materials

The main building materials used in constructions are: Concrete (cement, aggregates, water, additives, admixtures), steel, bricks, wood, glass, mortars and other materials. The fact that concrete has very good mechanical and durability properties explains why it has become the most important building material. It is mouldable, adaptable, relatively fire resistant, generally available and affordable. Nevertheless, concrete has an enormous environmental footprint. First of all its production each year creates a major need for natural resources. The production of Portland cement is energy intensive and is also responsible for CO_2 emissions. Moreover, the concrete industry requires large water consumption while construction and demolition waste have a high environmental impact as well.

Cement accounts for two-thirds of total energy use in the production of non-metallic minerals. In terms of CO_2 emissions, cement production is by far the most important activity in this category. Global cement production grew from 594 Mt in 1970 to 2,284 Mt in 2005, with the vast majority of the growth occurring in developing countries, especially China. The production of cement clinker from limestone and chalk is the main energy consuming process in this industry. The most widely used cement type is Portland cement, which contains 95% cement clinker. Clinker is produced by heating limestone to temperatures above 950 °C. Cement production is an energy-intensive process in which energy represents 20 to 40% of total production costs. Most of the energy used is in the form of fuel for the production of cement clinker and electricity for grinding the raw materials and finished cement. Since cement production consumes on average between 4 to 5 GJ per ton of cement, this industry uses 8 to 10 EJ of energy annually.

The electricity use in cement production varies between 90 and 150 kWh per ton. According to the GNR database, in the year 2006, the global average electricity consumption was 111 kWh per ton of cement. The electricity consumption of 90% of the 844 cement plants covered in the database are between 89 and 130 kWh/t. Significant variations exist between countries and regions. According to the IEA (IEA, 2007), electricity consumptions ranges from 90 to 120 kWh/t of cement, except for the United States, Mexico and Canada where typical figures are all above 120 kWh/t of cement. Grinding may account for a significant part of electricity consumption (up to 100 kWh/t) In a dry process, the electricity consumption share is 38% for cement grinding, 24% for raw material grinding, 22% for clinker production including grinding of solid fuels, 6% for raw material homogenisation, 5% raw material extraction and blending, and 5% for conveying, packing and loading.

There are two very different sources of carbon dioxide emissions during cement production. Combustion of fossil fuels to operate the rotary kiln is the largest source: approximately ¾ tons of CO_2 per ton of cement. But the chemical process of calcining limestone into lime in the cement kiln also produces CO_2: $CaCO_3 \rightarrow CaO + CO_2$. This chemical process is responsible for roughly ½ ton of CO_2 per ton of cement. Although, the main CO_2 emissions from concrete production are associated with cement manufacturing, other concrete constituents entail environmental loads, see Table 1.2. The CO_2 emissions from concrete production are the summation of the emissions from the chemical conversion process in clinker production (during cement manufacturing), from the energy consumption due to fossil fuel combustion (also during cement manufacturing), from the electrical energy required for the grinding of any additive materials and from the energy required (in terms of fuel consumption) for the transportation of the raw materials and of the final product (Penttala 1997, Flower and Sanjayan 2007).

Table 1.2 CO_2 emissions from cement and concrete production (Penttala 1997, Flower and Sanjayan 2007).

	lbs CO_2 per ton of cement	lbs CO_2 per cu. yd. of concrete	Percent of total CO_2 (%)
CO_2 emissions from energy use	1,410	381	60
CO_2 emissions from calcining of limestone	997	250	40
Total CO_2 emissions	2,410	631	100
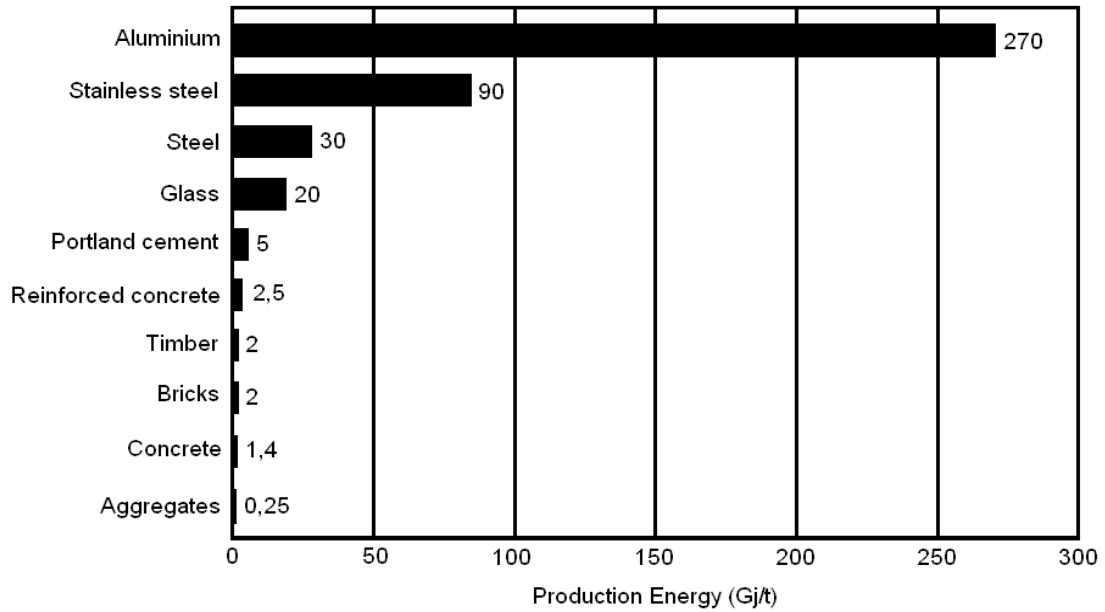
Figure 1.4 Energy consumption from production of building materials (EC DG Env. 2004).

Fig. 1.4 allows a comparative analysis of the energy that is consumed for the production of different building materials.

Fig. 1.5 and 1.6 are based on a life cycle assessment of building materials (Bribian *et al.* 2011). These figures show the relative contribution of some building materials to the primary energy demand and CO_2 emissions associated with a square meter in a Spanish standard block of flats. It is obvious that the most popular materials such as steel, cement and ceramics have a high impact.
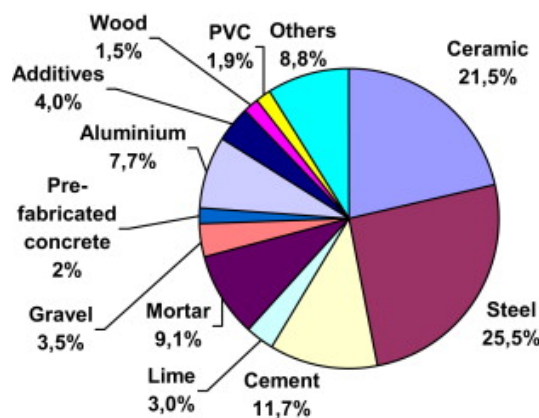
Figure 1.5 Contribution of primary energy demand for the manufacture of the materials needed in the construction of 1 m^2 gross floor area (Bribian et al. 2011).
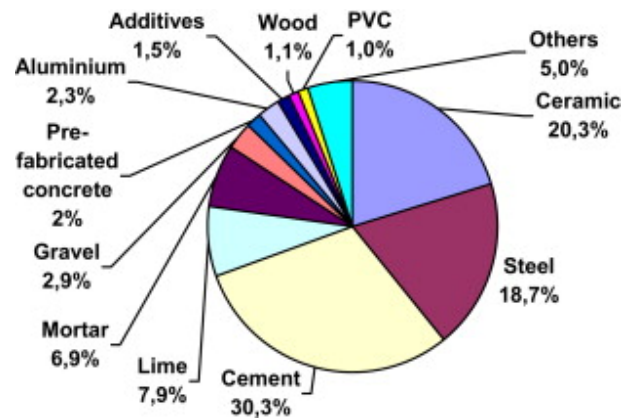
Figure 1.6   Contribution of CO_2 emissions associated with the manufacture of the materials needed in the construction of 1 m^2 gross floor area (Bribian et al. 2011).

Fig. 1.7 shows the CO_2 emissions for wooden and SRC (Steel Reinforced Concrete) type of construction, according to each life cycle stage (Gerilla *et al.* 2007). The carbon emissions in the operation stage have the highest rate compared to the other stages.
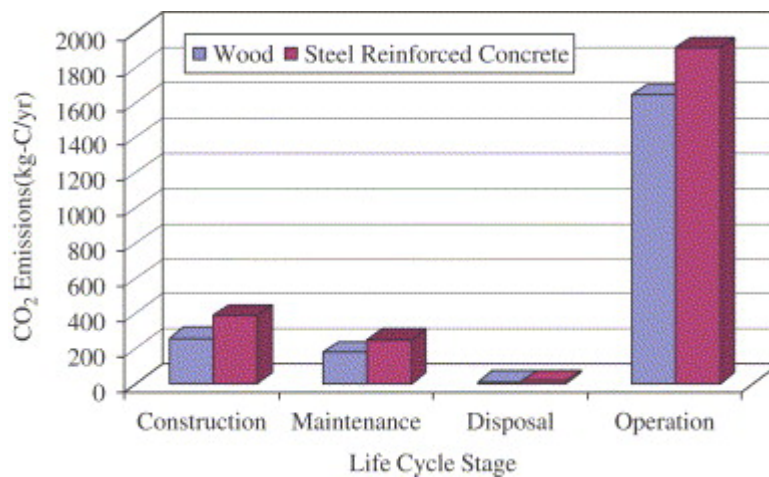
Figure 1.7   Environmental impacts of the calculated emissions (Gerilla et al. 2007).

Fig. 1.8 shows the environmental impacts of housing. The most serious environmental impact of building is Global Warming Potential because the highest air pollutants are from carbon emissions. SRC houses have a higher environmental footprint compared to the wooden type of construction (Gerilla *et al.* 2007).
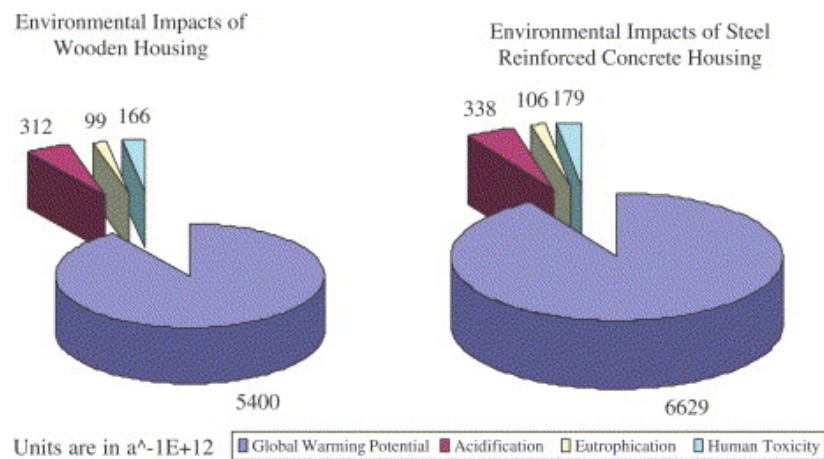
Figure 1.8 Total life cycle carbon emissions for each life cycle stage (Gerilla et al. 2007).

1.2.3   Reduction of the environmental cost

Decreasing the environmental cost is a matter of importance, thus a lot of measures are proposed such as restriction of residue production and emission responsible for the greenhouse phenomenon, extended use of industrial by- products and their various mixtures, more efficient use of mineral and metallic sources, increased use of recycled materials in conjunction with lengthening of the construction durability. In order to achieve a balance between sustainability and durability, as far as concrete design is concerned incorporation of supplementary cementing by –products, such as silica fume and fly ash, has been suggested (Tapali *et al.* 2013).

According to Meyer (2009) **the potential tools and strategies to meet the environmental challenges are:**

1. To replace as much Portland cement as possible by supplementary cementitious materials (SCM), especially those that are by-products of industrial processes, such as fly ash, ground granulated blast furnace slag and silica fume, etc.
2. To use recycled materials in place of natural resources.
3. To improve durability and service life of structures, thereby reducing the amount materials needed for their replacement.
4. To improve concrete's mechanical and other properties, which can also reduce the amount of materials needed.
5. To reuse wash water.

What follows is a brief report of the main methods and materials which can be used by concrete industry.

Fly ash

Fly ash is an important pozzolan with cementitious properties, which has a lot of advantages compared with regular Portland cement. The heat of hydration is lower, which means that fly ash can be used as a cement substitute for mass structures. Moreover, fly ash is a byproduct of coal combustion, which otherwise would be a waste product. It also improves the strength and durability properties of concrete and costs less than Portland cement.

The relatively slow rate of strength development of fly ash concrete is a disadvantage where high early strength is required (Papadakis 1999b, Papadakis 2000a). Another critical issue is the need for quality control since the sources of coal are different in power plants. So, the physical and chemical properties of fly ash can vary to a significant extend.

High Volume Fly Ash Concrete (HVFA) is constituted by the following minimum mix criteria:
- a minimum of 50% fly ash,
- a low water content (130 kg/m^3),
- less than 200 kg/m^3 cement content, and
- a low water-cementicious ratio (less than 0.4).

Ground granulated blast furnace slag (GGBFS)

GGBFS is a by- product of the steel industry which also has cementitious properties. It is the glassy granular material formed when molten blast- furnace slag is rapidly chilled, as by immersion in water (ACI Committee 233, 1995). GGBFS has a positive effect on many mechanical and durability properties of concrete and generates less heat of hydration.

Silica fume

Condensed silica fume is a by-product of the semiconductor industry which can improve the strength and durability of concrete. It has a lot of benefits both as a pozollan and a filler material, so it is now produced specifically for the concrete industry (Papadakis 1999a).

Recycled concrete

Because of the large amount of fines found in recycled concrete there are technical problems incorporating recycled concrete aggregates into new concrete. Recycled concrete aggregates (RCA) have generally lower densities than the original material used, because of the cement mortar that remains attached to the aggregate particles (De Pauw 1981). This fact is also the reason why there is larger water absorption of RCA in comparison with virgin aggregates. Moreover, as a result of the demolition of existing structures, there are a lot of contaminants in recycled concrete like plaster, soil, wood, gypsum, asphalt and rubber which can degrade the strength or durability of the concrete. RCA also causes a reduction in elastic modulus, an increase in creep and shrinkage deformations, as well as high permeability of concrete, whish decreases its durability (Meyer 2009). Another matter of concern is the fact that there is a large variability in quality of RCA obtained from different sources which may lead to significant variations in strength of concrete with RCA from different sources.

Post-consumer glass

Post- consumer glass can also be used as aggregate for concrete. Glass has many advantages such as zero water absorption, high hardness, good abrasion resistance, excellent durability, chemical resistance and aesthetic potential.

Other materials

There are also **many other and especially new by- products** that can be used as substitutes for conventional ingredients of concrete. For example various **biomass ashes** with pozzolanic properties can replace Portland cement. **Rice husk ash (RHA)** which is the residue from burning rice husk at rice industries can also be excellent for use in cement and concrete production.

1.2.4 Towards a sustainable construction

The implementation of environmental management in construction activities has a lot of benefits for the community and the contractors. EMS is an environmental management system defined in the standard ISO 14000 which can improve the environmental performance in construction, including or suggesting various environmental management measures such as:

- Legal requirements on environmental protection
- Reduction, reuse and recycling of construction and demolition wastes
- Imposing responsibilities of protecting environment on managerial staff

- Applying environmentally friendly technology
- Providing in- house training on environmental management
- Establishing waste management plan
- Continuous efforts in improving environmental management
- Inclusion of environmental management in tendering requirements
- Effective communication on environmental issue between all layers of subcontractors
- Close supervision at site level

There are many factors that can affect the environmental impact of a building, such as the choice of structural solutions and building materials. Furthermore, the length of the building's service life has an influence on the environmental assessment of a building. Numerous environmental assessment tools have been developed to allow scientists analyze the environmental performance of buildings.

Since decreasing the environmental cost is a matter of importance, a lot of measures are proposed such as restriction of residue production and emission responsible for the greenhouse phenomenon, extended use of industrial by- products and their various mixtures, more efficient use of mineral and metallic sources, increased use of recycled materials in conjunction with lengthening of the construction durability. Several different studies IEA (2008, 2009), CSI (2009), ECRA (2009), CCAP (2008), McKinsey (2008) have focused on potential cement industry emissions reduction.

Generally, there are four main levels concerning the reduction of carbon emissions:

1. Thermal and electric efficiency
2. Use of alternative fuels- use of less carbon-intensive fossil fuels and more alternative (fossil) fuels and biomass fuels in the cement production process
3. Clinker substitution by supplementary cementing materials (SCM)
4. Carbon capture and storage (CCS) – capturing CO_2 before it is released into the atmosphere and storing it securely so it is not released in the future (Cement Technology Roadmap 2009).

Considerable amount of work on developing analytical models for the evaluation of SCM in concrete using the concept of efficiency factors (or k-values, to compare the relative performance of supplementary cementing materials on concrete strength and durability) by Papadakis and Tsimas (2002) and preliminary work undertaken by Antiohos *et al.* (2013) on identifying and evaluating new promising industrial by products have identified the high-added value of incinerated residues from industrial by-products on cement and mortar. The k-factor, defined as the part of the SCM, which can be considered as portland cement, providing to the SCM-concrete equal property values with the

concrete without SCM, will allow the estimation of the relative value of these materials comparing to cement, an important factor of the mix design process for the preparation of the building product.
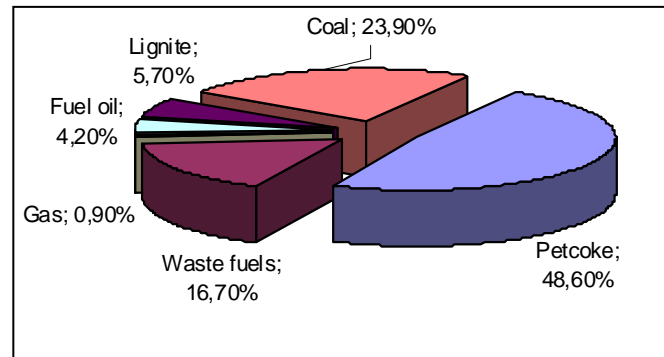
Figure 1.9 Fuel consumption in the EU-25 (EC DG Env. 2004).

In terms of fossil fuels, solid fuels such as coal (23.9%), petroleum coke (48.6%) and lignite are traditionally used (Fig. 1.9) in the burning process in clinker kilns (and to a lesser extent, natural gas and fuel oil). However, further waste and by-products with recoverable calorific value can be used as fuels in a cement kiln, replacing a portion of conventional fossil fuels, if they meet strict specifications (being 20-25% less carbon intensive than traditional coal and petcoke). In this way recycling wastes from one process as raw materials and fuels for another creates a web of relationships between industries that moves society closer to a zero-waste economy. Co-processing of these types of materials in the cement industry prevents equivalent CO_2 emissions at waste incineration disposal installations, plus any mineral content in alternative fossil fuels that is incorporated into the clinker matrix during its formation, thus there is no residual ash and associated heavy metal disposal, such as is typically found in incinerators.

In general, the **use of waste as an alternative energy source** varies widely across regions, influenced by the level of development of waste legislation, law enforcement, waste collection infrastructure and local environmental awareness. In Europe, where up to 70% of clinker production installations source energy from alternative fuels, 45% of installations source a small portion of energy from biomass, in contrast to Latin America, where 30% of energy used is derived from biomass. Overall, there is significant potential to further develop the sourcing of thermal energy from alternative fossil fuel, especially waste, and biomass across all regions of the world.
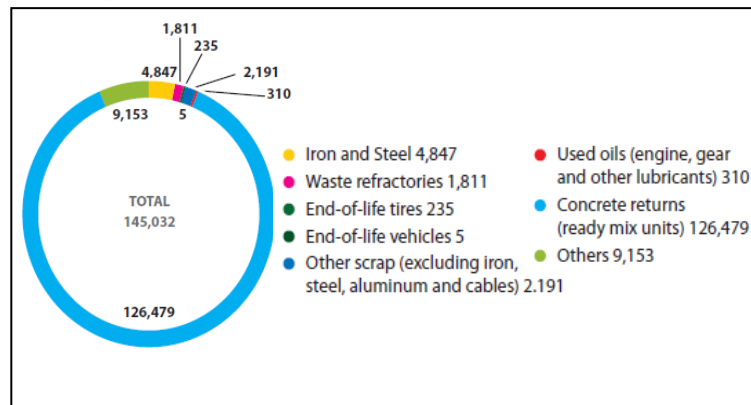
Figure 1.10   Waste materials utilised by TITAN Cement Company (TITAN, 2010).

Currently in Greece, TITAN Cement Company (Fig. 1.10) utilises 1.4% biomass derived energy in the cement manufacturing process (the largest source of thermal energy, 98.6% calorific basis, comes from conventional energy sources). Efforts however are being made to increase this percentage. An alternative fuel system that fires biomass (from sawdust flour, wood chips) to both the calciner and main burner was recently commissioned by TITAN in Roanoke cement plant in Virginia, USA. The goal of the project was to reduce the amount of coal consumed by the plant. The initial results have shown that the materials introduced through the calciner show great promise towards the ultimate goal of reducing coal consumption while at the same time not affecting clinker quality or increasing emissions. Furthermore, a considerable number of research projects initiated by TITAN provide additional efforts to address the current climate change challenges of the cement manufacturing process, by focusing on: the sustainability of both product and production process (ECOSERVE), on utilization of agricultural wastes in the cement industry (LABELAGRIWASTE), on the utilization of mineral industry by-products as raw materials for cement production (PERLITE REJECTS UTILIZATION), on the utilization of an aluminum industry by-product as raw material for the raw mix of clinker production (RED MUD FOR CLINKER) and on delivering roads constructed with minimal CO_2 burden, utilizing alternative raw materials and hydraulic binders with minimum clinker content (TEFRODOS Project). Further to the above, the fluctuation (increased at the moment) in prices of solid and liquid fuels, as well as the higher cost of electricity, in cement production leads the cement manufacturing companies to investigate and invest in the use of alternative fuels.

Considering all of the above, and bearing in mind that industrial ecology is "The Science of Sustainability" through minimising consumption of natural resources and production of waste with optimal utilization of raw materials in order to produce products with optimal performance and life expectancy, there is a wide sector that needs to be infiltrated by eco-cement and other relative sustainable products and techniques.

Utilisation of industrial by-products as cement replacement materials and as alternatives to fossil fuels will reduce the amount of the associated CO_2 emissions from both burning of fuel and the clinker calcination process, considerably. As fuel-related CO_2 emissions are about 40% of total emissions from cement manufacture, the CO_2 reduction potential from alternative fuel use can be significant. It has been estimated that utilisation of alternative fuels (to a certain percentage) can be 20-25% less carbon intensive than coal. Utilisation of 15,500 tons of sewage sludge in one of the coordinators cement plants, reduced the requirements for fossil fuels by about 5,000 tons, while lowering by about 18,000 tons the plant's CO_2 emissions.

By utilising the industrial by-products proposed in this thesis as cement replacing materials, rice husk for example, components of strength equal to a reference mixture can be obtained. At the same time, a similar durability in general is achieved, plus significant ecological benefits, due to industrial by-products use (reduction of pollution from incinerated residues of rice husk arbitrary disposal) and decrease in the cement quantity (energy saving and CO_2-emission reduction). As the k-value for treated residues of rice husk is estimated around 1 (equal to Portland cement), it means that this material can substitute equally cement, and by taking into account that 1 t of cement production emits 1 t CO_2, every 1 t of RHA used in building applications almost save 1 t of CO_2 emissions.
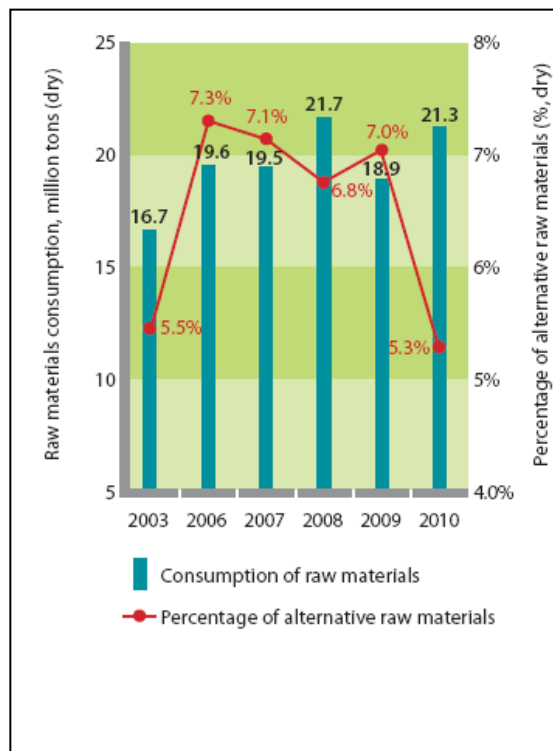
Figure 1.11   Consumption of raw materials and % of alternative raw materials used in clinker and cement production by TITAN Cement Company (TITAN, 2010).

In 2010, 21.3 million tons (dry basis) of raw materials were used by TITAN for cement production, in which approximately 5.3% of all raw materials (about 1.1 million tons dry basis) were alternative raw materials, namely by-products and waste disposals from other industries, such as fly ash, pyrite ash, blast furnace slag and industrial gypsum (Fig. 1.11). Overall the utilisation of the previously mentioned percentages of alternative materials resulted on 697.7 kg/t of cement direct CO_2 emissions. The aim is to increase the utilisation of alternative materials as cement replacements to 12% and combined with the utilisation rate of alternatives to fossil fuels previously mentioned, achieve an overall value of direct CO_2 emissions in the range of 628 kg/t of cement, by 2015.

1.3   Objectives and structure of the present thesis

1.3.1   Objectives of the present thesis

► *The present thesis targets on formulating in a structured way every process contributing on an optimization stage between the principles of* **sustainability, durability** *and economical aspects and on* **introducing new industrial by-products**, *easier to obtain throughout Europe and with less energy requirements for their processing than the ones currently used, in cement manufacturing (as clinker replacement materials), or as concrete additions, enforcing in this way an* **industrial ecology scheme**, *in achieving less greenhouse gas emissions from cement manufacturing.*

Through the formulation and utilisation of an **Integrated Design Process (IDP) tool**, the concept of minimizing greenhouse gas emissions, will be incorporated at the initial preliminary design stages of a reinforced concrete structure, at the materials selection stage, where by:

  - estimating the overall fixed environmental cost of materials
  - the operational environmental cost of the structure
  - its economical aspects
  - and the fulfilment of service life estimation for concrete deterioration,

the optimum balance among the previous will be estimated, in determining the best overall configuration for the **design of a durable RC structure, at the minimum environmental and economical cost.**

Overall the aim is to define the necessary structures of an analytical framework (IDP) and demonstrate its outputs (optimised process, suggestions for sustainable development, eco-concrete) in order to

introduce into everyday construction practice the principles of industrial ecology and enhancement of durability of structures, in achieving a considerable decrease of the associated CO_2 emissions.

The principal objective of this thesis is to provide an integrated approach of the environmental impacts in concrete industry by **enhancing an innovative software tool** (**EUCON**, Papadakis and Efstathiou 2005). The guidelines outlined herein would be very helpful for the engineers and the companies, whereas the manufactures would be encouraged to **promote "green" concrete and sustainable methods of building.**

A great challenge nowadays is the construction of durable concrete structures which are friendly to the environment and live longer. The basic conclusions that arise from this particular presentation must affect, apart from the scientific community, all other social and political groups, since the environmental problems caused by constructions have become really worrying.

The principles of Sustainable Development and Green buildings have dominated in recent years. The concrete industry in particular leaves an enormous environmental footprint; therefore the situation must be improved, as soon as possible. The use of supplementary cementing materials is suggested, in order to achieve a balance between sustainability and durability. Governments should give financial and legislative incentives to manufactures and industries and urge them to apply new methods and a more sustainable and "green" technology. Furthermore, construction organizations must improve their environmental performance by using environmental management systems (EMS). Life Cycle Analysis can contribute in the reduction of environmental impacts across the entire life cycle of materials, from production to disposal.

The technology (Fig. 1.12) for the development and production of eco-cement consists of the utilization of industrial by-products as cement replacement materials, (hence reducing clinker, which contributes to a large extent on greenhouse gas emissions) and of the incorporation of alternative fuels from the agro-industrial sector as rachis/pedicels from wine production, olive leaves and pruning from the olive/olive oil industry and biomass, to produce thermal energy for its manufacture. More specifically, specially treated (to a certain level of fineness) incinerated residues of industrial by-products, from the rice and paper making industries, with a high efficiency factor (an index of their pozzolanic activity, crucial in establishing cementitious properties) can be fed to the process, with the other typically used raw materials in cement manufacturing.

In order to achieve a **balance between sustainability and durability** in concrete design incorporation of supplementary cementing by–products, such as **biomass ashes** and more specifically **rice husk ash (RHA)** are examined. On the utilisation of rice husk ash, results from a National Research project

(PYRICE 2008) indicated that the specially physicochemical treated RHA, given its high specific surface and great amount of silica soluble in alkaline conditions, can be converted into advanced and high-added value cementitious materials, improving significantly the concrete strength and durability and decreasing the construction's environmental cost due to use of less cement and/or the extension of its lifetime. Considering the fact that approximately 600 million tonnes of rice paddy is produced on an annual basis and that on average 20% of the rice paddy is husk, and that production of paper sludge is estimated to be in the region of 1 million tonnes annually just in the UK, vast quantities of these incinerated residues are available and easy to obtain. At present, in Greece, most RHA quantities remain unexploited leaving significant space for successful applications towards a greener cement or concrete production.
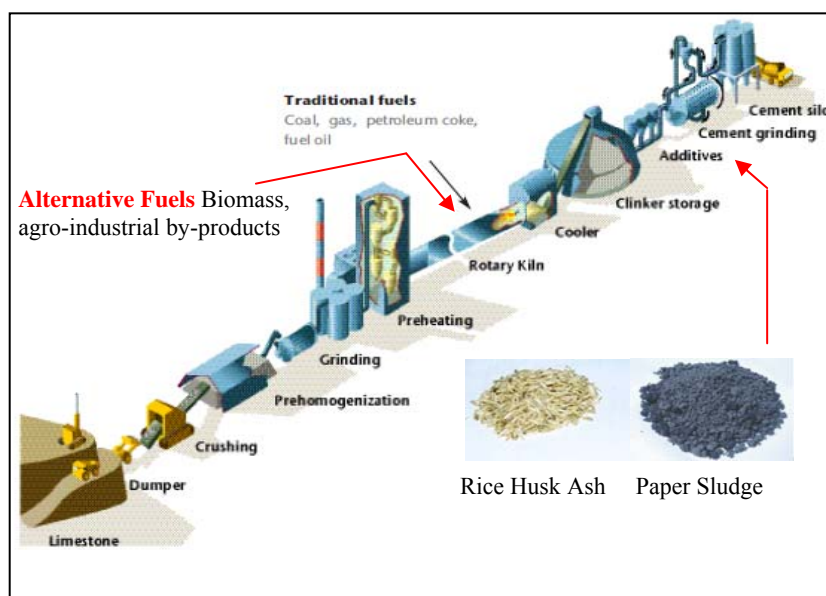
Figure 1.12   Schematic process of cement manufacture and ways for a greener production.

1.3.2   Innovative aspects of the thesis

Based on the previously stated arguments on defining the objectives and the environmental problem tackled in this thesis, its main aim can be defined as, **to focus on identifying and quantifying a structured framework of the appropriate methodologies in formulating an Integrated Design Process (IDP) for the design of durable and sustainable structures at the minimum possible environmental and economical cost** (without compromising issues of structural safety) and also in identifying and demonstrating ways (through the **use of various biomass ashes**) of industrial ecology for the sustainable development of the cement and construction industry.

For such a structured and comprehensive framework of processes as the IDP, counterbalancing issues of sustainability with durability and economical cost has yet to by developed. Analytical tools currently available cover, either the spectrum of environmental and economical constraints through life-cycle analysis, as the SUSCON (2008), GEMIS (Fritsche 2008), or SimaPro (Goedkoop *et al.* 2010) tools (not easy to follow by the key players involved in the field of the construction sector), or the service life estimation of concrete structures, as the DURACON (2006), Conclife (Bentz *et al.* 2001), Life-365 (Ehlen *et al.* 2009) tools and EUCON (Papadakis and Efstathiou 2009) which in addition to the service life and strength estimation incorporated economical aspects on the design procedure.

There is yet a certain tool to be developed offering a holistic approach and an accurate prediction of the service life of the structure, under harmful exposure conditions, with the minimum environmental and economical impact. Such is the purpose of the IDP tool (see Chapter 3).

Having said that, and bearing in mind the environmental burden of the cement manufacturing process (due to the clinker calcination process) several research solutions have been attempted.

• Innovative new types of clinker have been produced (or are being developed at the moment), as the types of Novacem (Ruffolo *et al.* 2010), a carbon-negative cement based on magnesium silicates (rather than limestone as the Ordinary Portland Cement), Calix (Sweeny and Sceats 2009) produced in a reactor by rapid calcination of dolomitic rock in superheated steam, Calera (Bren 2011) based on a mixture of calcium and magnesium carbonates and hydroxides and finally the type of clinker currently being developed by the AETHER Life+ project (Walenta and Morin 2011).

• In addition, efforts have been made in providing methodologies on recycling schemes of solid and liquid wastes from the production process of cement manufacturing, in cold climates (Betongindustri 2001) and in the Mediterranean Region (ECO-SERVE 2004).

The only restriction of the above mentioned types of research efforts is that they have to be accepted by the cement manufacturing companies, as their enormous (indeed) benefits on the reduction of the associated emissions it is estimated to be fully validated in a time frame of 5-10 years from today (Mehta and Monteiro 2006).

• What is actually currently being utilized is incorporation of cement replacement materials (replacing clinker to a certain percentage). It has been shown, that incorporation of fly ash, silica fume or ground granulated blast furnace ash, besides the effect they entail on early concrete strength and volume stability (Papadakis and Tsimas 2002, 2005), they improve to a great extend the overall environmental

contribution (Papadakis and Tsimas 2003). It has been calculated that 18% replacement of Portland cement results in a 17% reduction of the CO_2 emissions (Mehta and Monteiro 2006, Ecosmart Concrete 2008, WBCSD 2005, 2009).

Bearing all of the above in mind, it becomes prudent to identify and investigate new forms of materials, effective to be used as cement replacement, and easier to obtain on a European but also on a local level and also without having considerable energy requirements for their processing.

Industrial by-products, from the rice and paper making companies (or from the agro-industrial sector as rachis/pedicels from wine production, olive leaves from the olive/olive oil industry) can potentially be used as partial cement replacement materials. Rice husk ash (RHA), an agricultural waste material, produced by controlled burning of rice husk, or paper sludge ash, produced from the incineration at 800 °C of paper mill sludge, have shown to contain reactive silica and alumina (in the form of metakaolin) as well as lime (CaO) which could contribute chemically to the Portland cement ingredients. At present, in Greece, most RHA remains unexploited and is disposed as waste, resulting in a potential environmental threat and a factor of soil and atmosphere pollution.

It is believed that the approach presented in this thesis, although simple in principle, is currently missing and that it will provide considerable benefits in tackling the environmental burden of the construction sector and in providing:

• A structured framework of analytical methodologies, as an Integrated Design Tool, in evaluating in a balanced (optimized) way every aspect on material selection for the design of a RC structure (environmental cost, durability and service life, economical cost)

• A new type of cement with reduced clinker content, or concrete incorporating simple in principle, but innovative in results, new types of pure industrial by-products (hence enhancing the principle of industrial ecology), easily accessible in the majority of the European Countries.

1.3.3   Structure of the thesis

According to the above introduction and analysis of the thesis' objectives, the structure of the thesis has as follows:

Chapter 1:   *Introduction*. First, a brief description of the building sector is presented in terms of basic characteristics, production rates, and relevance with the economy growth. The

various environmental impacts of the building sector are then analysed and grouped, whereas the potential measures, products and techniques for reducing the environmental cost of the constructions are outlined. Then, the objectives and structure of the present thesis are given.

Chapter 2: *Durability and sustainability of concrete constructions*. Service life and durability of concrete are strongly related with the environmental footprint of constructions. It is obvious that a structure with a longer service life is less harmful to the environment during the phase of operation. In this chapter, therefore the concrete durability according to the European Standard EN 206 is first presented, then, the development of a concrete mix design is given including the concrete constituents and, finally, the concrete service life estimation tool (EUCON) is presented with the improvements made in the present work on environmental cost assessment.

Chapter 3: *Environmental cost of concrete production – Estimation & optimization*. First, the concept of the environmental cost is analysed and then it is estimated for the concrete production according to literature and industry data. A structured methodology for concrete mix design optimization (*Integrated Design Process*) is then presented in details and utilized for typical applications offering a significant tool towards sustainable concrete constructions.

Chapter 4: *Investigation on the effectiveness of biomass ashes as pozzolanic materials*. The main aim is to shed light on the specific influence of the main characteristics of biomass ashes on concrete strength development and performance in chloride exposure, exploring in this way their future utilization in cement and concrete manufacturing. Types and evaluation methodology for biomass ashes are presented together with results and discussion on their evaluation as concrete constituents.

Chapter 5: *Utilization of rice husk ash in the building sector – Technoeconomical analysis and environmental benefits*. Focusing on rice husk ash - a main biomass ash and efficient pozzolanic material, provided its amorphous and fine state – techno-economical aspects are analyzed in detail. A technical and financial study and a preliminary design for the industrial production of the RHA-derivatives for building applications, including an environmental analysis, are performed. The limitations that may arise are examined, such as the registration of these new materials according to EU and national regulations. Knowing the above components, the rate of return on investment is estimated and the

first conclusions for the undertaking of this investment are drawn, offering as well high environmental benefits to the construction industry.

Chapter 6:   *Conclusions*. The main conclusions drawn from all thesis chapters are presented and the corresponding suggestions for engineers, manufacturers, practitioners and all interesting parties are given as well.

Chapter 2. Durability & sustainability of concrete constructions

2.1 Introduction

Concrete is the most widely used building material. Its good performance in service, including *durability*, is the second important characteristic after the usual required mechanical properties. However, during the last decades the problems of unsatisfactory durability of structures, especially reinforced concrete ones, are in a dramatic increase. This causes not only *economic impacts,* because the repairing expenses of deteriorated structures are almost equal to the cost of construction of new ones, but also *industrial, **environmental** and social problems* due to decrease of reliability and safety (see Fig. 2.1). **Service life and durability are strongly related with the environmental footprint of constructions**. *It is obvious that a structure with a longer service life is less harmful to the environment during the phase of operation.*
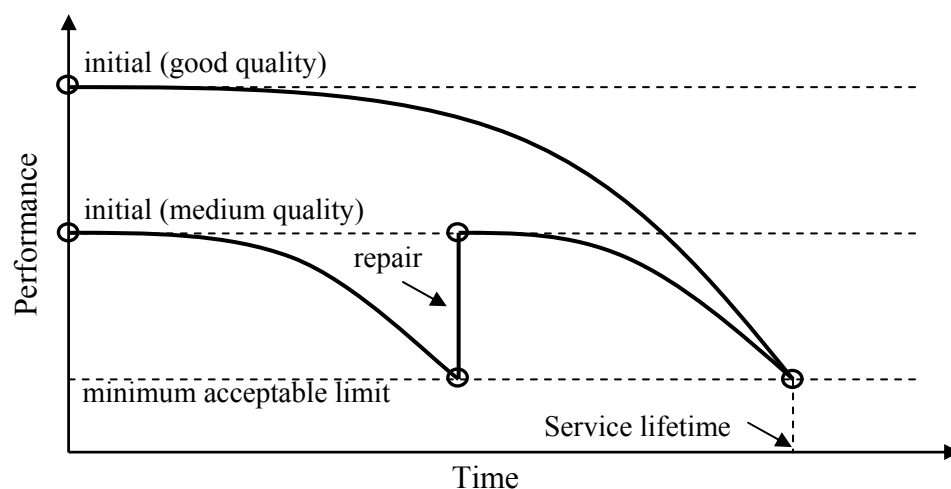
Figure 2.1   Relationship between concrete performance and service life (Papadakis 2005).

The type and rate of degradation processes for concrete and reinforcement determines the resistance and the rigidity of the materials, the sections and the elements making up the structure. This reflects in the *safety*, the *serviceability* and the *appearance* of a structure, i.e., determines the **performance of the structure**. **Concrete working life or service lifetime** is the period of time during which the performance of the concrete structure will be kept at a level compatible with the fulfilment of the performance requirements of the structure, provided it is properly maintained. As observed in Fig. 2.1, this service life may be achieved either due to initial good quality, or due to repeated repair of a not so good structure. The modeling of the deterioration mechanisms and the quantitative approach of the service life is the main objective of the present chapter.

As **durability** of a structure is called the ability to resist against environmental attacks without its performance to drop below a minimum acceptable limit. Three following main factors define the concrete durability: the *initial mix design* (quality and relevant quantity of the concrete constituents), *structure* design, construction and maintenance, and the specific *environmental conditions*.

Deterioration of building materials in service is every loss of performance, and it may be the result of a variety *of mechanical, physical, chemical or biological processes*. Concrete (and cement products in general) is also susceptible to all these types of deterioration (CEB 1989, Mehta 1997, Neville 1995, Illston and Domone 2001, Richardson 2002). The final result of these mechanisms is mainly *cracking*. Cracking will occur whenever the tensile strain to which concrete is subjected exceeds the tensile strain capacity of the concrete.

As <u>mechanical processes</u> causing cracking can be considered the direct loading and the imposed deformations:

- Cracking caused by *direct loading* is the result of normal load effects (i.e., bending, shear, tension, etc.) applied to sections.
- As *imposed deformations* causing cracking can be considered differential settlement of foundations, earthquakes and other natural catastrophes.
- A mechanical process causing deterioration of the surface is the *erosion either by abrasion or cavitation.*

Concrete cracking due to the reinforcement corrosion (and creation of internal expansion tensions) will be included in the chemical processes, because these are responsible for the corrosion.

As <u>physical processes</u> causing cracking can be considered the plastic shrinkage, the plastic settlement, the temperature differences, the shrinkage, and the frost action:

- *Plastic shrinkage* is caused by capillary tension in pore water when the water loss by vaporization exceeds the supply by bleeding water (mainly map surface cracking).

- If *settlement* of concrete is hampered by the reinforcement or by the formwork, cracking can, also, occur (longitudinal cracks).

- One of the major causes of cracking is movement resulting from the cooling of members from the *temperatures* generated by hydration of cement during a specific use of concrete.

- *Shrinkage* is the load independent, long-term deformation of concrete because of its decrease in volume due to drying.

- In the case of *water freezing* in concrete, the following physical processes are of major importance: Transition from water to ice involves an increase in volume by 9% and the freezing point is depressed as the pore diameter decreases. In the case of completely water-filled pores such expansion will cause splitting of concrete. Owing to this fact, a sufficient quantity of pores not filled with water shall be available.

The *chemical processes* causing concrete deterioration can be divided into two categories according to the medium they influence: *concrete or reinforcement*:

The first category includes the chemical attack *of aggressive substances* (ions and molecules) on concrete. A precondition for chemical reactions to take place within the concrete is the presence of water in some form (liquid, vapor). In general, the reactions between the aggressive substance (present in the concrete or transported from the environment) and the reactive substance of the concrete take place as they meet each other. However, often because of the low rate of transport of these substances, these reactions may take many years to show their detrimental effect. For practice, the most important chemical attacks on concrete are the acid, the sulphate and the alkali attack:

- The *action of acids* (as well ammonium salts, magnesium salts, and soft water) on the hardened concrete is practically a conversion of all the calcium compounds to the calcium salts of the attacking acid. These salts are very soluble and can be removed by dissolution or abrasion destroying the binding capacity of the cement.

- *Sulphate attack* on concrete is the reaction of sulphate ions with the aluminate phase of the cement, which causes expansion of the concrete, leading to cracking and disintegration.

- In the case of the *alkali attack*, alkalis from the cement present in the pore solution can react with silica containing aggregates resulting in the formation of alkali-silica gel (alkali-aggregate reaction). This may lead to destructive expansion if enough water is present, starting with small surface cracks and followed eventually by complete disintegration.

Reinforcing bars in concrete are protected from corrosion by a thin oxide layer that is formed on their surface due to high alkalinity, i.e., the high pH-value, of the surrounding concrete. *Corrosion* may start when this protective layer is destroyed:

- either by *chloride penetration* (and the chloride content exceeds a critical value),
- or due to a reduction in the pH value of concrete to values below 9. Such a reduction in alkalinity is the result of *carbonation* of the $Ca(OH)_2$ in the concrete mass, i.e., of its reaction with the atmospheric CO_2 that diffuses through the concrete pores.

In marine or coastal environments, and when deicing salts come in contact with the concrete surface, chloride penetration is the main mechanism that paves the way to initiation of reinforcement corrosion. In all other cases, and especially in CO_2-rich urban and industrial areas, carbonation of concrete is the main mechanism leading to steel corrosion. Furthermore, the two mechanisms are synergetic, i.e., chloride action is accelerated by carbonation. However, corrosion of the reinforcement is possible, *if sufficient moisture and oxygen are available*.

Finally, many <u>*biological processes*</u>, such as *growth* on concrete structures may lead to mechanical deterioration caused by lichen, moss, algae and roots of plants:

- *Microgrowth* may cause chemical attacks by developing humic acid, which dissolves the cement paste.
- In practice, the most important type of biological attack occurs in sewer systems, where *hydrogen sulfide* (formed during anaerobic conditions) may be oxidized by bacteriological action to form sulfuric acid, thus resulting in an acid attack on concrete.

Fig. 2.2 summarises various possible causes of concrete deterioration and gives some indication of the age at which the various forms of cracking can be expected to occur.

Nowadays, an issue of importance is the durability design of reinforced concrete structures with a minimum service life of at least 50 years. However, a great number of concrete structures especially in coastal and urban areas begin to deteriorate in 20 to 30 years or even less time. This fact has serious economic impacts, as the repair of structures demands large financial amounts. Freyermuth (2001) has emphasized on these matters and suggested a service life time of 100 to 120 years for future structures. For the assessment of durability two basic indicators are used: in order to evaluate the carbonation exposure, carbon dioxide penetration front is calculated, while for chloride ingress, the adequate concrete cover needed to sustain that ingress for a period of also 50 years is estimated.

MECHANICAL		direct loading				
		imposed deformations				
PHYSICAL	plastic shrinkage					
	plastic settlement					
		temperature differences				
			shrinkage			
		early	frost action		late	
CHEMICAL						acid, sulfate, alkali attack
						reinforcement corrosion
BIOLOGICAL						micro-growth
						H$_2$S attack
HOUR		*DAY*	*WEEK*	*MONTH*	*YEAR*	*CENTURY*

Figure 2.2 Deterioration mechanisms and possible time of appearance of cracking or damage (Papadakis 2005).

During the past years, a lot of experimental work has been conducted in this scientific field since durability is considered as one of the most serious issues that concern engineers all over the world. Nowadays, there is an increasing awareness of the durability problems that appear in many concrete structures. In spite of significant advances made in concrete technology in recent years, the problems of unsatisfactory durability of structures are still among the serious issues concerning the international community of engineers today. *Corrosion of steel reinforcement is the most serious durability problem of reinforced concrete structures.* It impairs not only the appearance of the structure, but also its strength and safety, due to the reduction in the cross-sectional area of the reinforcement, the deterioration of bond with the surrounding concrete, and the significant reduction of the steel ductility properties (Richardson 2002, Apostolopoulos and Papadakis 2008, Apostolopoulos *et al.* 2013).

Over the past decades, an enormous amount of energy has been expended in laboratory and field studies on concrete durability. The results of this research are still either scattered widely in the journal literature or mentioned briefly in popular textbooks; having although partially been included in the

relevant industry consensus documents as well as in the relevant codes for construction. Moreover, the theoretical approaches of deterioration mechanisms with a predictive character are limited to some complicated mathematical models not widely applicable in practice. A significant step forward could be the development of appropriate software for computer estimation, including reliable mathematical models and strengthened by adequate supporting experimental data. Durability design should get as much attention as structural design since it has to quantify the anticipated functional lifespan. There is opportunity for both simulation computer-aided modelling as well as full-scale engineering corroboration both in the laboratory and in the field.

In the present Chapter, the basis of the development of a computer estimation of the concrete service life is presented. After the definition of concrete mix design and structure characteristics, as well as the consideration regarding the environmental conditions where the structure will be found, the concrete service life can be reliably predicted using fundamental mathematical models that simulate the deterioration mechanisms. The prediction is focused on the basic deterioration phenomena of reinforced concrete, such as carbonation and chloride penetration. Basic principles of chemical and material engineering are applied to simulate the physicochemical processes, yielding simple and accurate mathematical models for design and prediction. Aspects on concrete strength and the production cost are also considered. Field observations and data collection from existing structures are compared with predictions of service life using the above model. A first attempt to develop a database of service lives of different types of reinforced concrete structure exposed to varying environments is finally included. The work approach presented herein is in full compliance with the European Standards; for cement: EN 197 and concrete: EN 206; however, after a short modification it can be applied to any other standard.

On the European Standard for concrete, EN 206 durability is approached by the definition of limiting parameters on cement and concrete composition (water-to-cement ratio, cement content, etc.), as well as by the development of *performance-related methods (PRMs)*. Such a method (*PRM*) is necessary when a service life significantly higher of 50 years is required, or when the environmental actions are particularly aggressive. A *PRM* considers each relevant deterioration mechanism, in addition to the service life of the structure, and the criteria which define the end of this service life, in a quantitative way. It can be based on data derived from established performance test methods for each relevant mechanism, or on the use of proven predictive models. Considering that in reinforced concrete the most serious deterioration mechanisms are those leading to reinforcement corrosion, it is therefore necessary, if a long service life is required, the modeling attempts to focus on these types of mechanisms/chemical attack processes. Bearing all of the above in mind, a significant step forward could be the development of appropriate software for the estimation of concrete service life, using reliable mathematical proven models, based on performance-related methods.

In this chapter, a deterministic simulation tool in full compliance with the European Standards for cement and concrete, based on proven predictive models developed by Papadakis *et al*, for estimation of concrete service life and strength is briefly presented. Emphasis is given on the concept of service life estimation and on tool validation and utilisation schemes. Based on this software tool (EUCON), an environmental assessment of the concrete production is performed and use is possible offering significant input for a life cycle analysis.

2.2   Concrete durability and the EN 206 approach

The European Standard EN 206 specifies requirements for the constituent materials of concrete, the properties of fresh and hardened concrete and their verification, the limitations for concrete composition, the specification of concrete, the delivery of fresh concrete, the production control procedure, the conformity criteria, and evaluation of conformity. It defines tasks for the specifier, producer, and user. During its development, consideration was given to detailing a performance-related approach to the specification of durability, but it was concluded that test methods to specify durability are not yet sufficiently developed to include them in the standard. However, this standard permits the continuation and development of performance-related methods for assessing durability, as does the present chapter.

According to EN 206, environmental actions are those chemical and physical actions to which the concrete is exposed and that result in effects on the concrete or reinforcement or embedded metal that are not considered as loads in structural design. The main deterioration actions considered are corrosion of reinforcement induced either by carbonation or chlorides, cyclic freezing and thawing, and chemical attack. The environmental actions are classified in exposure classes; their selection depends on the provisions valid where concrete will be used. Durability is then specified either through the traditional practice of limiting values of concrete composition (more widely used) or by performance-related methods. The requirements shall take into account the intended service life of the concrete structure.

2.2.1   Limiting values for concrete composition

In the absence of European standards for absolute performance testing of concrete, requirements for the method of specification to resist environmental actions are given in EN 206 in terms of established concrete properties and limiting values for concrete composition. The requirements for each exposure class shall be specified in terms of permitted types and classes of constituent materials, maximum

water-cement ratio, minimum cement content, minimum concrete compressive strength class (optional), and, if relevant, minimum air-content of the concrete.

Due to lack of experience on how the classification of the environmental actions on concrete reflect local differences in the same nominal exposure class, the specific values of these requirements for the applicable exposure classes are given in the provisions valid in the place of use. A recommendation for the choice of limiting values for concrete composition and properties is given in Annex F (informative) of EN 206. These values are based on the assumption of an intended service life of the structure of 50 years, and refer to the use of cement type CEM I conforming to EN 197.

2.2.2   Performance-related design methods

The requirements related to exposure classes may be established by using performance-related methods for durability and may be specified in terms of performance-related parameters, e.g., scaling of concrete in a freeze/thaw test. Guidance on the use of an alternative performance-related design method with respect to durability is given in Annex J (informative) of EN 206. The application of an alternative method depends on the provisions valid in the place of use of the concrete.

The performance-related method considers each relevant deterioration mechanism, the service life of the element or structure, and the criteria which define the end of this service life, in a quantitative way. Such a method may be based on satisfactory experience with local practices in local environments, on data from an established performance test method for the relevant mechanism, or on the use of proven predictive models.

A general guidance and some applications are given:

➢   Some aggressive actions are best dealt with a prescriptive approach, e.g., alkali-silica reaction, sulphate attack, or abrasion.
➢   Performance-related design methods are more relevant to corrosion resistance and possibly, freeze-thaw resistance of concrete. This approach may be appropriate where:

  -   a service life significantly differing from 50 years is required;
  -   the structure is "special" requiring a lower probability failure;
  -   the environmental actions are particularly aggressive, or are well defined;
  -   standards of workmanship are expected to be high;
  -   a management and maintenance strategy is to be introduced, perhaps with planned upgrading;

- significant populations or similar structures, or elements, are to be built;
- new or different constituent materials are to be used;
- method based on limiting values for concrete composition has been used in design, but there has been a failure to conform.

➢ In practice, the level of durability achieved depends on a combination of design, materials, and execution.

➢ The sensitivity of the design concept, the structural system, the shape of members and structural/ architectural detailing are all significant design parameters for all methods of durability design.

➢ Compatibility of materials, the construction method, the quality of workmanship, levels of control and quality assurance are significant parameters for all methods of durability design.

➢ The required durability performance depends on the required service life, on the possible future use of the structure, on the particular protective measures, on the planned maintenance in service, and on the consequences of failure, in the particular local environment.

➢ For any required level of performance, it is possible to derive alternative equivalent solutions from different combinations of design, material and construction factors.

➢ The level of knowledge of the ambient and local micro-climate is important in establishing the reliability of performance-related design methods.

The performance-related methods that may be used include:

✓ The refinement of the method of limiting values for concrete composition, based on long-term experience of local materials and practices, and on detailed knowledge of the local environment.

✓ Methods based on approved and proven tests that are representative of actual conditions and have approved performance criteria.

✓ Methods based on analytical models that have been calibrated against test data representative of actual conditions in practice.

The orientation of the present work included in this chapter is towards the development of performance-related methods based on predictive models that have been calibrated against test data representative of actual conditions in practice.

First, however, basic information on concrete mix design as well on physicochemical characteristics of concrete constituents will be given.

2.3   Concrete mix design

2.3.1   Constituent materials for concrete composition

Concrete is the material formed by mixing cement, aggregates and water, with or without the incorporation of admixtures and additions, which develops its properties by hydration of the cement. The general concept for concrete mix design as presented herein is in full compliance with the most spread existing standards for concrete production, such as the *European Standard for concrete: EN 206*. For the present application, a concrete volume is assumed that contains certain amounts of **cement, additions (optional), aggregates, water, and admixtures (optional)** *only*, see Fig. 2.3. To the above materials **entrained or entrapped air** should be added.

All these materials have to comply with the corresponding standards for the constituent materials, for instance in the case of European Standards: EN 197 (Cement), EN 450 (Fly ash for concrete), EN 13263 (Silica fume for concrete), EN 12620 (Aggregates for concrete), EN 1008 (Mixing water for concrete), EN 934-2 (Admixtures for concrete), etc.

CONCRETE :

Cement:	main constituents: portland clinker, blast furnace slag, silica fume, pozzolanic materials (natural or natural calcined pozzolanas), fly ash (siliceous or calcareous), burnt shale, and limestone
	minor additional constituents: all main constituents except clinker
	calcium sulphate, additives

+

Additions:	type I (filler aggregate, pigments), type II (fly ash, silica fume)

+

Aggregates:	fine, coarse

+

Water:	mixing water

+

Admixtures:	retarder, accelerator, air-entraining, plasticizer, superplasticizer, etc.

+

Air:	entrained, entrapped

Figure 2.3   Constituent materials for concrete composition (European Standard EN 206-1, 2000).

a. **Cement**

Cement is a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste that sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water. General suitability for concrete production is established for cement conforming to EN 197-1. Cement conforming to this European Standard, termed CEM cement, shall, when appropriately batched and mixed with aggregate and water, be capable of producing concrete or mortar which retains its workability for a sufficient time and shall after defined periods attain specified strength levels and also possesses long-term volume stability.

Hydraulic hardening of CEM cement is primarily due to the hydration of calcium silicates but other chemical compounds may also participate in the hardening process, e.g., aluminates. The sum of the proportions of reactive calcium oxide (CaO) and reactive silicon dioxide (SiO_2) in CEM cement shall be at least 50% by mass when proportions are determined in accordance with EN 196. CEM cements consist of different materials that are statistically homogeneous in composition resulting from quality assured production and material handling processes. According to this standard, a cement may comprise of ***main constituents, minor additional constituents, calcium sulphate and additives,*** see Table 2.1.

A ***main constituent*** is a specially selected inorganic material in a proportion exceeding 5% by mass related to the sum of all main and minor additional constituents. As main constituents the following are used: portland cement clinker, blast furnace slag, silica fume, pozzolanic materials (natural or natural calcined pozzolanas), fly ashes (siliceous or calcareous), burnt shale, and limestone. *Portland cement clinker* is the main constituent that all cement types contain (CEM I to CEM V). It is made by sintering a precisely specified mixture of raw materials (raw mill, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. It is a hydraulic material which shall consist of at least 2/3 by mass of calcium silicates ($3CaO. SiO_2$ and $2CaO. SiO_2$), the remainder consisting of aluminium and iron containing clinker phases and other compounds. The ratio by mass CaO/SiO_2 shall be not less than 2.0. The content of magnesium oxide (MgO) shall not exceed 5.0% by mass.

All other main constituents (except clinker), defined only in the present work as *supplementary* *cementing materials (SCM),* may be divided into *natural materials* and *artificial* ones. To the former natural pozzolanic materials and limestone belong. To the second category granulated blast furnace slag, silica fume, calcined pozzolanas, fly ashes, and burnt shale belong. In EN 197 these materials are defined as follows:

Table 2.1   Types of common cements according to European Standard EN 197-1*.

Main types	Nota-tion	Main constituents**									Minor addit. const.
		K	S	D	P	Q	V	W	T	L/LL	
PORTLAND CEMENTS											
CEM I	I	95-100	-	-	-	-	-	-	-	-	0-5
PORTLAND-COMPOSITE CEMENTS											
CEM II	II/A-S	80-94	6-20	-	-	-	-	-	-	-	0-5
	II/B-S	65-79	21-35	-	-	-	-	-	-	-	0-5
	II/A-D	90-94	-	6-10	-	-	-	-	-	-	0-5
	II/A-P	80-94	-	-	6-20	-	-	-	-	-	0-5
	II/B-P	65-79	-	-	21-35	-	-	-	-	-	0-5
	II/A-Q	80-94	-	-	-	6-20	-	-	-	-	0-5
	II/B-Q	65-79	-	-	-	21-35	-	-	-	-	0-5
	II/A-V	80-94	-	-	-	-	6-20	-	-	-	0-5
	II/B-V	65-79	-	-	-	-	21-35	-	-	-	0-5
	II/A-W	80-94	-	-	-	-	-	6-20	-	-	0-5
	II/B-W	65-79	-	-	-	-	-	21-35	-	-	0-5
	II/A-T	80-94	-	-	-	-	-	-	6-20	-	0-5
	II/B-T	65-79	-	-	-	-	-	-	21-35	-	0-5
	II/A-L	80-94	-	-	-	-	-	-	-	6-20	0-5
	II/B-L	65-79	-	-	-	-	-	-	-	21-35	0-5
	II/A-M	80-94			6-20						0-5
	II/B-M	65-79			21-35						0-5
BLASTFURNACE CEMENTS											
CEM III	III/A	35-64	36-65	-	-	-	-	-	-	-	0-5
	III/B	20-34	66-80	-	-	-	-	-	-	-	0-5
	III/C	5-19	81-95	-	-	-	-	-	-	-	0-5
POZZOLANIC CEMENTS											
CEM IV	IV/A	65-89	-		11-35			-	-	0-5	
	IV/B	45-64	-		36-55			-	-	0-5	
COMPOSITE CEMENTS											
CEM V	V/A	40-64	18-30	-	18-30		-	-	-	0-5	
	V/B	20-38	31-50	-	31-50		-	-	-	0-5	

*   The composition is expressed as % by mass of the main and minor additional constituents.

** Notation **exclusively** for the present table: portland clinker (K), blast furnace slag (S), silica fume (D), pozzolana (natural, P or natural calcined, Q), various fly ashes (siliceous, V or calcareous, W), burnt shale (T), and limestone (L or LL).

Granulated *blast furnace slag* is made by rapid cooling of a slag melt of suitable composition, as obtained by smelting iron ore in a blast furnace slag and contains at least 2/3 by mass of glassy slag and possesses hydraulic properties when suitably activated. It shall consist of at least 2/3 of the sum of $(CaO+MgO+SiO_2)$, the remainder contains Al_2O_3 together with small amounts of other compounds. The ratio by mass of $(CaO+MgO)/(SiO_2)$ shall exceed 1.0.

Silica fume originates from the reduction of high purity quartz with coal in electric arc furnaces in the production of silicon or ferrosilicon alloys and consists of very fine spherical particles containing at least 85% by mass amorphous SiO_2.

In EN 197, *pozzolanic materials* are defined as the *natural substances* of siliceous or silico-aluminous composition or a combination thereof (in general, however, pozzolanic materials are also fly ash and silica fume). Pozzolanic materials do not harden in themselves when mixed with water but, when finely ground and in the presence of water, they react at normal ambient temperature with dissolved calcium hydroxide, $Ca(OH)_2$, to form strength-developing calcium silicate and calcium aluminate compounds. These compounds are similar to those which are formed in the hardening of hydraulic materials. They consist essentially of reactive SiO_2 (>25.0 % by mass) and Al_2O_3, the remainder contains Fe_2O_3 and other oxides. These materials may be *natural pozzolanas* (materials of volcanic origin or sedimentary rocks) or *natural calcined pozzolanas* (materials of volcanic origin, clays, shales or sedimentary rocks, activated by thermal treatment).

Fly ash is the combustion residue (coal mineral impurities) in coal-burning electric power plants, which flies out with the flue gas stream and is removed by electrostatic or mechanical precipitation. Ash obtained by other methods shall not be used in cement that conforms the EN 197-1. Fly ash may be siliceous or calcareous in nature. The former has pozzolanic properties; the latter may have, in addition, hydraulic properties. *Siliceous fly ash* is a fine powder of mostly spherical particles having pozzolanic properties. It consists essentially of reactive SiO_2 and Al_2O_3, the remainder contains Fe_2O_3 and other compounds. The proportion of reactive CaO shall be less than 10.0% by mass and the content of free CaO shall not exceed 1.0% by mass. The reactive SiO_2 content shall not be less than 25.0% by mass. *Calcareous fly ash* is a fine powder having hydraulic and/or pozzolanic properties. It consists essentially of reactive CaO, reactive SiO_2 and Al_2O_3, the remainder contains Fe_2O_3 and other compounds. The proportion of reactive CaO shall not be less than 10.0% by mass and the content of free CaO shall not exceed 1.0% by mass. The reactive SiO_2 content shall not be less than 25.0% by mass, if the reactive CaO is between 10-15% by mass; if the reactive CaO is greater than 15% by mass certain strength levels should be required.

Burnt shale, specifically burnt oil shale, is produced in a special kiln at temperatures of approximately 800 $^{\circ}$C. Owing to the composition of the natural material and the production process, burnt shale contains clinker phases, mainly dicalcium silicate and monocalcium silicate. It also contains, besides small amounts of free calcium oxides and calcium sulphate, larger proportions of pozzolanically reacting oxides, especially SiO_2. Consequently, in a finely ground state burnt shale shows pronounced hydraulic properties like Portland cement and in addition pozzolanic properties.

Limestone shall meet the following requirements: The $CaCO_3$ content shall be at least 75% by mass, the clay content shall not exceed 1.20% by mass, and the total organic carbon content shall conform to one of the following criteria, LL: shall not exceed 0.20% by mass, L: shall not exceed 0.50% by mass

In general, but not accepted in EN 197, to the above SCM may be added slags from metallurgical furnaces producing steel, copper, nickel and lead, bottom ashes, ashes from incinerators and waste treatment sludge, metakaolin, red mud from alumina production, etc. These materials may, in some future revised edition of the standards, be included as cement constituents. However, either experimentally or at industrial scale all the above additions are extensively used the recent years especially as ingredients in blended cements and at a lower degree as separately batched constituents in concrete. *Almost only silica fume and siliceous fly ash are used as separately additions in concrete (see below: concrete additions).* However, for all these materials, whatever is their origin in concrete, besides the effect on usual structural properties, such as strength and volume stability, *the concrete durability should seriously be considered.*

A **minor additional constituent (mac)** is a specially selected inorganic material used in a proportion not exceeding 5% by mass related to the sum of all main and minor additional constituents. As minor additional constituents can be used inorganic natural materials, inorganic mineral materials derived from the clinker production process or main constituents as specified earlier unless they are included as main constituents in the cement. Inert materials, such as limestone and dust derived from the clinker production process (materials known as fillers) are usually used. Thus, mac affects only the physical properties of concrete, such as workability and water retention. However, they shall not increase the water demand of the concrete appreciably, impair the resistance to deterioration or reduce the corrosion protection of the reinforcement.

Calcium sulphate (between 3 % and usually 5% by weight of cement) in the form of gypsum or anhydrite is added to the above constituents to control the clinker flash setting.

Various ***additives*** may also be added (up to 1% by weight of cement) to improve either the cement production or cement properties. They shall not promote the corrosion of the reinforcement or impair the properties of cement, mortar or concrete.

Regarding ***durability requirements*** it is stated that, in many applications, particularly in severe environmental conditions, the choice of cement has an influence on the durability of concrete, mortar and grouts, e.g., frost resistance, chemical resistance and protection of the reinforcement. The choice of cement, particularly as regards type and strength class for different applications and exposure classes shall follow the appropriate standards and/or regulations for concrete or mortar valid in the place of use.

b. Additions

Addition is a finely divided material used in concrete in order to improve certain properties or to achieve special properties. The EN 206 deals with two types of inorganic additions:

- *nearly inert additions (**type I**)*
- *pozzolanic or latent hydraulic additions (**type II**)*

General suitability as type I addition is established for *filler aggregate* conforming to EN 12620 and *pigments* conforming to EN 12878. General suitability as type II addition is established for ***fly ash*** conforming to EN 450 and ***silica fume*** conforming to EN 13263. However, EN 206 notes that certain constituents no conforming to some European Standard may be used in concrete; the establishment of suitability may result from: a European Technical Approval, or a relevant national standard or provisions. In general, type II additions may by all the above called supplementary cementing materials (SCM).

c. Aggregates

Aggregate is a granular mineral material suitable for use in concrete. Aggregates may be natural (natural collected or just natural, and natural crushed), artificial or recycled from material previously used in construction. General suitability is established for:

- *normal and heavy-weight aggregates* conforming to EN 12620. Normal-weight aggregate has an oven-dry particle density between 2000 – 3000 kg/m^3, when determined according to EN 1097-6. Heavy-weight aggregate has an oven-dry particle density $\geq$ 3000 kg/m^3, when determined according to EN 1097-6.

- *light-weight aggregates* conforming to EN 13055-1. Light-weight aggregate of mineral origin has an oven-dry particle density ≤ 2000 kg/m^3 when determined according to EN 1097-6 or a loose oven-dry bulk density ≤ 1200 kg/m^3 when determined according to EN 1097-3.

Aggregate type, grading and categories, e.g., flakiness, freeze/thaw resistance, abrasion resistance, fines, **shall be selected** taking into account the execution of the work, the end use of the concrete, the environmental conditions and any requirements for exposed aggregate. The *maximum nominal upper aggregate size* (D_{max}) shall be selected taking into account the concrete cover to reinforcement and the minimum section width. When aggregates contain varieties of silica susceptible to attack by alkalies (Na_2O and K_2O originating from cement or other sources) and the concrete is exposed to humid conditions, actions shall be taken to prevent deleterious alkali – silica reaction using procedures of established suitability.

c. Water

Suitability is established for **mixing water** and for recycled water from concrete production conforming to EN 1008. *Total water content* is the added water plus water already contained in the aggregates and on the surface of aggregates plus water in the admixtures and in additions used in the form of a slurry and water resulting from any added ice or steam heating. *Effective water content* is the difference between total water present in the fresh concrete and the water absorbed by the aggregates.

d. Admixtures

Admixture is a material (usually organic) added during the mixing process of concrete in small quantities related to the mass of cement to modify the properties of fresh or hardened concrete. General suitability is established for admixtures conforming to EN 934-2.

In general, the admixtures for concrete can be divided into:
- admixtures modifying set and hardening:
  - accelerators
  - retarders
- admixtures modifying the mix rheology and the air content:
  - water-reducing admixtures (superplasticizers, plasticizers)
  - water-retaining admixtures
  - thickening admixtures
- admixtures entraining air into the mixes:
  - air-entraining and air-detraining admixtures

- gas-forming admixtures
- foam-forming admixtures

- admixtures modifying the resistance to physical and chemical actions:
    - frost-resisting and anti-freezing admixtures
    - water-repelling admixtures
    - permeability-reducing admixtures
    - corrosion-inhibiting admixtures
    - improving resistance to chemical actions

However, the most largely used products are *retarders* (0.2-0.4% by mass of cement), *accelerators* (0.5-6% by mass of cement), *air-entraining admixtures* (0.05-0.2% by mass of cement), *plasticizers* (0.3-0.5% by mass of cementitious materials), and *superplasticizers* (0.8-1.5% by mass of cementitious materials). These representative dosages refer to the total solution of admixtures (as supplied: solids plus solvent water).

The total amount of admixtures, if any, shall not exceed the *maximum dosage* recommended by the admixture producer and not exceed 50 g of admixture (as supplied) per kg cement unless the influence of the higher dosage on the performance and durability is established. If the total quantity of liquid admixtures exceeds 3 l/m^3 of concrete, its water content shall be taken into account when calculating the water/cement ratio.

e. *Entrained or entrapped air*

Entrained air are the microscopic air bubbles intentionally incorporated in concrete during mixing, usually by use of a surface active agent; typically between 10 – 300 μm in diameter and spherical or nearly so. *Entrapped air* is voids in concrete which are not purposely entrained.

2.3.2 Design strategy

The *concrete mixture composition* and the *constituent materials* for designed or prescribed concrete shall be chosen to satisfy the requirements specified for fresh and hardened concrete, including consistence, density, strength, durability, protection of embedded steel against corrosion, taking into account the production process and the intended method of execution of concrete works. As *designed concrete* called the concrete for which the required properties and additional characteristics are specified to the producer who is responsible for providing a concrete conforming to the required properties and additional characteristics. As *prescribed concrete* called the concrete for which the composition and the constituent materials to be used are specified to the producer who is responsible

for providing a concrete with the specified composition. Where not detailed in the specification, the producer shall select types and classes of constituent materials from those with established suitability for the specified environmental conditions.

In all specifications regarding concrete production, among the main design parameters are the *cement content (C)* and the *water-to-cement ratio (W/C)*. Thus, minimum values of cement content and maximum values of W/C ratio are specified according to the *aggressiveness class* of the surrounding environment. Despite the exposure classes, in all cases, the *total equivalent cement content* should be taken into account.

After having specified the *fresh concrete composition (mix design: cement C, silica fume S, fly ash F water W, aggregates A, admixtures D, and entrained or entrapped air ε_{air})* that fulfils the strength expectations and standard requirements (e.g., minimum C, maximum W/C ratio, etc.), the *concrete durability* should be examined. *Let us suppose that the **designed service life is Z years***. Thus, this specific concrete composition must be examined if it ensures service life greater than the designed one, as regards the possible deterioration environment in which the concrete will be exposed.

First the case of **concrete carbonation**, if any, must be taken into account. The **concrete cover, c,** must be higher than the expected carbonation depth within the lifetime Z. An accurate prediction of this carbonation depth can be obtained using the equations presented in the sequence. If an *unacceptable* (due to various technical or economic reasons) cover is predicted then either a different concrete composition (e.g., lower W/C ratio, higher cement content, etc.) or a protective coating application shall be proposed. Then the calculation must be repeated until satisfaction.

Having specified the concrete composition and cover as above, the case of **chloride penetration**, if any, must then be considered. The equations presented in the sequence have to be solved using the corresponding parameters, in order to predict the chloride profile into the concrete as a function of time. Using the Cl-profile at the time equal to Z, the *minimum concrete cover* can be found at which and onwards the chloride concentration takes lower values than the *critical threshold* for corrosion. If an unacceptable cover is predicted then again either a denser concrete composition or a coating application should be considered and the calculations are repeated.

If any other deterioration mechanism could take place, e.g., a specific **chemical attack**, it has to be considered in a similar way. Finally, the ***cost of concrete production*** has to be estimated.

For the initially selected concrete composition the most essential properties have been predicted, such as ***strength, service life and cost***. The *specifier* can then alter accordingly the concrete composition

and/or the protection measures to improve further every desired property. The design parameters that ensure *full protection* (the higher concrete cover and the denser concrete composition or the best protection measures) among them predicted for resistance against carbonation and chloride penetration, chemical attack, etc., at the lowest cost, *must be finally proposed.*

2.4   Concrete service life estimation tool

Many software tools have been developed for the estimation of service life and the computation of environmental cost in the construction sector. The combination of these models with new technologies can contribute in the establishment of sustainable building. One of these tools, the EUCON® software package, is a complete and comprehensive solution in calculating: (a) concrete mix design, (b) concrete service life under harsh environmental agents, (c) corrosion prevention measures. EUCON is a useful tool based on proven predictive models (according to performance-related methods for assessing durability), developed and validated by Papadakis *et al.* (2005, 2007, 2012, 2014), well published and awarded by the American Concrete Institute (ACI), for the estimation of concrete service life when designing for durability under harsh environments.

As shown in Fig. 2.2, all physical and mechanical mechanisms for concrete deterioration, except direct loading and imposed deformations, may exhibit their effect on concrete performance during the first year of the service life. Chemical and biological mechanisms actually start from the beginning; however, their detrimental results are observed typically long after the first year. In reinforced concrete, the most serious deterioration mechanisms are those leading to corrosion of the reinforcement, which occurs after depassivation due to carbon dioxide or chloride ion penetration. It is therefore necessary, if a long service life is required, that the modelling attempts to address corrosion initiation mechanisms and chemical/biological attack processes.

Fig. 2.4 shows the logic diagram followed in the software program development (EUCON) for the estimation of concrete service life. The underlined actions, connected with the **environmental cost**, have been developed under the present Thesis. First, the essential parameters that characterize a concrete composition (mixture proportions) are selected, and this is the main source on which all other concrete characteristics depend. Thereafter, the main chemical and volumetric characteristics of concrete are calculated (chemical composition of hydrated cementitious materials, porosity and related characteristics) and this is also another source to receive more information. Based on the selected mixture proportions (cement type and strength class, cement content, water-cement ratio, air content, aggregate type, type and activity of additions, etc.), the compressive strength class of concrete is estimated.

CONCRETE MIX DESIGN (according to EN 197, EN 206)		
INPUT	Cement Type	Selection between 27 cement types (EN-197) and of Standard Cement Strength Class. Composition in clinker, other main constituents, minor constituents, gypsum. Cement density and content
	Additions	Type I (filler aggregate and/or pigments), Type II (siliceous/calcareous fly ash, silica fume), additions density and content
	Admixtures	Type (retarder, accelerator, air-entraining, plasticizer, superplasticizer), density, solid content, dosage. Total admixture content
	Water	Water added, water from admixtures and aggregates, water density and content
	Aggregates	Aggregate type, aggregate density, maximum nominal aggregate size
	Air	Entrapped-air content, entrained-air content, total air content
OUTPUT	Aggregate content, fresh concrete density	

↓

CHEMICAL & VOLUMETRIC CHARACTERISTICS OF CONCRETE	
INPUT	Cement Composition, Oxide Analysis	Oxide analysis of clinker, oxide analysis and activity of other main constituents of cement, oxide analysis and activity of silica fume and fly ash
OUTPUT	Reaction degree of other main constituents of cement and concrete additions. Contents of calcium hydroxide, calcium silicate hydrate, chemically-bound water, porosity	

↓

ESTIMATION OF CONCRETE STRENGTH	ESTIMATION OF SERVICE LIFE WITH RESPECT TO CARBONATION	ESTIMATION OF SERVICE LIFE WITH RESPECT TO CHLO-RIDE PENETRATION	COST & ENVIRONMENTAL ASPECTS
INPUT	**INPUT**	**INPUT**	**INPUT**
All of the previous	All of the previous, plus environmental conditions • Exposure class • Relative humidity, • CO_2-content in air • Use of mortar or other coating (type, chemical analysis, width)	All of the previous, plus environmental conditions • Exposure class • Internal concentration of Cl^- • External source of Cl^- • Cl^- concentration at concrete surface • Degree of exposure • Relative humidity • Use of corrosion inhibitors, coatings, etc.	All of the previous, plus • **Financial input** purchase cost of materials, mixing, transport. and delivery cost • **Environ. input environmental impact from materials production**
OUTPUT	**OUTPUT**	**OUTPUT**	**OUTPUT**
• Mean compressive strength • Strength Class • Strength ratio 2/28 days • Strength Development	• corrosion-initiation period, • corrosion-propagation period, • total service life	• Adequate concrete cover needed to sustain a corrosion free structure, for a given service life • corrosion-initiation period	• Concrete production cost • **Environmental cost**

↕

TECHNICAL, ENVIRONMENTAL AND ECONOMICAL OPTIMIZATION
Mixture proportions optimization to achieve the specified strength and durability at the lowest cost.

Figure 2.4 Logic tree of software for estimation of concrete service life, strength, economical & environmental cost (underlined: developed in the present Thesis).

For each significant deterioration mechanism, according to the specific environment where the structure would be found, an appropriate proven predictive model is used. Concrete carbonation and chloride penetration are the most common causes for reinforcement corrosion onset, and for further concrete deterioration. The service life of the structure found in these environments, which cause either carbonation or chloride penetration, is calculated. The degree of deterioration from a possible chemical attack is also estimated, either as a reduction in the effective concrete section (in the case of acid or biological attack) or as a reduction in strength of the affected concrete (in the case of sulphate or alkali attack). Finally, cost and environmental aspects regarding concrete composition are analysed. Now, for the initially selected concrete composition, the most essential properties have been predicted, such as strength, service life and cost. The designer can then modify the concrete composition accordingly to improve further every required property.

Concrete service life is reliably predicted using fundamental mathematical models that simulate the basic deterioration mechanisms of reinforced concrete (carbonation, chloride penetration). Principles of chemical and material engineering have been applied to model the physicochemical processes leading to concrete carbonation, as well as the processes of chloride diffusion in the aqueous phase of pores, their absorption and binding in the solid phase of concrete and their desorption.

The procedure suggested in order to export the desired results is the following: First, the essential parameters that characterize a concrete composition (mix design) are selected. Thereafter, the main chemical and volumetric characteristics of concrete are calculated (chemical composition of hydrated cementitious materials, porosity and related characteristics).

Based on the selected mixture proportions the compressive strength class of concrete is estimated. For each significant deterioration mechanism, according to the specific environment where the structure would be found, an appropriate proven predictive model is used. The service life of the structure in these environments, which cause either carbonation or chloride penetration, is calculated. Finally, cost and environmental aspects regarding concrete composition are analyzed. The designer evaluates the values of predicted properties (strength, service life, cost) and modifies the initially selected concrete composition, if necessary, in order to improve one or more of these properties.

2.4.1   Modeling for carbonation exposure

In terms of carbonation exposure, a system of non-linear differential equations developed by Papadakis *et al.* models in a quantitative way the physicochemical processes leading to concrete carbonation. These include the diffusion of CO_2 in the gas-phase of pores, its dissolution in the aqueous film of these pores, the dissolution of solid $Ca(OH)_2$ in pore water, its ultimate reaction with

the dissolved CO_2 and the reaction of CO_2 with calcium silicate hydrate (CSH). The solution of the set of differential equations permits the calculation of the carbonation depth x_c, at a given time t, as well as the estimation of the critical time, $t_{cr,carb}$, required for the carbonation front to reach the reinforcement located at a distance c (concrete cover to reinforcement), for both Portland and blended cements, as well as when additions of supplementary cementing materials (SCM) are used separately in concrete, according to the following equation:

$$x_c = \sqrt{\frac{2D_{e,CO2}(CO_2/100)t}{0.33CH + 0.214CSH}} \ , \quad t_{cr,\,carb} = \frac{(0.33CH + 0.214CSH)c^2}{2D_{e,CO2}(CO_2/100)} \tag{2.1}$$

where, CO_2 is the CO_2-content in the ambient air at the concrete surface (%), CH and CSH are the contents of calcium hydroxide and calcium-silicate-hydrate in concrete volume (kg/m³), $D_{e,CO2}$ the effective diffusivity of CO_2 in carbonated concrete (m²/s), where in an ambient relative humidity, RH (%), is calculated as:

$$D_{e,CO2} = 6.1 \cdot 10^{-6} \left(\frac{\varepsilon_c - \varepsilon_{air}}{1 - \dfrac{A}{d_A} - \varepsilon_{air}} \right)^3 \left(1 - RH/100\right)^{2.2} \tag{2.2}$$

where, ε_c is the porosity of the carbonated concrete, ε_{air} the volume fraction of entrapped or entrained air in concrete (m³/m³), A the aggregate content in concrete volume (kg/m³) and d_A the aggregate density (kg/m³).

Once the carbonation front reaches the embedded bar, corrosion can take place with its known consequences, including concrete cracking. At that point it can be reasonably assumed that major repair will be necessary. Hence the appearance of generalized cracking may be considered to signal the end of the service life of the structure (Z_{carb}). Overall, the time required to crack the concrete cover can be expressed (see Fig. 2.5) as the time required for the carbonation front to reach the bar (initiation period of corrosion, $t_{cr,carb}$, estimated as mentioned above) plus the time necessary for the layer of rust to build up around the bar and split the cover (corrosion propagation period, $t_{pr,carb}$). However, in certain cases the corrosion rate in carbonated concrete at high relative humidity values can be of such magnitude, that the arrival of the carbonation front at the bar is followed shortly by splitting of the concrete cover. Therefore the time $t_{cr,carb}$ required for the carbonation front to penetrate the concrete cover c can be considered with good approximation as a narrow lower bound to the service life of reinforced concrete.
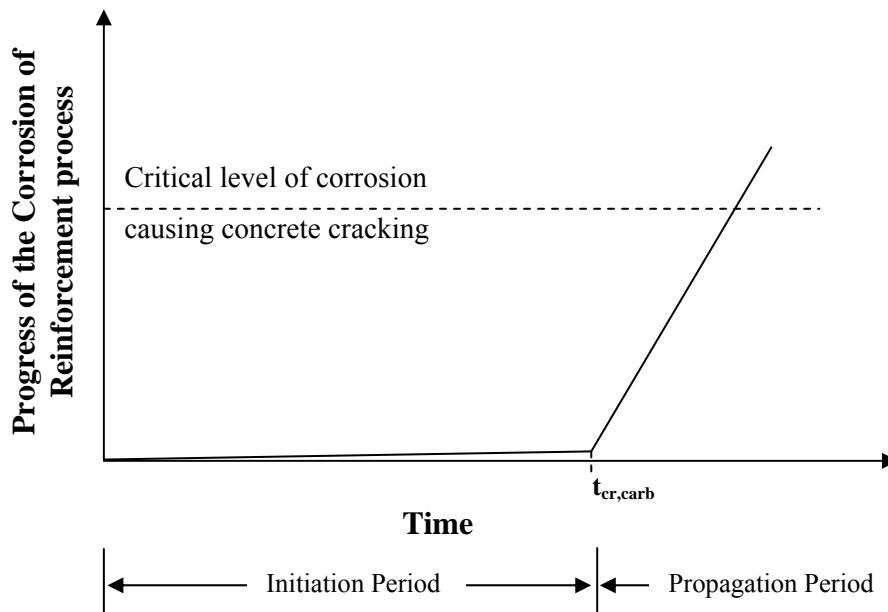
Figure 2.5   Schematic illustration of initiation and propagation periods of corrosion in a reinforced concrete element (Papadakis 2005).

If an approximation of the propagation period is required, then a model of the physicochemical processes of corrosion and cracking has to be applied. However, until now there is no a generally accepted fundamental model for corrosion propagation of the concrete reinforcement, attributed to the complex phenomena of corrosion as well to the definition of detectable effects that define the limit of an acceptable damage, such as the level of cracking.

An alternative approach would be to assume a zero propagation period ensuring at least the lower limit for service life. However, this assumption is not valid, especially for low relative humidity when the propagation period is much higher than the initiation period due to lack of moisture. As a general conclusion from various works (Morinaga 1991, Richardson 2002), the propagation period depends strongly on relative humidity. For example 70 % RH results in a propagation period almost double of the initiation period, while for 80 % RH the propagation period is about half of the initiation period and for 90 % RH, the propagation period is about 1/5 of the initiation period.

2.4.2 Modeling for chloride ingress

In many studies, chloride transport in concrete is modeled using Fick's second law of diffusion, neglecting the chloride interaction with the solid phase. However, the latter process is very important

including binding of chlorides by cement hydration products, ionic interaction, lagging motion of cations and formation of an electrical double layer on the solid surface, etc.

The physicochemical processes of chlorides (Cl⁻) diffusion in the aqueous phase, their adsorption and binding in the solid phase of concrete, and their desorption, are described by the non-linear partial differential Eq. (2.3) (Papadakis et al. 1996, 2000). Solution of Eq. (2.4), allows the calculation of the Cl⁻ bound in the solid phase [Cl⁻(s)].

$$\frac{\partial \left[Cl^-(aq) \right]}{\partial t} = \frac{D_{e,Cl^-}(1 + K_{eq}\left[Cl^-(aq) \right])^2}{K_{eq}\left[Cl^-(s) \right]_{sat} + \varepsilon(1 + K_{eq}\left[Cl^-(aq) \right])^2} \frac{\partial^2 \left[Cl^-(aq) \right]}{\partial x^2} \tag{2.3}$$

$$\left[Cl^-(s) \right] = \frac{K_{eq}\left[Cl^-(aq) \right]}{1 + K_{eq}\left[Cl^-(aq) \right]} \left[Cl^-(s) \right]_{sat} \tag{2.4}$$

initial condition: $[Cl^-(aq)] = [Cl^-(aq)]_{in}$ at t = 0   (initial concentration)

boundary conditions: $[Cl^-(aq)] = [Cl^-(aq)]_0$ at x = 0   (concrete surface),

$\partial[Cl^-(aq)] / \partial x = 0$ at x = M   (axis of symmetry)

where, x is the distance from the concrete surface (m), t is the time (s), K_{eq} the equilibrium constant for Cl⁻ binding (m³ of pore volume/kg), $[Cl^-(s)]_{sat}$ the saturation concentration of Cl⁻ in the solid phase (kg/m³ concrete), $[Cl^-(aq)]$ the concentration of Cl⁻ in the aqueous phase, D_{e,Cl^-} is the intrinsic effective diffusivity of Cl⁻ in concrete (m²/s), calculated as:

$$D_{e,Cl^-} = \frac{2.4 \cdot 10^{-10}}{\left(\dfrac{C + \sum (kP_{ACT})}{d_c} + \dfrac{W}{d_W} \right)^2} \left(\varepsilon_{eff} \right)^{3.5} \tag{2.5}$$

with ε_{eff} being the effective (for diffusion) concrete porosity (m³ pore volume/m³ concrete), calculated as:

$$\varepsilon_{eff} = W/d_W - 0.226 \cdot 10^{-3} \left\{ C + \sum (kP_{ACT}) \right\} \tag{2.6}$$

where, C cement content (kg cement / m³ of concrete), P_{ACT} the active content of each SCM added either as cement constituent or as concrete addition, having an efficiency factor k, and d_c, d_w, cement and water densities, respectively,

Furthermore, the solution of Eq. (2.3) allows the calculation of the adequate (minimum) concrete cover needed in order to sustain a chloride-induced corrosion free structure for a given service life, as well as the estimation of the time (critical time for chloride-induced corrosion, $t_{cr,chlor}$) required for the total chloride concentration surrounding the reinforcement (located at a distance c from surface) to increase over the threshold for depassivation. Afterwards, the propagation of corrosion process takes place at a rate that depends strongly on the availability of both oxygen and water. The service lifetime of a structure, regarding chloride penetration, can be considered to be at least $t_{cr,chlor}$.

In the case of a reinforced concrete (RC) structure where the concrete cover is not crack-free, the model can be adjusted accordingly. It is widely understood that cracks increase the transport properties of concrete, creating perfect pathways for gas and liquid transportation, thus, facilitating the ingress of deleterious species such as CO_2 or chlorides into concrete and accelerating the initiation time for the corrosion of the steel reinforcement. The estimation of the life span of reinforced concrete structures having cracks is influenced by characteristics, such as crack width and length, in addition to the concrete properties and the environmental exposure conditions. The models presented briefly in the current study to estimate the service life of reinforced concrete structures (as far as chloride ingress and the action of carbon dioxide from the atmosphere is concerned), take under consideration parameters influenced by the appearance of cracks on the concrete cover. Research has shown that the presence of cracks increases the diffusion coefficient of both chloride ions and carbon dioxide. A comparison of chloride diffusion coefficients for cracked and uncracked concrete showed an increase in the diffusion coefficient for cracked concrete by one or two orders of magnitude (Raharinaivo *et al.* 1986, Sahmaran *et al.* 2007), while a crack width of 0.2 mm was found to increase the carbon dioxide diffusion coefficient about three orders of magnitude compared to an average quality crack-free concrete (Alekseev and Rosenthal, 1976). In the model, by adjusting the values of the effective chloride and/or carbon dioxide diffusion coefficients and by taking under consideration the initial conditions (Cl⁻ concentration of the surface, environmental exposure, etc.), an initial profile corresponding to a cracked concrete surface is created, which will be used by the model as a starting point on the calculation of the service life estimation parameters.

2.4.3   Cost and environmental aspects

Cost and environmental aspects regarding concrete composition are also addressed. As it is the main aim of the current study to elaborate in detail on these features of the model especially the environmental aspects, for reasons of completeness a very brief introduction is given herein (please see more details in Chapter 3).

In terms of economic cost, the concrete production cost KT ($€/m^3$) is calculated (per volume unit of 1 m^3 of fresh concrete) by taking into account factors as materials purchasing cost (K_P, $€/m^3$), mixing cost for concrete production (K_M, $€/m^3$), cost of transportation and delivery (K_B, $€/m^3$), and other operational costs (K_G, $€/m^3$), as it shown in the following equation.

$$KT = K_p + K_M + K_B + K_G$$

$$= \left(CU_C + SU_S + FU_F + AU_A + WU_W + DU_D\right) + \left(P_M t_M U_E\right) + \left(K_T + \frac{P_B}{Q}U_E\right) + K_G \tag{2.7}$$

where, $U_{C,S,F,A,W,D}$, are the cement, silica fume, fly ash, aggregate, water, admixtures values ($€/kg$), C, S, F, A, W, D, are the cement, silica fume, fly ash, aggregate, water, admixtures content (kg/m^3 of concrete), P_M the mixing power / m^3 of concrete ($J/s.m^3$), U_E the cost of energy ($€/J$), t_M the mixing time (s), K_T the cost of transportation ($€/m^3$), P_B the pumping power (W), Q the concrete flow (m^3/s).

It should be noted that in the calculation of the concrete mixing cost, the parameters P_M and t_M depend on concrete workability and density and, therefore, on concrete composition parameters. The cost of transportation K_T depends on the distance between project location and plant, hence is independent of concrete compositional parameters. At the project location, the cost is burdened with pumping and application expenses. Fixed and operational costs include the fixed cost of purchase and establishment of equipment (depreciation values), labor and administration costs and general operational costs.

In terms of environmental cost (see Chapter 3), the CO_2 emissions from concrete production can be expressed as the summation of the emissions from, the chemical conversion process in clinker production (during cement manufacturing), from the energy consumption due to fossil fuel combustion (also during cement manufacturing), from the electrical energy required for the grinding of any additive materials and from the energy required (in terms of fuel consumption) for the transportation of the raw materials and of the final product. A more precise estimation of the environmental footprint of concrete E_{conc}, taking under consideration the environmental factors of each individual concrete component, based on a large set of concrete production data (from the literature and from cement production companies) can be expressed as:

$$E_{conc} = CE_c + SE_S + FE_F + AE_A + WE_W + DE_D \tag{2.8}$$

where,   C, S, F, A, W, D are the cement, silica fume, fly ash, aggregate, water and admixtures content (kg of material / m^3 of concrete), E_C, E_S, E_F, E_A, E_W, E_D, are the environmental costs of cement, silica fume, fly ash, aggregates, water and admixtures respectively (kg of CO_2 / kg of material).

The above approach introducing the **environmental cost** indicator is the contribution of the present Thesis in this prediction tool as well as the overall optimization process (see Chapter 3).

2.4.4   Validation and verification

Having presented the structure and the concept behind the modeling of the physicochemical processes leading to concrete deterioration, the results of a wide validation study (Papadakis and Demis 2011), in terms of carbonation exposure, are given in this section. A comparison between experimental measurements and model predictions of chloride concentration for various concrete specimens has been presented elsewhere (Papadakis 2000). Currently, an ongoing field study is taking place, for a thorough validation based on data derived from structures showing signs of chloride induced corrosion. In the case of carbonation exposure, such a study has been completed and the validation results are briefly presented bellow.

Carbonation depth results were collected from the recent published literature, under either accelerated conditioning or natural ageing, for different exposure times. Parameters as cement type, mix design characteristics, chemical composition of the clinker and pozzolanic materials, levels of relative humidity and carbon dioxide concentration (where the reinforced concrete element was exposed) were recorded and inserted into the model. The calculated carbonation depth values were compared with the corresponding values taken from the literature (see Fig. 2.6). A very good correlation was observed (an average variation of 7.6 % was calculated).
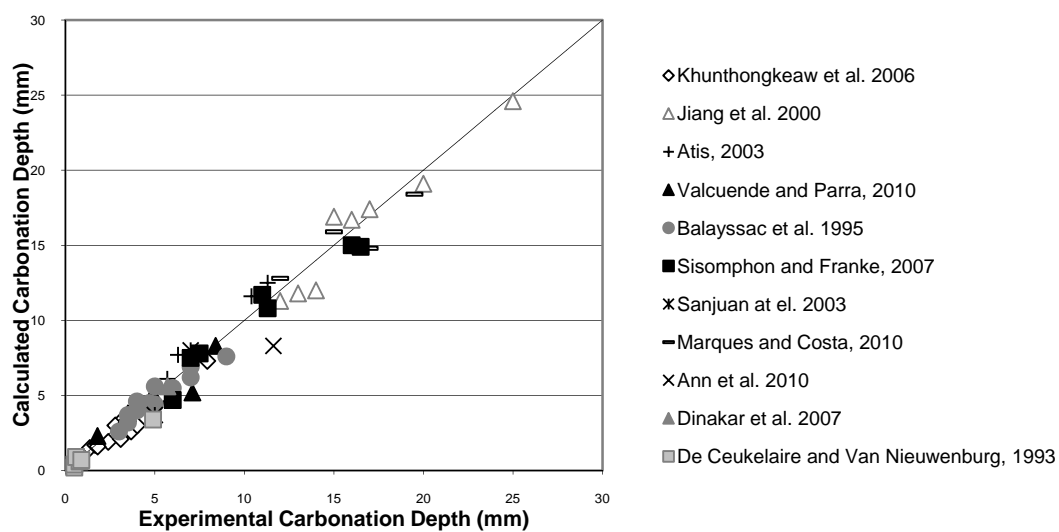
Figure 2.6 Comparison of calculated to experimental carbonation depth values (Papadakis and Demis 2011).
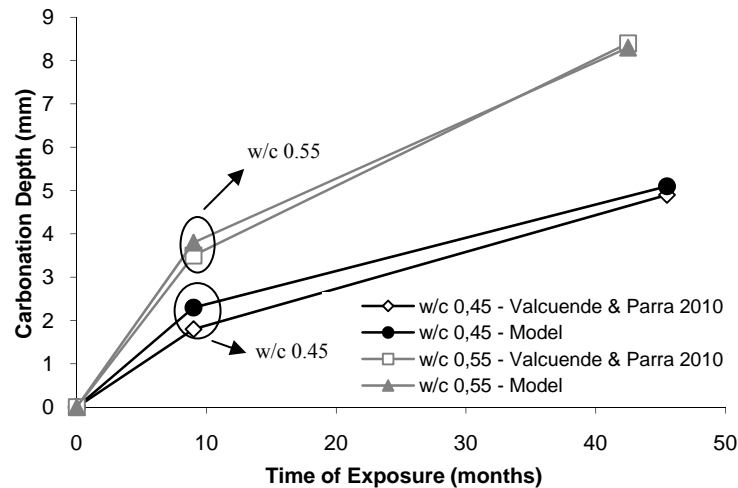
Figure 2.7 Calculated and experimental carbonation depth values for different W/C ratios of a CEM II/B-M type of cement (Papadakis and Demis 2011).

From the characteristic data given in Table 2.2 it can be seen that the model yields very accurate predictions for a range of both accelerated (up to 1 year) and natural exposure times (up to 18 years, where considering the experimental value of 11.62 mm with a standard deviation of 2.45, the 8.3 mm calculated is a very good approximation) and for different cement and concrete compositions. In Fig. 2.7, just as a representative example, an excellent agreement between calculated and experimental values is observed, for a longer natural exposure time (up to 4.5 years) and for different W/C ratios.

Table 2.2 Characteristic estimated and measured carbonation depth values (Papadakis and Demis 2011).

Reference	*Cement type*	*w/c*	*RH (%)*	*CO_2 (%)*	*Exp. X_c (mm)*	*Calc. X_c (mm)*	*Exposure Time*
Khunthongkeeaw et al. 2006	CEM I	0.67	72.5	0.0625	5.68	5.30	2 year
Sisomphon & Franke 2007	CEM I + fa	0.68	65.0	3	7.50	7.80	4 weeks [*]
Sisomphon & Franke 2007	CEM I + fa	0.68	65.0	3	11.0	11.7	9 weeks [*]
Ann et al. 2010	CEM I	0.45	60.0	0.08	11.62 (2.45)	8.30	18 years
Valcuente & Parra, 2010	CEM II/B-M	0.55	60.8	0.035	3.50	3.80	9 months
Valcuente & Parra, 2010	CEM II/B-M	0.55	60.8	0.035	8.40	8.30	42 months
Balayassac et al. 1995	CEM II/B-L	0.48	60.8	0.035	3.00	2.60	6 months
Balayassac et al. 1995	CEM II/B-L	0.48	60.8	0.035	3.50	3.70	12 months
Balayassac et al. 1995	CEM II/B-L	0.48	60.8	0.035	4.00	4.60	18 months
Marques and Costa, 2010	CEM II/A-L	0.60	65.0	5	15.0	15.9	42 days [*]
Dinakar et al. 2007	CEM II/A-V	0.54	65.0	5.0	5.71	5.6	1 year [*]
Sisomphon, 2007	CEM III/B	0.60	65.0	3	16.00	15.0	9 weeks [*]
Marques and Costa, 2010	CEM IV/B	0.55	65.0	5	19.50	18.4	42 days [*]

[*] denotes accelerated exposure

In addition, data from a set of characteristic structures showing signs of carbonation-induced deterioration were derived. Using the simulation tool (EUCON), based on information as, the age they were erected, their environmental exposure, the type of cement used and the concrete compressive strength measured, the carbonation depth was estimated and a very good correlation (average variation of 7.2 %) was observed (Fig. 2.8, Table 2.3).

Table 2.3 Characteristic estimated and measured carbonation depth values from field studies.

Structure		Age (years)	Carbonation Depth (mm)	
			Measured	**Calculated**
1	Industrial facility, Patras, Greece (mortar coating)	70	8	6
1	Industrial facility, Patras, Greece (no mortar coating)	70	20	19
2	School, Mesologi, Greece	66	45	43
3	Hospital, Lixouri, Greece	51	43	41
4	Town Hall, Voia, Greece	38	35	32
5	Cooling Tower, Megalopolis, Greece (internal)	25	2	2
5	Cooling Tower, Megalopolis, Greece (external)	25	18	16.9
6	School, Nafpaktos, Greece	30	52	50.5
7	Hotel, Galatas, Greece	37	30	32
8	City Hall, Sami, Greece	40	55	50
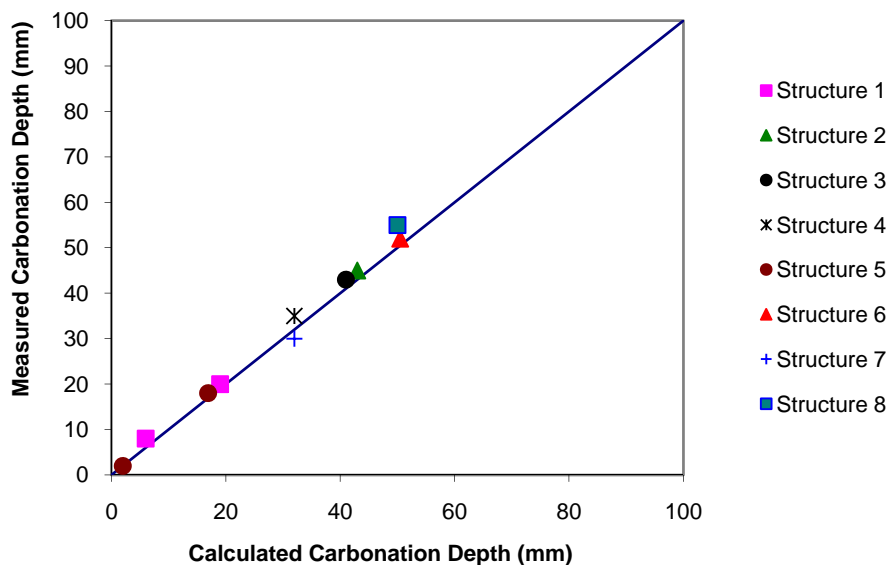
Figure 2.8 Comparison of calculated to measured carbonation depth values from field studies (see Table 2.3).

2.5 Life cycle analysis for constructions

Life-cycle analysis (LCA) is a process whereby the material and energy flows of a system are quantified and evaluated. Environmental life cycle analysis for constructions can actually access the environmental burden caused by buildings and show measures of reduction as well. Moreover, numerous environmental assessment tools have been developed to allow scientists analyze the environmental performance of buildings (see Chapter 1).

LCA focuses to quantify the full range of environmental impacts associated with a product by considering all inputs of resources and materials and all outputs of wastes and pollution at each stage of the product's life — including acquiring raw materials (e.g., mining), manufacturing and distributing the product, the consumer's use and maintenance of the product, and its ultimate disposal (Dimoudi and Tombra 2008).

Fig. 2.9 shows the system boundary in a life cycle analysis which means the inputs and outputs and of course all the intermediary stages that must be taken into account.
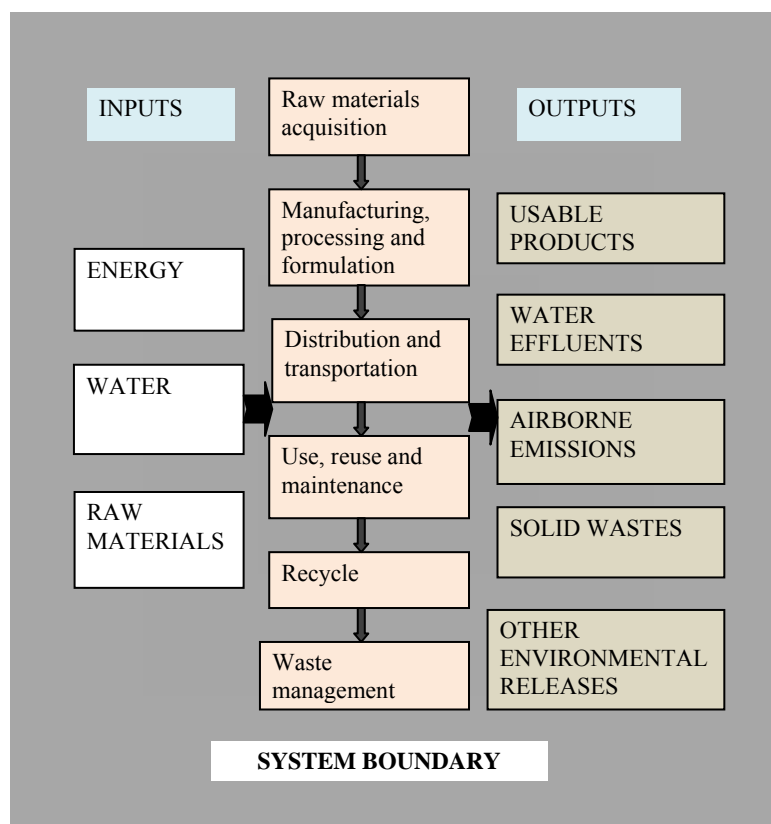
Figure 2.9   Life Cycle Analysis (LCA) scheme.

Life cycle assessment involves three stages:

1. An inventory of materials and energy used and environmental releases from all stages in the life of a product or process.

2. Impact assessment examining potential and actual environmental and health effects related to the use of resources (materials and energy) and environmental releases.

3. An improvement assessment, identifying the changes needed to bring about environmental improvements in the product or process.

Figure 2.10   The life cycle concept and the calculation of the net present value for environmental cost.

Especially, for a construction or building, the phases of the initial construction, rehabilitation, maintenance and salvage should be analysed in details, as well as the total service lifetime should be estimated, see Fig. 2.10. The initial construction includes energy, water and raw materials consumption as well as the several rehabilitation and maintenance actions during the construction's service life; whereas during demolition phase some materials could be regained. All these actions can be characterized by a total cost in terms of CO_2 emissions, grey energy consumed, or by economical terms. The net present value (NPV) of this cost can be calculated by Eq. (2.9) representing the **net fixed environmental cost** and having as units CO_2 emissions, grey energy consumed, or economical units.

$$NPV = IC + \sum_{k=1}^{N} RC_k / (1+i)^{n_k} \tag{2.9}$$

where,   IC the initial cost, RC the recurring costs, N the number of recurring costs, i the discount rate, n_k the number of years when the k recurring cost happens.

In the above fixed environmental cost the operational environmental costs should be added by using the net present value concept as well. These costs refer to the use of the construction or building, i.e., the electricity or other energy sources consumed during operation, heating, ventilation and air conditioning (HVAC systems), cooking, washing, etc. However, their analysis and estimation are outside of the scope of the present study.

The total service life time of the construction or building is calculated by the models and the tools presented in section 2.4, where the concept and the main principles of a software tool (based on deterministic proven predictive models) for the estimation of concrete service life, are presented. The tool presented offers a comprehensive approach on concrete service life estimation, in terms of:

- Defining the concrete mix design and the main chemical/volumetric characteristics of concrete.
- Estimating the compressive strength class
- Accurately predicting the concrete service life, for carbonation and chloride exposure, by taking under consideration the relative exposure classes and by utilising proven predictive mathematical models of the physicochemical processes leading to such deterioration.

In the next Chapter (Chapter 3), the **environmental cost** for concrete production will be analysed, quantified and optimized by using the above software tools and models.

Chapter 3. Environmental cost of concrete production – Estimation & optimization

3.1 Introduction

Today, the cement and concrete industry is still the dominant type of materials industry within the construction sector. As referred in the Introduction, concrete is recognized to be the most widely used construction material of nowadays with huge quantities consumed by our society. It has been estimated that its average consumption is about 1 ton per year per every person on the planet (Flower and Ganjayan 2007). Despite the economical crisis, previous studies from CEMBUREAU (2011) showed a 0.7% rise in the EU construction activity in 2011, with the index of cement manufacturing showing a positive trend. It is predicted that global demand for cement is expected to rise 4.1% yearly, to 3.5 billion metric tons in 2014.

Such levels of demand however, are associated with significant environmental burden. It is well known that any type of construction material entails certain aspects of environmental cost (in the form of carbon dioxide and other gasses emissions and energy consumed) from its manufacturing stage to its end-use (fixed environmental cost). During concrete production the main emissions to atmosphere are associated with the cement-making process, where during the stage of clinker formation, CO_2 and other greenhouse gases are emitted to the atmosphere (CEMBUREAU 2009). These types of emissions are both raw material-related and energy-related. Raw material-related emissions are produced during limestone decarbonation and account for about 50% - 60% of total CO_2 emissions (Ecosmart Concrete 2008, WBSCD 2005). Energy-related emissions are generated both directly through fuel combustion and indirectly through the use of electrical power. It is estimated that burning of 1 ton of clinker releases up to 0.97 tons of CO_2 (Habert *et al.* 2010, IEA 2010). Considering that on average 900 kg of clinker are used to produce 1 ton of cement, the CO_2 emissions per ton of cement are estimated in the magnitude of 0.87 tons (Ecosmart Concrete 2008, WBSCD 2005). Just to get an

indication on the overall magnitude of related emissions, it should be noted that the construction sector accounts for a considerable share of the total EU final energy consumption (more than 42%) and produces more than 35% of all the greenhouse emissions (WBSCD 2005, 2009), with cement manufacturing contributing 5% of the global man made CO_2 emissions.

Bearing all of the above in mind, increasing emphasis should be placed on investigating and enforcing ways and methodologies to make the cement and the construction industry in general a more environmental friendly sector. On that note, altering the nature of clinker, or reducing the clinker content of cement with other constituents, should influence directly the levels of the derived CO_2 emissions. Several innovative new types of cements with altered clinker properties are being (and have been) developed, including carbon-negative cement based on magnesium silicates (rather than limestone as the Ordinary Portland Cement) (Ruffolo *et al.* 2010), cement produced in a reactor by rapid calcination of dolomitic rock in superheated steam (Sweeny and Sceats 2009) and cement based on a mixture of calcium and magnesium carbonates and hydroxides (Bren 2011), with however limited appeal on the cement manufacturing companies. Reasons for such a withheld acceptance can be found on the fact that it is estimated that their substantial benefits on the reduction of the associated emissions will by fully utilized in a time frame of 5-10 years from today (WBSCD 2005, 2009). Overall, they do not provide a feasible economical and operational solution on tackling the environmental burden of cement manufacturing, today.

What is actually promising is direct reduction (up to a certain extent) of the clinker content in cement through utilization of industrial by-products as supplementary cementing materials *SCM* (fly ash, silica fume, rice husk ash, ground granulated blast-furnace slag, etc.). It has been estimated that 18% replacement of Portland cement results in a 17% reduction of the CO_2 emissions and that, if just 30% of cement (Ecosmart Concrete 2008) used globally were replaced with SCMs, the rise in CO_2 emissions from cement production could be reversed (see Fig. 3.1).

However, equally important on achieving a **"green" mix design**, by utilizing industrial by-products as cement replacement materials, is to be able to further "fine tune" this particular mix design in order to safeguard certain concrete strength and service life requirements. The challenge is to be able to guarantee not only reduced environmental contribution but also, accepted mechanical properties, workability, strength development and service life of a structure utilizing an environmentally friendly cement type.
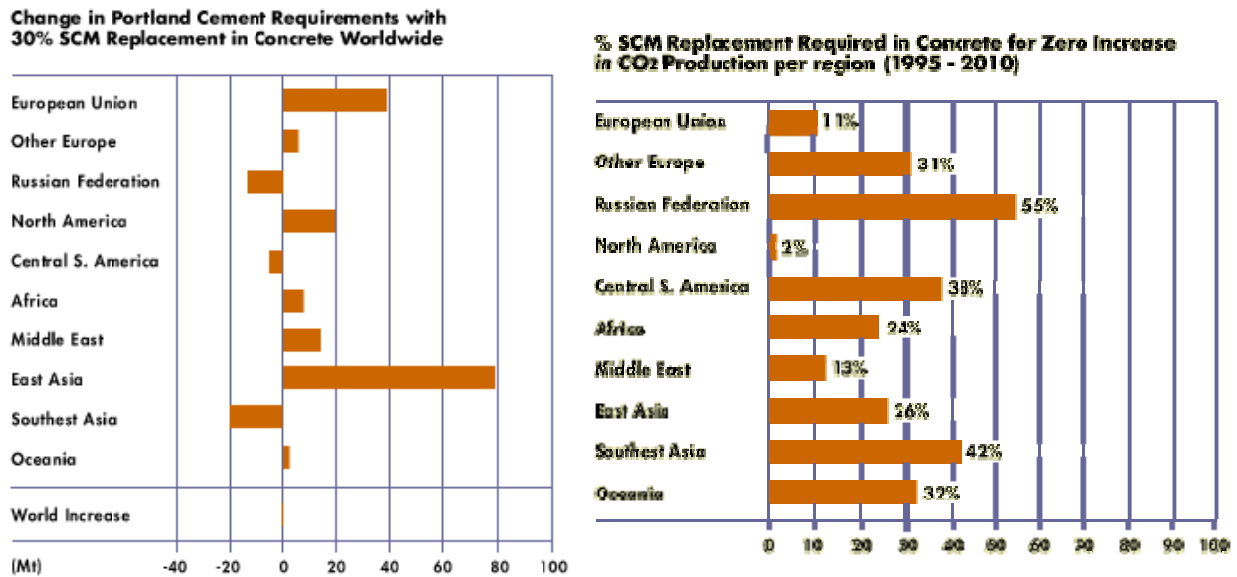
Figure 3.1   Effect of SCM utilization in CO₂ emissions (Ecosmart Concrete 2008).

Previous research studies (Antiohos *et al.* 2007, Demis and Papadakis 2012, Papadakis and Demis 2013) have identified the high added values of SCM incorporation in concrete strength and service life under harsh environmental factors. Considerable amount of work on developing analytical models for the evaluation of SCM in concrete using the concept of efficiency factors (or k-values, to compare the relative performance of supplementary cementing materials on concrete durability) by Papadakis (1999a, 1999b, Papadakis *et al.* 2002) has identified the high-added value of certain types of these materials (as Type II additives in CEM I type of cement) and their pozzolanic properties on cement and mortar and the effects they entail on early concrete strength and volume stability (Antiohos *et al.* 2007, Papadakis and Tsimas 2002).

What is needed is to be able to achieve an optimum, balanced approach, between sustainability and durability design of reinforced concrete structures, an effort put by the present Thesis. After all, the very definition of sustainability (CEN EN 15643 2011) as "*… the ability of a system (a structure) to be maintained for the present and future generations*" incorporates to a great extend the end result of the durability design (*maintenance of a structure for the present and future*). It should be noted, that the linkage between durability and sustainability is also emphasized, on the newly imposed EN Standards on the sustainable assessment of buildings (CEN EN 15643 2011), where a combination of the assessments of *environmental and economic performance* taking into account the *technical* and *functional requirements* of a *building* is approached, and on the next generation structural codes (*f*ib 2010), where repair and maintenance of concrete structures, will be subjected to strict requirements

both with regard to environmental, economical and service life constraints.

The question that needs to be answered is how their relationship is affected. How a 30% reduction in clinker content (for example) or a reduction in the overall cement or water content affect the service life of a structure? Does an accepted sustainable design (from an environmental aspect point of view) provides automatically a durable design that meets certain target values, or certain modification in the mix design have to be made (and to what extent)?

The scope of this particular study is to provide answers to the previously mentioned questions, on the relation between sustainable and durable design of reinforced concrete. To achieve this, a (4-step) structured methodology is proposed on estimating the reduction of environmental cost (in principle) and the strength and service life of concrete incorporating cement replacement materials, aiming to achieve the best possible (optimum) mix design configuration. Although the previously mentioned methodology is presented in detail in Section 3.3 of this chapter, it can be summarized as follows. Upon defining a set of design parameters, in terms of concrete compressive strength and service life, a typical (referenced as control) mix design (no SCM) is selected that produces strength and service life values higher than the design parameters, but at a high environmental cost. The aim is to reduce considerable that cost, without compromising on strength or service life. To achieve this, a particular SCM is utilized at certain incremental percentages and the environmental and service life properties are calculated. On reaching a rate of pozzolanic reaction bellow 1, further fine-tuning of the concrete compositional parameters is achieved resulting in reduced environmental cost and at the same time strength and service life values higher than the predefined ones. As it is also mentioned in Section 3.3, on every step, the service-life, and compressive strength, evaluation was made using a software tool (EUCON), based on proven predictive models (according to performance-related methods for assessing durability) developed and validated elsewhere (Papadakis and Efstathiou 2005, Demis and Papadakis 2012, Papadakis *et al* 1991, 2007, Papadakis and Demis 2013) well published and awarded by the ACI, for the estimation of concrete service life when designing for durability under harsh environments.

On this note, fly ash and silica fume were evaluated as Type II additives on a common CEM I type of cement. The first step however is the estimation of the environmental output of concrete incorporating these types of materials, as it illustrated in the following section.

3.2   Estimation of environmental cost of concrete

It was previously mentioned that during the concrete production the main emissions to air are

associated with the cement manufacturing process. However, other concrete constituents also contribute in that sense. In general, it can be said that the CO_2 emissions from concrete production are the summation of the emissions from, the chemical conversion process in clinker production (during cement manufacturing), from the energy consumption due to fossil fuel combustion (also during cement manufacturing), from the electrical energy required for the grinding of any additive materials and from the energy required (in terms of fuel consumption) for the transportation of the raw materials and of the final product. Overall, the initial environmental cost of concrete $E_{I,conc}$ (expressed in kg CO_2 / m³ of concrete) taking under consideration every environmentally contributing parameter from the materials supply to concrete production, delivery and casting can be expressed as:

$$E_{I,conc} = E_M + E_P + E_T + E_G \qquad (3.1)$$

where E_M is the environmental cost of materials, E_P the environmental cost for concrete production, E_T the environmental cost for concrete transportation and delivery, and E_G the cost for concrete casting, placing and finishing (all expressed in kg CO_2 / m³ of concrete).

A more precise estimation of the environmental footprint (environmental factors) of each individual concrete component, based on the literature and on data derived from a Greek cement manufacturing company, is presented in this section. The total fixed environmental footprint of concrete materials (E_M, kg CO_2 / m³ of concrete) can be calculated as:

$$E_M = C \cdot E_c + \Sigma (SCM \cdot E_{SCM}) + A \cdot E_A + W \cdot E_W + D \cdot E_D \qquad (3.2)$$

where C, SCM, A, W, and D: are the contents (in kg / m³ of concrete) of cement, supplementary cementing materials, aggregate, water and admixtures, respectively, in the concrete volume, and E_C, E_{SCM}, E_A, E_W, and E_D: their corresponding environmental costs (in kg of CO_2 / kg of material).

By taking under consideration the chemical equation of complete combustion of coal (Eq. 3.3), where 94 kcal/mol of energy is produced (Q), since it is an exothermic reaction, the amount of CO_2 produced from energy consumption of 1kWh is calculated as 0.404 kg (1 cal is equal to $1.162 \cdot 10^{-6}$ kWh, hence 94 kcal equal to 0.109 kWh producing 44 g of CO_2).

$$C + O_2 \rightarrow CO_2 + Q \qquad (3.3)$$

The related to cement production CO_2 emissions vary from 0.65-0.92 tons per ton of cement produced based on a cement plant with a modern technology and equipment, according to the literature (Flower and Ganjayan 2007, Hoenig *et al.* 2007), or from 0.61 – 0.80 according to data from cement

manufacturing companies (ACC 2010, CRH 2011, Heidelberg Cement 2009, Holcim 2011, Italcementi Group 2011, Lafarge 2011) (see Table 1). It should be noted that the levels of CO_2 emissions derived from cement manufacturing companies (Table 3.1) represent the average levels of emissions produced of the total range of different cement types produced annually by each company. Hence, they do not reflect on the actual levels of emissions of a CEM I type of cement.

Table 3.1 Cement production data and CO_2 emissions from the industry (ACC 2010, CRH 2011, Heidelberg Cement 2009, Holcim 2011, Italcementi Group 2011, Lafarge 2011).

Reference	Cement Produced (million t/year)	Electrical Energy Consumed (kWh/t cement)	CO_2 Emissions (t/year)	(t/t cement)
CRH 2011	15.6	180	$10.3 * 10^6$	0.735
Heidelberg 2009	3.90	131	$3.70 * 10^6$	0.739
Holcim 2011	144.3	100	$102. * 10^6$	0.608
Italcementi 2011	71.8	122	$34.4 * 10^6$	0.708
Lafarge 2011	145	-	$98.0 * 10^6$	0.611
ACC 2010	-	118	$43.1 * 10^6$	0.798

For the purposes of this study, based on operational and production data from the Greek cement-manufacturing company, the level of CO_2 emissions from cement manufacturing was accurately estimated. By taking into account data as, the amount of cement produced (1,700,000 t/year), the electrical energy required (500,000 kWh/day) the level of CO_2 emissions measured (3,801,000 kg/day) and the total days of operation per year (335), the total CO_2 emissions were calculated to be in the range of 1,341,005 t/year. Hence in order to produce 1 t of cement 0.79 t of CO_2 are emitted into the atmosphere. In addition to the later, the derived CO_2 emissions from transportation should be added. Considering that on average 2.74 kg of CO_2 is emitted per litre of fuel, using vehicle transport, and that fuel consumption is estimated to be 1 lt / 3 km for 5 t of raw materials, the overall emissions arise from transportation are estimated to be 0.183 kg / km / t of raw material (GHG Protocol 2001).

According to data from a cement manufacturer (ItalCementi 2011), in order to extract, process and grind aggregates the overall CO_2 emissions are estimated to be 5.96 kg / t of aggregates (considering that 2.53 kWh are required for the production of 1 ton of aggregates and that 9 lt of fuel are required for the transportation of a 5 tons shipment, resulting in 4.94 kg of CO_2 / t of aggregates).

When fly ash is used as an SCM, since it is a by-product of coal burning in electrical power stations, the emissions associated with power generation are not considered of being part of the environmental burden of fly ash. A small amount of energy required for the grinding of the raw material into very fine powder and for its transportation are the only sources of greenhouse gasses. According to the literature (IPPC 2010, US Environmental Protection Agency 2008) the previously mentioned energy requirement is estimated to be in the order of 20 kWh per ton of fly ash produced, hence 8.06 kg of CO_2 per ton of fly ash (emissions from transportation, similar to cement transportation, should also be added). In the case of silica fume, since it is available from limited regions on European level, the related emissions arise from its transportation. For reasons of simplicity, since the aim of the current study is to produce an estimation of the environment impact of concrete the previously mentioned source of emissions are assumed to be twice of those of fly ash transportation.

As far as water is concerned, the only source of emissions arises from the electrical energy required to pump the water, which in this study is considered to be negligible. Since no admixtures were used on the mix design of the different concrete configurations used in this study, the environmental impact of admixtures is ignored.

In this way, based on the proportions of the concrete constituent materials used and on the environmental factors, as derived above, the overall environmental cost of concrete was calculated. These calculations were incorporated on every step of the structured methodology presented in the following section.

3.3 Structured methodology for concrete mix design optimization

A schematic illustration of the (4-step) methodology proposed in this study, for the evaluation of the effectiveness of industrial by-products as cement replacement materials in achieving a robust mix design (in terms of concrete properties and service life) with minimum environmental cost is presented in Fig. 3.2.

The concept can be briefly described as follows:

- For given design parameters, as concrete compressive strength and service life (e.g. 40 MPa and 50 years), an initial set of concrete compositional parameters (CCP; cement, water, aggregate) is selected (achieving the target values) but with an initial high environmental cost (*Step 1*). This particular mix design is referenced as the control mix (with 95% clinker, no SCM) and its corresponding properties as the control values (strength, service life, environmental cost).

- A particular SCM is utilized as cement replacement material (*Step 3*) at a certain percentage (e.g. 10%, 20%, 30% for fly ash and 5%, 10%, 15% for silica fume, since it is a more intense pozzolanic material than fly ash). The environmental cost and the corresponding concrete properties are calculated, per incremental step of SCM addition. In order to provide a level of comparison in terms of concrete properties of the utilization of SCM (with the control mix, from step 1), these materials are also inserted in the mix as aggregate replacement materials (*Step 2*). Eventhough they do not replace cement, hence we do not achieve a reduction in environmental cost, at the same time we do not particularly increase it, since the aggregate associated levels of CO_2 emissions are very small (5.96 kg / t of aggregates).

- Based on the best performed mix design configuration from Step 3 (in terms of environmental cost and target values) further reduction in the CCP properties is achieved (*Step 4*), through incremental reductions of cement (10 kg per step) and water (10 kg per step, for each decrease in cement content). In essence we are altering the water-to-cement (w/c) ratio of the best performed mix at Step 3, keeping at the same time the percentage of SCM constant.

In terms of service life as indicators of performance, the critical time for initiation of corrosion due to the action of carbon dioxide from the atmosphere (and the corresponding depth of carbonation), as well as the critical time for initiation of chloride induced corrosion (and the adequate concrete cover needed in order to sustain a chloride free concrete cover for a period of 50 years), were selected.

On every step, the service-life, and compressive strength, evaluation was made using a software tool (EUCON), based on proven predictive models (according to performance-related methods for assessing durability) developed and validated elsewhere (Papadakis and Efstathiou 2005, Demis and Papadakis 2012, Papadakis *et al* 1991, 2007, Papadakis and Demis 2013) well published and awarded by the ACI, for the estimation of concrete service life when designing for durability under harsh environments. Concrete service life is reliably predicted using fundamental mathematical models that simulate the basic deterioration mechanisms of reinforced concrete (carbonation, chloride penetration). Principles of chemical and material engineering have been applied to model the physicochemical processes leading to concrete carbonation, as well as the processes of chloride diffusion in the aqueous phase of pores, their absorption and binding in the solid phase of concrete and their desorption.

Figure 3.2 Logical diagram of structured methodology for obtaining CCP values for minimum environmental cost (EC) with optimum strength and durability properties (C, P, W: cement, SCM and water contents, in kg/m³; Z_{carb}, $Z_{Cl\text{-}}$: service life in carbonation and chloride exposure, in years)

3.4 Utilization of structured methodology for concrete mix design optimization

3.4.1 Step 1: Selection of initial CCP values

A compressive strength of 40 MPa and a service life of 50 years were selected as the defined target values. A typical CEM I mix (w/c: 0.5, cement content: 300 kg/m³, crushed aggregates of 31.5 mm maximum size, no additives, no admixtures), water cured for 28 days, was selected as the control mix. Its overall environmental contribution was calculated to be 311.47 (kg CO_2/m³ of concrete). The control mix produced a concrete compressive strength of 44.6 MPa and gave a service life of 119.9 years under carbonation exposure (for a concrete cover: 30 mm) and 53.1 years under chloride

exposure (for a concrete cover: 30 mm). These values (environmental cost, strength and service life) are regarded as the *reference (control)* values on every mix design optimisation procedure followed in the current study.

3.4.2   Steps 2 and 3: Replacing aggregates or cement by SCM

On every mix design a constant volume unit (1 m³) of concrete was chosen as a common basis. When an SCM was added to this unit, then an equal volume of another component, either cement (Step 3) or aggregate (Step 2), was removed in order to keep the same total volume and the common comparison basis. Several mix design configurations were considered (see Table 3.2), where each time addition of a Type II additive took place, at certain proportions, as cement and as aggregate replacement.

Table 3.2   Mix design, service life indicators and environmental cost (Steps 1-3).

SCM type	SCM %	C kg/m³	W kg/m³	w/c	A kg/m³	P kg/m³	f_c MPa	Z_{carb} years	Z_{Cl-} years	E_C kg CO_2/m³ con.	ΔE_C %
Control	*0*	*300*	*150*	*0.5*	*1925*	*-*	*44.6*	*119.9*	*53.1*	*311.47*	*-*
SFA	Replacing aggregates										
s-fa 1a	10	300	150	0.50	1890	30	47.4	175	187.5	311.52	0.02
s-fa 2a	20	300	150	0.50	1856	60	50.3	>200	>200	311.58	0.03
s-fa 3a	30	300	150	0.50	1821	90	50.4	>200	>200	311.63	0.05
	Replacing cement										
s-fa 1c	-10	270	150	0.56	1915	30	41.8	98.4	81.3	281.67	-9.57
s-fa 2c	-20	240	150	0.63	1905	60	38.0	74.3	106.3	251.87	-19.14
s-fa 3c	-30	210	150	0.71	1895	90	31.7	47.6	45.8	222.07	-28.70
CFA	Replacing aggregates										
c-fa 1a	10	300	150	0.50	1896	30	51.4	180.2	118.8	311.56	0.03
c-fa 2a	20	300	150	0.50	1866	60	58.0	> 200	>200	311.64	0.05
c-fa 3a	30	300	150	0.50	1837	90	64.4	> 200	>200	311.72	0.08
	Replacing cement										
c-fa 1c	-10	270	150	0.56	1920	30	45.8	102.3	70.8	281.70	-9.56
c-fa 2c	-20	240	150	0.63	1916	60	46.9	86.2	93.8	251.94	-19.11
c-fa 3c	-30	210	150	0.71	1911	90	48.0	72.2	187.5	222.16	-28.67
SF	Replacing aggregates										
sf 1a	5	300	150	0.50	1908	15	50.8	135.3	137.5	311.39	-0.03
sf 2a	10	300	150	0.50	1890	30	56.9	146.5	>200	311.30	-0.06
sf 3a	15	300	150	0.50	1873	45	62.0	164.8	>200	311.21	-0.08
	Replacing cement										
sf 1c	-5	285	150	0.53	1920	15	48.0	102.9	81.3	296.46	-4.82
sf 2c	-10	270	150	0.56	1915	30	51.4	85.2	143.8	281.45	-9.64
sf 3c	-15	255	150	0.59	1910	45	51.2	70.9	156.3	266.43	-14.46

SCM:	Replacement level (%) with supplementary cementing material
C:	cement content (kg/m³)
A:	aggregate content (kg/m³)
P:	SCM content (kg/m³) of fly ash *FA* (siliceous "*SFA*" or calcareous "*CFA*") and of silica fume *SF*
f_c:	Concrete compressive strength (MPa)
Z_{carb}, Z_{Cl-}	Service life for carbonation and chloride exposure, respectively (years)
E_C, ΔE_C:	Environmental cost (kg CO_2 / m³ of concrete) and change (%) compared to control

W: Water content (kg/m³)
w/c: Water/cement ratio

In the case of fly ash, 10, 20 and 30 % replacement levels of the control cement mass were chosen, while in the case of silica fume, since it is a more intense pozzolanic material than fly ash (hence the degree of pozzolanic reactions drops bellow one for lesser quantities than fly ash) 5, 10 and 15% replacement levels were used. The water content (kg/m^3) was kept constant for all specimens.

Overall, in terms of concrete and durability properties, it was seen (Tables 3.2 and 3.3) that when SCM was used for cement or aggregate replacement, the derived strength and service life values were higher than the target values initially set (40 MPa and 50 years). When SCM was used as aggregate replacement, incorporation of calcareous fly ash (CFA) in CEM I type of cement produced a better performance than siliceous fly ash (SFA) (Fig. 3.3). Addition of 30% of CFA produced similar service life (more than 200 years for carbonation exposure) values to SFA but increased the compressive strength considerably higher (Table 3.3) than SFA, compared to control (44.4% strength increase for CFA, compared to 13% increase for SFA).

Additionally and more important the derived strength values were 61% and 26% higher than the target strength value initially set (40 MPa) in the case of CFA and SFA correspondingly. Silica fume (SF) although it produced concrete and durability values higher than the target set values, compared to FA it did not proved to be as effective in inhibiting carbonation exposure. The service life was increased, but to a lesser extent. To draw a level of comparison between performances, 10 % addition of SF increased the service life for carbonation by 22.2% (compared to the control value of 119.9 years of the control mix), compared to the 46% and 50.3% increase observed when 10% of siliceous and calcareous fly ash was added.
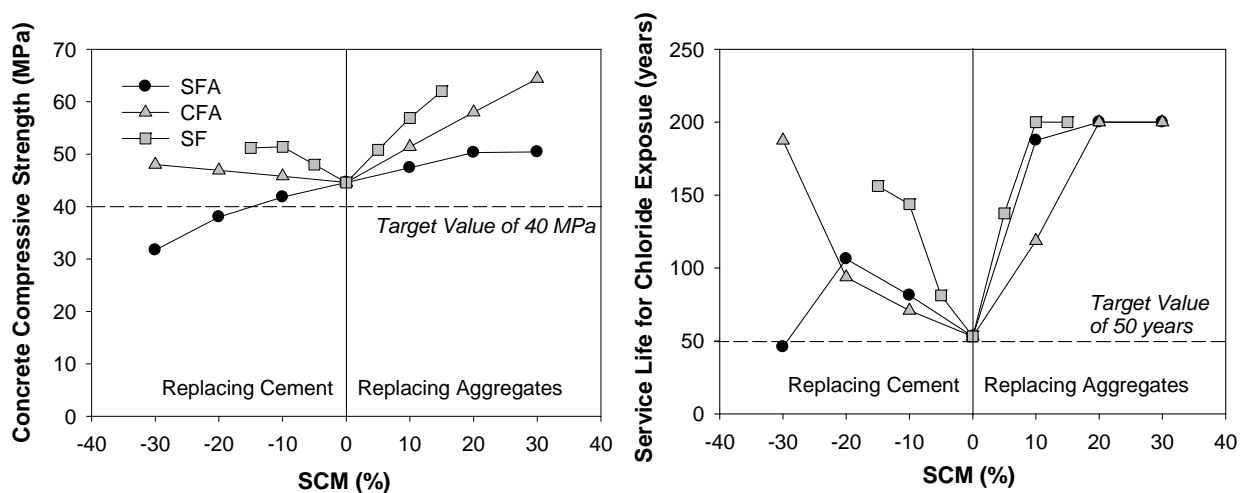
Figure 3.3   Comparison of SF and FA performance in terms of target values for strength (left) and service life for chloride exposure (right).

Table 3.3 Comparison of strength and servie life values to initial set target values (Steps 1-3).

SCM type	SCM	f_c	Δf_c	$f_c >$ set value	Z_{carb}	ΔZ_{carb}	$Z_{carb} >$ set value	Z_{Cl-}	ΔZ_{Cl-}	$Z_{Cl-} >$ set value
	%	MPa	%	%	years	%	%	years	%	%
Control	*0*	*44.6*	-	-	*119.9*	-	-	*53.1*	-	-
SFA		Replacing aggregates								
s-fa 1a	10	47.4	6.3	18.5	175	46.0	>150	187.5	252.9	>150
s-fa 2a	20	50.3	12.8	25.8	>200	66.8	>150	>200	276.5	>150
s-fa 3a	30	50.4	13.0	26.0	>200	66.8	>150	>200	276.5	>150
		Replacing cement								
s-fa 1c	-10	41.8	-6.3	4.5	98.4	-17.9	96.8	81.3	52.9	62.5
s-fa 2c	-20	*38.0*	-14.8	-5.0	74.3	-38.0	48.6	106.3	100.0	112.5
s-fa 3c	-30	*31.7*	-28.9	-20.8	*47.6*	-60.3	-4.8	*45.8*	-13.7	-8.3
CFA		Replacing aggregates								
c-fa 1a	10	51.4	15.2	28.5	180.2	50.3	>150	118.8	123.5	137.5
c-fa 2a	20	58.0	30.0	45.0	>200	66.8	>150	>200	276.5	>150
c-fa 3a	30	64.4	44.4	61.0	>200	66.8	>150	>200	276.5	>150
		Replacing cement								
c-fa 1c	-10	45.8	2.7	14.5	102.3	-14.7	104.6	70.8	33.3	41.7
c-fa 2c	-20	46.9	5.2	17.3	86.2	-28.1	72.4	93.8	76.5	87.5
c-fa 3c	-30	48	7.6	20.0	72.2	-39.8	44.4	187.5	252.9	275.0
SF		Replacing aggregates								
sf 1a	5	50.8	13.9	27.0	135.3	12.8	>150	137.5	158.8	>150
sf 2a	10	56.9	27.6	42.3	146.5	22.2	>150	>200	276.5	>150
sf 3a	15	62	39.0	55.0	164.8	37.4	>150	>200	276.5	>150
		Replacing cement								
sf 1c	-5	48	7.6	20.0	102.9	-14.2	105.8	81.3	52.9	62.5
sf 2c	-10	51.4	15.2	28.5	85.2	-28.9	70.4	143.8	170.6	>150
sf 3c	-15	51.2	30.0	28.0	70.9	-40.9	41.8	156.3	194.1	>150

Δf_c: ΔZ_carb ΔZ_Cl-: Change in concrete compressive strength and service life values compared to control (%)

> set value Percentage of concrete compressive strength and service life above target values set (40 MPa, 50 years)

In the case where SCM were used as cement replacement materials, the service life to carbonation exposure was decreased for every type of SCM used. In other words, the corresponding carbonation depth values calculated by the models utilised in this study were increased, with increasing content of SCM. As far as chloride exposure is concerned (Fig. 3.3b), specimens incorporating SCM whether aggregate or cement was substituted, produced increased service life values compared to control. Silica fume proved to inhibit chloride diffusion more efficiently than FA. A staggering 170% increase on the service life (compared to control) was noticed for 10% SF utilization, in contrast to 33.3% and 52.9% increases in the cases of CFA and SFA (correspondingly). Is should also be noted, that at higher levels of SFA (30%) the service life values to both carbonation and chloride exposure dropped below the target service life value initially set (of 50 years). The reasons for such a performance are explained in the following section.

In terms of environmental performance, utilization of 30% FA, as cement replacement material, reduced the concrete environmental footprint by 28.7% (to 222.07 kg CO_2 / m^3 of concrete), compared to a 14.5% reduction achieved when 15% of SF was utilized. Of course, when SCM were used as aggregate replacements the environmental output of concrete did not change. A comparative assessment of every strength, durability and environmental cost indicator, calculated in this study, for CFA and SF is given in Fig. 3.4. In this way, the reduction of environmental cost observed can be weighed against the strength and service life values.
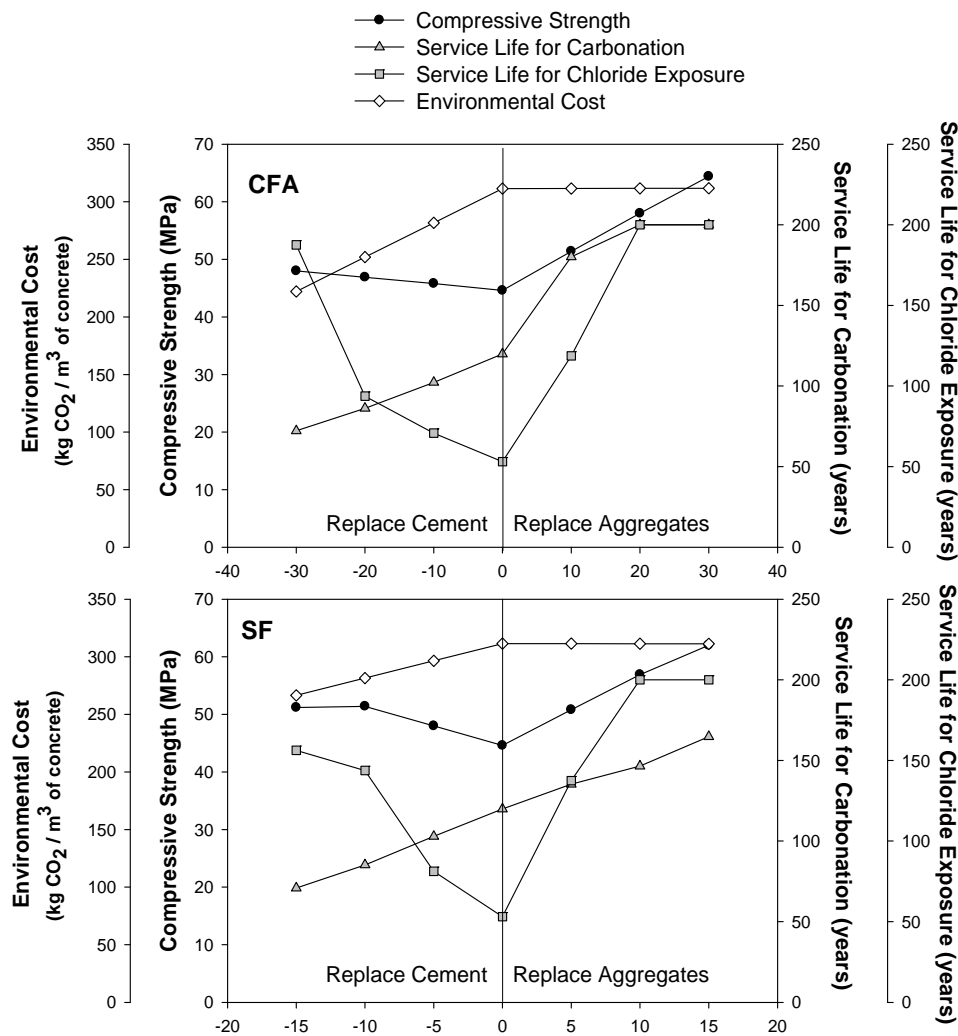
Figure 3.4 Overall performance of CFA and SF mixes in terms of environmental cost, concrete strength and service life properties.

It can be seen that even though in terms of environmental cost CFA outperformed SF (28.7% reduction compared to a 14.5% reduction for SF), in terms of concrete properties SF performed better than FA in general. A 10% utilization of SF increased the concrete compressive strength by 15.2% (compared to

the control value of 44.6 MPa), in contrast to a mere 2.7% increase achieved when CFA was used. In terms of service life, for chloride exposure each SCM gave comparable significant increases to control. For carbonation exposure however, the service life was reduced compared to the control value (119.9 years) but remained higher than the target set value (of 50 years) by 41.8% and 44.4% when SF and CFA were used respectively.

Such a behavior, in terms of reduction in environmental cost and trends in service life and strength was also noticed for

- different w/c ratios (Fig. 3.5a), other than the control value of 0.5, but for the same initial cement content (300 kg/m^3 concrete, as in the control mix),
- different initial cement content from (300 up to 400 kg/m^3) for w/c ratio of 0.5 (Fig. 3.5b).
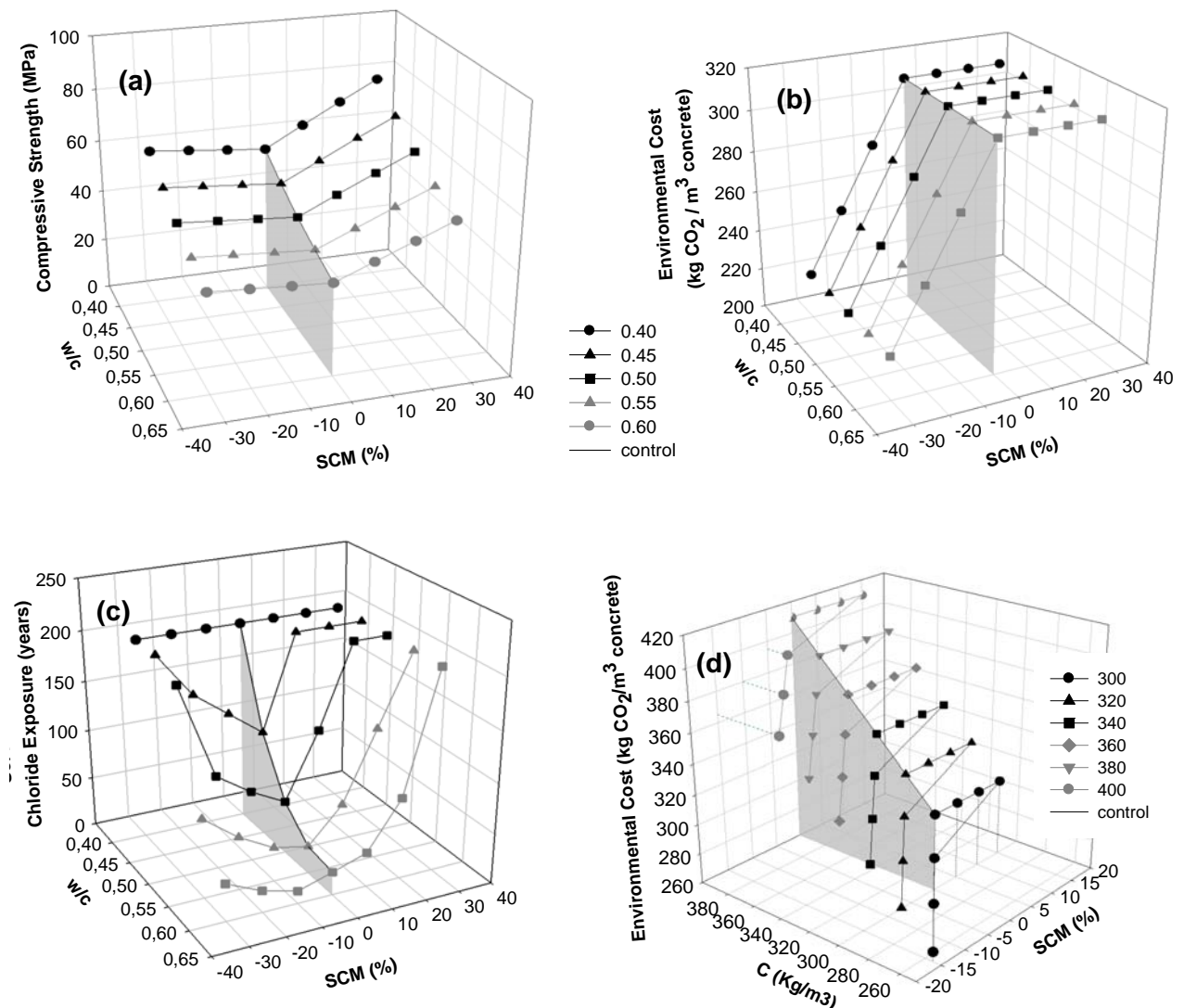
Figure 3.5   Overall performance of SCM in terms of environmental cost (b), concrete strength (a) and service life properties (c) for a range of w/c ratios and for different cement content (d).

The rate and the overall reduction in environmental cost was very similar on every different mix design with either different w/c ratio (but for the same cement content) or with different initial cement content (but for the same w/c ratio), since the cement replacement level follows the same incremental increase. Overall the 28.7% reduction in environmental cost (in the case of FA) is achievable with a 30% utilization of SCM as Type II additive (with accepted strength and service life properties).

Considering the fact that at higher SCM replacement levels, the degree of the pozzolanic reaction drops quickly below one, the question is, how can we further reduce the environmental cost without compromises on strength and durability properties? Such a solution is attempted on "Step 4" of the methodology previously described (Fig. 3.2) and utilized in this study, for the optimum mix design configuration in terms of environmental cost at one end and concrete and durability properties at the other.

3.4.3   Step 4: Further reduction of W and/or C contents

As previously described, on the best performed mix design configuration from Step 3 further reduction in the CCP properties can be achieved, through incremental reductions of cement (by 10 kg/m^3) and water (per 10 kg/m^3), for each decrease in cement content. Overall, we are altering the w/c ratio of the best performed mix at Step 3, keeping at the same time the percentage of SCM constant.

Such a mix design configuration, in the case of FA utilization, is given in Tables 3.4 and 3.5. Compared to the initial control mix (0.5 w/c ratio, 300 kg/m^3 cement content, no SCM), two CFA mix designs were further investigated (with 20 % cement replacement by CFA and with 30%, illustrated in Tables 3.4 and 3.5 respectively). On each SCM mix initially the cement content was reduced by 10 kg/m^3, followed by a step by step decrease of the water content by 10 kg/m^3. These reductions, were stopped when either strength or service life values dropped below the target values initially set (40 MPa and 50 years).

It should be noted that such reductions in cement and water content (although have been approached in the literature, Newlands *et al.* 2012), might fail to meet certain minimum composition criteria (minimum cement content, maximum w/c ratio) for certain exposure classes, as defined in the relevant standard. However, better and more realistic reductions can be achieved if a mix design other than the control is selected as the base line of comparisons (e.g. with more increased cement content). After all, the main aim of this study is to demonstrate the effectiveness of altering the concrete compositional parameters (cement, water, SCM, etc.) in principle, in achieving a reduced environmental cost with accepted at the same time concrete and service life properties.

Table 3.4　Strength and durability indicators compared to initially set target values for strength and service life, of a 20% CFA mix (Step 4).

	C kg/m³	W kg/m³	A kg/m³	f_c MPa	f_c > set value %	Z_{carb} years	Z_{carb} > set value %	Z_{cl-} years	Z_{cl-} > set value %	E_c kg CO_2 / m³con	ΔE_c %
Control mix	*300*	*150*	*1925*	*44.6*	*-*	*119.9*	*-*	*53.1*	*-*	*311.47*	*-*
20% SCM mix	**240**	**150**	**1916**	**46.9**	**17.3**	**86.2**	**72.4**	**93.8**	**87.5**	**251.94**	**19.11**
	240	**140**	1942	50.6	26.5	118.1	136.2	187.5	> 150	252.09	19.06
C stable	240	130	1967	54.8	37.0	175.4	> 150	262.5	> 150	252.24	19.02
W-10-40 kg/m³	240	120	1994	59.7	49.5	203	> 150	200	> 150	252.40	18.97
	240	110	2020	65.1	62.8	203	> 150	200	> 150	252.56	18.92
	230	**140**	1949	48.6	21.5	95.6	91.2	118.8	137.5	242.13	22.26
C- 10 kg/m³	230	130	1976	52.8	32.0	136.5	> 150	237.5	> 150	242.29	22.21
W-10-40 kg/m³	230	120	2001	57.4	43.5	203	> 150	200	> 150	242.44	22.16
	230	110	2028	62.8	57.0	203	> 150	200	> 150	242.60	22.11
	200	**140**	1974	42.7	6.75	53.3	6.6	70.8	41.7	212.28	31.85
C – 40 kg/m³	200	130	2000	46.4	16.0	71.3	42.6	118.8	137.5	212.44	31.80
W-10-40 kg/m³	200	120	2026	50.7	26.8	102.4	104.8	200	> 150	212.59	31.75
	200	110	2052	55.6	39.0	163.3	> 150	200	> 150	212.75	31.70
C – 70 kg/m³	**170**	**120**	2051	43.8	9.50	51.1	2.2	106.3	112.5	182.74	**41.33**
W-10-40 kg/m³	170	110	2077	48.3	20.8	73.3	46.6	200	> 150	182.90	**41.28**

Table 3.5　Strength and durability indicators compared to initially set target values for strength and service life, of a 30% CFA mix (Step 4).

	C kg/m³	W kg/m³	A kg/m³	f_c MPa	f_c > set value %	Z_{carb} years	Z_{carb} > set value %	Z_{cl-} years	Z_{cl-} > set value %	E_c kg CO_2 / m³con	ΔE_c %
Control mix	*300*	*150*	*1925*	*44.6*	*-*	*119.9*	*-*	*53.1*	*-*	*311.47*	*-*
30% SCM mix	**210**	**150**	**1911**	**48**	**20**	**72.2**	**44.4**	**187,5**	**> 150**	**222.16**	**28.67**
	210	**140**	1937	51.8	29.5	97.6	95.2	200	> 150	222.32	28.62
C stable	210	130	1963	56.1	40.25	141.7	> 150	200	> 150	222.47	28.57
W-10-40 kg/m³	210	120	1989	61	52.5	200	> 150	200	> 150	222.63	28.52
	210	110	2015	66.5	66.25	200	> 150	200	> 150	222.78	28.47
	200	**140**	1945	49.9	24.75	78.6	57.2	200	> 150	212.37	31.82
C stable	200	130	1971	54	35	110.9	121.8	200	> 150	212.52	31.77
W-10-40 kg/m³	200	120	1997	58.8	47	171.1	> 150	200	> 150	212.68	31.72
	200	110	2023	64.2	60.5	200	> 150	200	> 150	212.83	31.70
C stable	**160**	**120**	2030	46.1	15.25	57	14	200	> 150	172.87	**44.50**
W-10-40 kg/m³	160	110	2056	50.6	26.5	78.6	57.2	200	> 150	173.03	**44.45**

A first overall observation is that the environmental cost can be further reduced (up to 44.5%) in providing a mix design with guaranteed concrete compressive strength above 40 MPa and a service life of more than 50 years.

A closer look of the environmental and concrete strength and service life values achieved (Table 3.4), per step by step reductions of cement and water contents, reveals that the further reduction in cement content is associated with the desirable decrease of the environmental cost of concrete. The associated water reductions (from 10 to 40 kg/m^3) for each step by step reduction in cement content are associated with the further enhancement of strength and service life properties. Just to emphasize the validity of this particular point (illustrated in Fig. 3.6) it should be noted that for a 10 kg/m^3 reduction in cement content of the 30% CFA mix (from 210 kg/m^3 to 200 kg/m^3), the corresponding water content was reduced from 10 – 40 kg/m^3. Overall, for such a further cement reduction, a 31.7% decrease (on average) in environmental cost was noted (31.82% and 31.7% for 10 $kg/^3$ and 40 kg/m^3 reductions in water content, correspondingly). However, in terms of water content reduction, the mix design with its water content reduced by 40 kg/m^3 provided higher compressive strength and service life values (especially for carbonation exposure) than any other smaller reduction in water (10 – 30 kg/m^3).
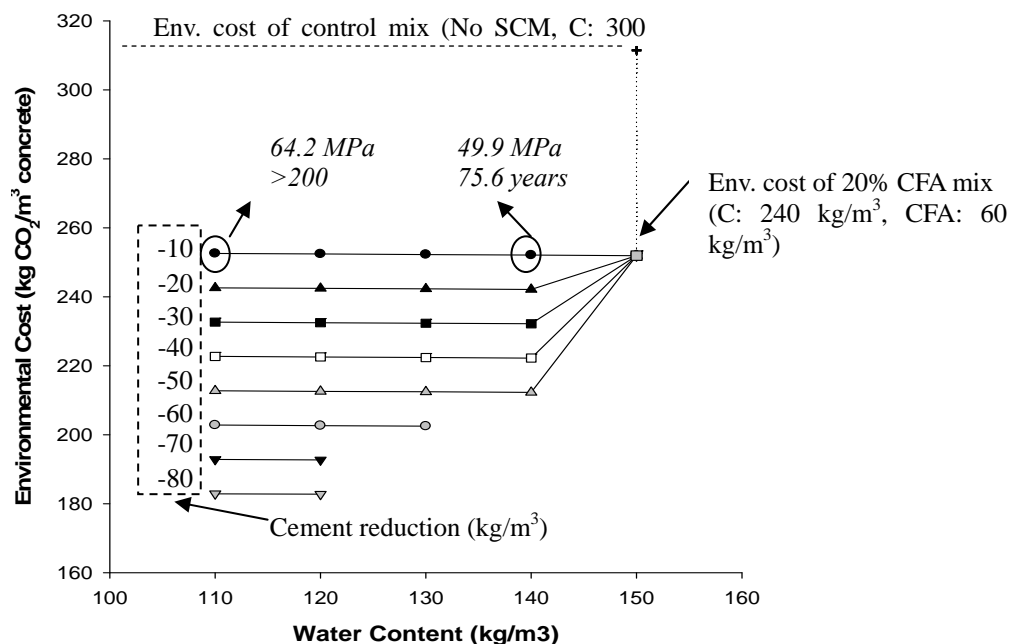
Figure 3.6   Effect of step/step reduction of cement and water contents on the environmental cost of a 20% CFA mix.

The best behavior in terms of environmental cost and concrete/service life properties of the further reduction in cement and water content of a 30% CFA mix is illustrated in Fig. 3.7.
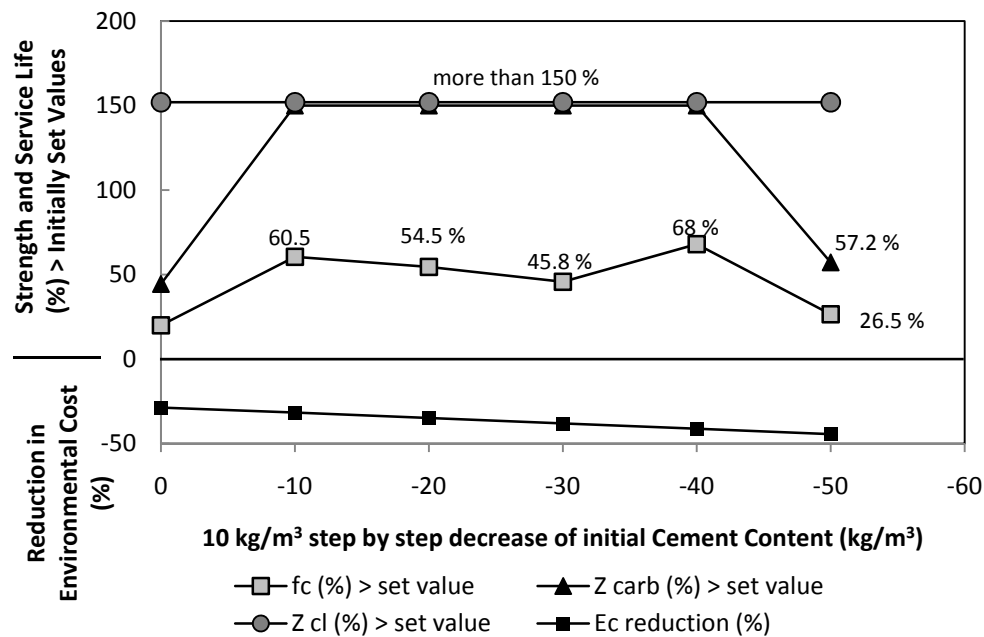
Figure 3.7   Effect of step by step reduction of cement and water contents on the environmental cost and strength and service life values of a 30% CFA mix.

It can be seen, how a further (to a 30% replacement by CFA) reduction in cement content alters the environmental cost of concrete. Furthermore, Fig. 3.7, shows how such a reduction affects strength and service life compared to the initially set target values (of 40 MPa and 50 years). For example, a further cement content reduction by 30 kg/m^3, on a 30% CFA mix, reduces the environmental cost of concrete by 38 %. More important is the fact that it provides a concrete compressive strength of 58.3 MPa and a service life in carbonation and chloride exposure of more than 200 years, values higher than 45.8% and more than 150% compared to the target 40 MPa strength and 50 years service life. Hence, considerable reductions in environmental cost of concrete can be achieved, without compromising on strength and service life (in essence on structural safety).

3.5   Discussion

The aim of this study was to investigate the relationship of sustainable and durable design, in terms of concrete mix proportioning, in providing a valid mix design with accepted strength and service life properties, but with the minimum environmental cost. To achieve this, a (4-step) structured

methodology (Fig. 3.2) was developed. Upon defining a set of target strength and service life values, an initial mix design is selected with 95% clinker (Step 1). Its strength and service life (in terms of carbonation and chloride exposure) values are estimated, using proven predictive models developed and validated by some of the authors of this study. In addition, its environmental output (in terms of kg CO_2/m^3 of concrete) is calculated, according to the concept described in section 2 of this study, using data from the literature and from cement production companies. At the next step, the effectiveness of SCMs (fly ash and silica fume) as cement (clinker) and aggregate replacement materials (Steps 2 and 3) is investigated, in reducing the environmental cost and in providing accepted strength and service life properties. The best performed mix design with a certain percentage of SCM is further optimized (Step 4) in reducing further its environmental output.

When SCM were utilized as aggregate replacement materials (Step 2) their environmental output was not improved (which is expected since they do not replace clinker). However, the strength and service life in carbonation exposure were considerably increased, compared to control. When SCM replaced cement (Step 3), smaller service life and strength values to control (hence larger carbonation depths), were produced, still higher than the target values set (50 years and 40 MPa) and their environmental output was considerably reduced (Table 3.2).

Although it has been noted (Atis, 2003) that there is no general agreement as to whether fly ash utilization tends to lessen the rate of carbonation, similar behavior (in terms of service life values for cement replacement) as the one observed in this study, has been observed also by other researchers. Khunthongkeaw (*et al.* 2006) stated that the carbonation depth increased along with the increase in the fly ash content (became critical for 30% fly ash). On a similar note, Lo (*et al.* 2010) observed that at high PFA replacement levels (more than 40%) carbonation depth was considerably increased. The explanation for such a behavior, lays in the way these materials were incorporated into the mix. In the first case (SCM replacing aggregates), the total amount of carbonatable constituents remains almost the same, resulting in decreased porosity and lower carbonation rates (Papadakis 2000). While in the second case (SCM replacing cement), by reducing the cement and clinker content, the amount of carbonatable materials is also reduced (due to the decrease in total CaO), resulting in higher carbonation rates (Khunthingkeaw et al. 2006; Lo et al. 2009). In general SCM materials (as cement replacements) proved to be less resistant to carbonation, mainly due to their low binding capacity of CO_2, caused by their smaller concentrations of $Ca(OH)_2$, compared to control (due to the consumption by pozzolanic reaction, and lower cement content).

Under chloride exposure they all behaved much better than control. It has been noticed that specimens incorporating an SCM, whether it substitutes aggregate or cement, exhibit significantly lower total chloride content for all depths from the surface (Chalee. *et al* 2010, Hosam *et al.* 2010).

Silica fume proved to be most efficient in inhibiting chloride ingress, than fly ash (since a 10% replacement by SF resulted in a 170% increase of service life compared to control, than the 33.3% and 52.9% for SFA). Silica fume, composed by very small spherical particles, due to its ultra fineness and activity led to the formation of intense pozzolanic reaction products (with increased chloride ion binding capacity than fly ash) within the capillary pore spaces and as a consequence, a finer and more segmented pore system is produced (Hosam *et al.* 2010; Nochaiya *et al.* 2010).

When fly ash was used, a study pozzolanic reaction level was observed for calcareous fly ash (rate of pozzolanic reaction equal to 1) resulting in higher service life to chloride exposure (at high, 30% concentration level). CFA due to its high calcium oxide content, apart of being pozzolonic active, reacts faster than siliceous reach cement replacement materials, since it contains higher amounts of aluminate-cementing compounds (C_3A, C_4AF), leading to a more increased chloride ion binding capacity. On the contrary, when siliceous fly ash was used smaller than the control values (in both strength and service life) were obtained. Such a behaviour, can be explained by the very nature of a rich in silica material. In general, when pozzolanic materials with high active silica content are added to cement, the silica (SiO_2) present in these materials reacts with free lime released during the hydration of cement and forms additional calcium silicate hydrate (CSH) as new hydration products which improve the mechanical properties of concrete formulation (Ganesan and Thangavel 2007). However when all the available free lime is depleted, the pozzolanic reactions stops and the remaining levels of silica remain inactive. Such an observation is further reinforced by the rate of the pozzolanic reaction of SFA, which at high replacement levels (30%) drops bellow 0.5. That is the reason why at these quantities of SFA, the strength and the service life in carbonation was reduced compared to control.

In terms of environmental cost fly ash (in general) produced bigger reductions (28.7%) of the associated CO_2 emissions, compared to silica fume (14.5%). These reductions and the overall trends observed in strength and service life were also observed on other mix designs investigated, with the same content level of SCM (up to 30%) and initial cement content (300 kg/m^3), but with different *w/c* ratios (Fig. 3.5). Even at mix designs with different initial cement contents than control (from 300-400 kg/m^3), with the same replacement level of SCM (up to 30%) and of 0.5 w/c ratio, the percentage reductions in environmental cost was constant.

Taking under consideration that any further SCM addition would result in a bellow 1 (or even 0.5) degree of pozzolanic reaction, in order to further reduce the environmental cost incremental cement and water reductions took place (Step 4). Each reduction of cement content (by 10 kg/m^3) is associated with a reduction in environmental cost, while at the other hand, the water reduction (again by 10 kg/m^3,

for each cement reduction) enhances the concrete and service life properties (as illustrated in Fig. 3.6).

It was shown that the environmental cost of a 30% CFA mix (reduced already by 28.7 % compared to the control mix) can be further reduced up to 45%, with step by step cement (by 10 kg/m^3) and additional water reductions. Such a mix design, except the considerable reduced level of associated CO_2 emissions, produces strength and service life (for chloride exposure) values of more than 26.5 % and 150 % above the initial target values of 40 MPa and 50 years, respectively.

Taking under consideration the effects of each incremental cement and water reduction on the associated environmental cost, strength (Fig. 3.8) and service life (Fig. 3.9) properties, in essence an area of accepted performance (in terms of strength and service life) can be defined. On each Figure, for each reduction in cement content, apart of the decrease in environmental cost, the gain in strength and service per water content reduction is also illustrated, expressed as a percentage above the initial set target values for strength (40 MPa) and service life (50 years).
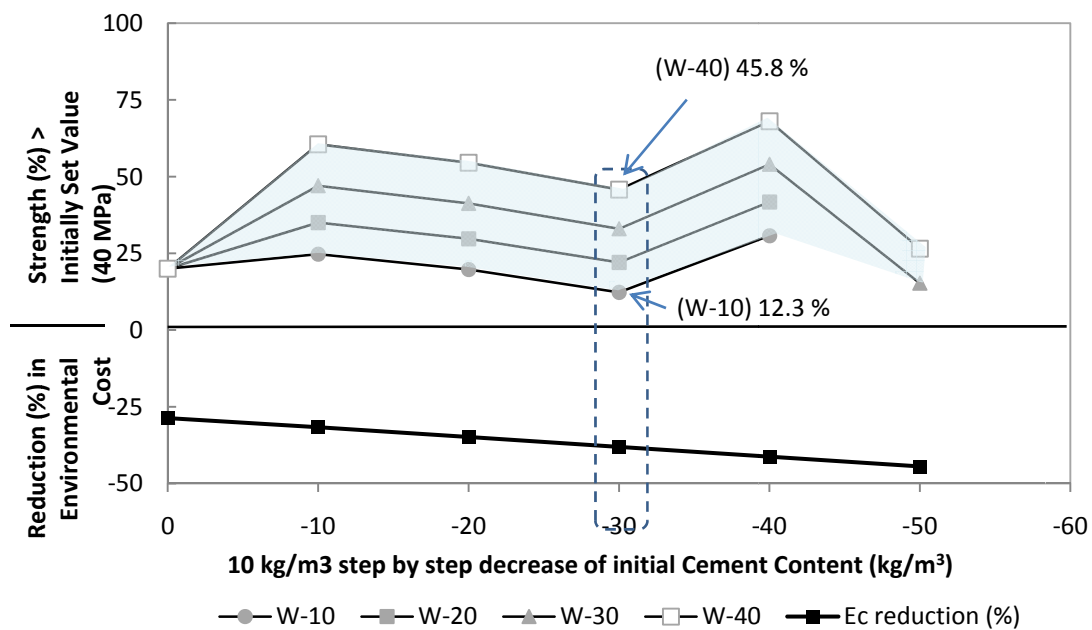
Figure 3.8   Effect of reduction of water and cement contents on strength and environmental cost.

For a reduction of the initial cement content of the 30% CFA mix by 30 kg/m^3, we can achieve a 38.2% reduction in environmental cost. At the same time, the associated strength would be 12.3% higher than 40 MPa for a 10 kg/m^3 water reduction and 45.8 %, for a 40kg/m^3 water reduction (the corresponding service life values would be 3.4% and more than 150% for the same water reductions).
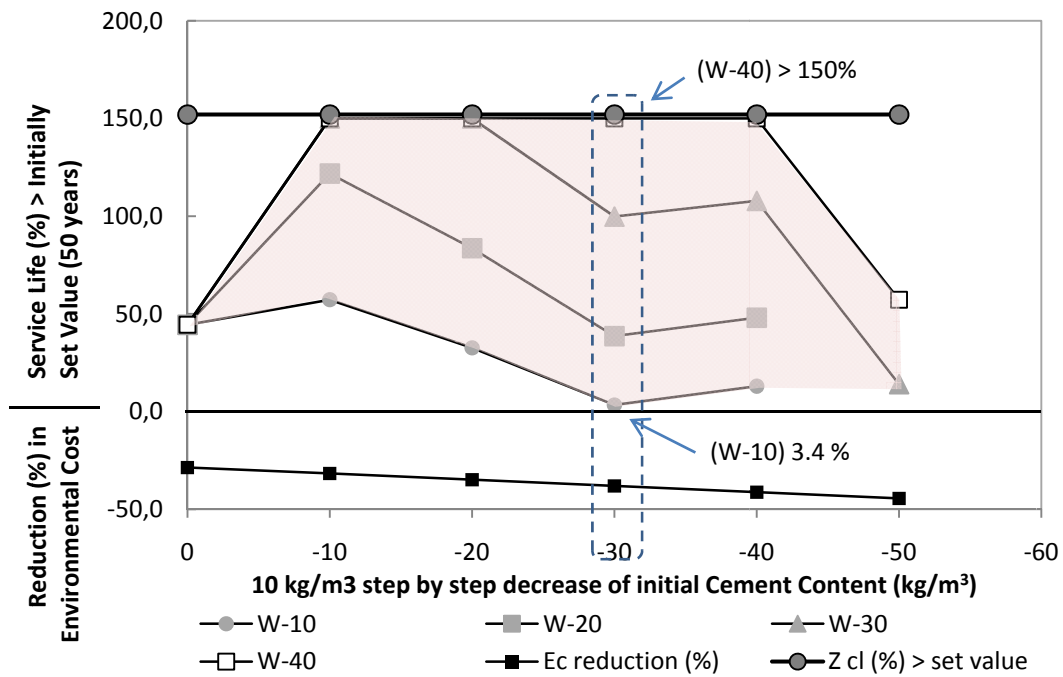
Figure 3.9   Effect of reduction of water and cement contents on service life and environmental cost.

Hence the designer can adjust the mix design configuration of a particular concrete mix design incorporating SCM, in achieving further reduction in environmental cost (in addition to those achieved through clinker replacement), and at the same time can select, for this particular cement reduction the levels of required strength and service life.

Chapter 4. Investigation on the effectiveness of biomass ashes as supplementary cementing materials

4.1 Introduction

Portland cement is well recognized as the major construction material throughout the world. Given its known environmental issues (in terms of energy and raw materials required for its production), direct reduction of its clinker content through utilization of industrial by-products as supplementary cementing materials (*SCM*), is a very promising first step in reducing considerably the associated environmental burden (see Chapter 3). Just to reinforce this observation, it has been estimated (Ecosmart Concrete 2008) that 18 % replacement of Portland cement would result in a 17 % reduction of CO_2 emissions and that, if just 30% of cement used globally were replaced with SCM, the rise in CO_2 emissions from cement production could be reversed.

Industrial by-products, such as blast furnace slag, fly ash and silica fume have been used as traditionally supplementary cement replacement materials (both in the production of clinker and in partial replacement of Portland cement in mortars and concrete) for the last 30 years. A number of investigations have demonstrated the validity of using these materials from both technical, environmental reasons and, at times, even economical (Papadakis *et al.* 2002, Antiohos *et al.* 2007, Papadakis and Tsimas 2002). Today, research studies (Genesan *et al.* 2007, Frias *et al.* 2007, Tangchirapat and Jaturapitakkul 2010, Sousa-Coutinho and Papadakis 2011) are indicating the feasibility of using pozzolans originating from the agricultural industry, through biomass utilization. Biomass in general, considered as one of the major renewable energy sources (in absolute terms), accounts for more than 4% of the total energy consumption in the European Union (EU) (IEA 2011). However, despite its wide use as energy source much of the waste produced remain unprocessed (Von Bergs and Feuerborn 2005). Various types of biomass, from agro-industrial processes, produces ash (as rice husk ash, palm oil fuel ash, sugar cane bagasse ash, etc.) which under certain conditions

(chemical configuration, level of fineness) can have a similar pozzolanic activity to coal fly ash (Genesan *et al.* 2007, Frias *et al.* 2007, Tangchirapat and Jaturapitakkul 2010, Sousa-Coutinho and Papadakis 2011, Wang *et al.* 2008). These agro-waste ashes, containing a large amount of silica in amorphous form, have potential for use as pozzolanic materials replacing cement (Rajamma *et al.* 2009).

Strict interpretation of ASTM C618 2012 (and of most standards in other countries addressing a similar issue) precludes the use of any material (including biomass ash) not derived from coal combustion, in cement and concrete utilization. The fraction of fly ash that qualifies under this strict interpretation for use in concrete is in rapid decline due to issues such as co-firing fuels with coal and injecting a variety of materials for emission control (Wang *et al.* 2008). This observation is essential, due to the fact that biomass ash can be originated through a number of processes including pure solid biomass combustion or co-firing (of a less than 10% biomass by energy content) with coal. In terms of the latter, eventhough biomass co-firing is a way of producing cost effective and efficient renewable power, the relatively low amounts of biomass in the co-firing process leads in general to low contents of the biomass derived ash. Solid biomass combustion is a proven technology for heat and power production, where the technologies of fluidized bed and grate furnace combustion are mainly used (Loo and Koppejan 2003, Yin *et al.* 2008). The quantity and quality of ashes produced in a biomass power plant are strongly influenced by the characteristics of the biomass used: agriculture wastes or herbaceous biomass, wood or bark (Loo and Koppejan 2003, Masia *et al.* 2007). Combustion of wood, for example, generates fewer amounts of ashes to be managed, because herbaceous biomass, agriculture wastes and bark have higher ash content when compared to wood (Rajamma *et al.* 2009). Biomass ashes differ from coal ashes, in terms of chemistry and mineralogy. The characteristics of ashes from biomass combustion vary widely and are influenced by: (i) biomass characteristics (for example, herbaceous material, wood or bark), (ii) combustion technology (for example, fixed bed or fluidized bed), (iii) the location where the ashes are collected (for example, bottom ashes or fly ashes) (Loo and Koppejan 2003, Yin *et al.* 2008, Obernberger *et al.* 1997). Typically, fly ash from neat biomass combustion has more alkali (Na and K) and less alumina (Al_2O_3) than coal fly ash (Llorente and Garcia 2006, Thy *et al.* 2006).

Most of the biomass ash produced in thermal power plants is either disposed of in landfill or recycled on agricultural fields or forest (Loo and Koppejan 2003). Considering that the disposal cost of biomass ashes and biomass ash volumes are increasing (worldwide), a sustainable ash management has to be established. In addition, exploitation by the cement/concrete industry of agro-industrial ashes can be an attractive activity for several countries which use great volumes of rice husk, palm oil fuels and sugar cane bagasse as biomass in processes of energy cogeneration (such as China, India, Brazil and Thailand).

Considerable amount of work on developing analytical models for the evaluation of (traditional) SCM in concrete using the concept of efficiency factors (or k-values, to compare the relative performance of supplementary cementing materials on concrete durability, Papadakis *et al.* 2002, Antiohos *et al.* 2007, Papadakis and Tsimas 2002) has identified the high-added value of certain types of these materials and their pozzolanic properties on cement and mortar and the effects they entail on early concrete strength and volume stability (Papadakis 1999a, Papadakis 1999b, Papadakis and Demis 2013).

The same principle can be applied to biomass ashes, as presented in this chapter. By selecting data from representative biomass ashes from the literature, the feasibility of their utilization in cement manufacturing, as pozzolanic materials is investigated. An evaluation of the ashes in terms of the derived efficiency factors for 28 days compressive strength (as calculated based on the analytical models of strength prediction developed and validated elsewhere; Papadakis and Demis 2013), further enhanced by their performance in chloride penetration (as defined in ASTM C 1202 2012) is presented in this study. The main aim is to try to shed some light on the specific influence of the main characteristics of biomass ashes on concrete strength development and performance in chloride exposure, exploring in this way their future utilization in cement and concrete manufacturing.

4.2 Types and evaluation methodology for biomass ashes

4.2.1 Types of biomass ashes investigated

Based on data from the literature, a range of characteristic types of biomass (and other) ashes was selected, including rice husk ash and mixtures (*RHA*), palm oil fuel ash (*POFA*), sugar cane bagasse ashes (*SCBA*) and wood ashes (*WA*). Their origin and main points concerning their chemical composition is briefly discussed bellow and presented in Table 4.1.

Rice husk ash (*RHA*), an agricultural waste material, produced by controlled burning of rice husk has shown to contain highly reactive silica which could contribute chemically to Portland cement ingredients. Typical highly reactive *RHA* ashes (Hwang *et al.* 2011, Saraswathy and Song 2007, Ganesan *et al.* 2008) with SiO_2 content of more than 90% were selected. Their reactivity is attributed to the high content of amorphous silica, and to the very large surface area governed by the porous structure of the particles. Generally, the reactivity is also favored by increasing the fineness of the *RHA* (expressed in this study as the median size d_{50} in μm). In addition certain *RHA* mixtures, utilizing eucalyptus bark (*RHBA*) and chop wood (*BRWA*) were also selected. Rice husk–bark ash (Chalee *et al.* 2013) is a by-product produced from burning a mixture of rice husk (65%) and eucalyptus bark (35%)

by fluidized bed combustion process in a biomass power plant (used as fuel). The level of SiO_2 (of more than 74%) indicates a high potential for pozzolanic reactivity. According to ASTM C 618, this particular type of biomass ash can be said to be Class N pozzolan since the sum of SiO_2, Al_2O_3, and Fe_2O_3 are higher than or close to 70%, SO_3 content is not higher than 4%, and loss of ignition (LOI) is close to 10%.

Table 4.1 Chemical composition and characterization of biomass ashes.

Type		SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	SO_3 (%)	Na_2O_3 (%)	K_2O (%)	LOI	d_{50} (µm)	Density (kg/m³)	*
Rice	GRHBA[1]	87.0	1.08	2.58	1.25	0.09	0.08	1.0	5.71	10.8	2150	k
Husk	GRHBA[2]	74.8	0.20	0.80	5.90	0.50	0.20	2.0	11.2	10.8	2150	k
Ash	BRWA[3]	78.4	2.60	1.70	7.40	1.10	0.20	3.7	3.60	15.5	2100	k
	RHA[4]	91.0	0.35	0.41	1.95	1.21	0.08	3.21	8.50	12.0	2060	k
	RHA[5]	87.3	0.22	0.28	0.48	-	1.02	3.14	2.10	3.80	2060	k, RCPT⁻
	RHA[6]	92.9	0.31	0.26	0.53	-	0.08	2.06	1.97	-	-	RCPT
	RHA[7]	91.6	0.35	0.40	0.60	-	0.30	1.60	3.70	7.41	2050	RCPT
Palm	GPOFA[8]	65.3	2.50	1.90	6.40	0.40	0.30	5.70	10.0	19.9	2170	k
Oil	GPOFA[9]	65.3	2.50	1.90	6.40	0.40	0.30	5.70	10.0	10.1	2330	k
Fuel	GPOFA[10]	65.3	2.60	2.00	6.40	0.50	0.30	5.70	10.1	10.1	2330	k
Ash	POFA[11]	55.5	9.20	5.60	12.4	2.30	-	-	7.90	10.7	2530	k
	POFA[12]	63.6	1.60	1.40	7.60	0.20	0.10	6.90	9.60	7.20	2250	RCPT
Sugar	SCBA[13]	78.3	8.90	3.60	2.20	-	0.10	3.50	-	2.70	2530	k
Cane	SCBA[14]	64.2	9.05	5.52	8.14	-	0.92	1.35	4.90	5.40	1850	k, RCPT
b. ash	SCBA[15]	78.4	8.55	3.61	2.15	-	0.12	3.46	0.42	-	2530	k, RCPT⁻
Wood	W(S)A[16]	31.8	28.0	2.64	10.5	0.45	6.50	10.4	27.0	-	2130	k
Ash	HCWA[17]	28.0	4.10	2.50	39.0	1.00	1.00	7.40	7.22	5.16	2520	k

[1] GRHBA: Ground rice husk bark ash, 65% rice husk and 35% eucalyptus bark, Chalee *et al.* 2013
[2] GRHBA: Ground rice husk bark ash, Sata *et al.* 2007
[3] BRWA: Bagasse rice husk wood ash, 15% rice husk, 82.5% bagasse ash and 2.5% chop wood, Horsakulthai *et al.* 2011
[4] RHA: Rice husk ash, Hwang *et al.* 2011
[5] RHA: Rice husk ash, Ganesan *et al.* 2008
[6] RHA: Rice husk ash, Saraswathy and Song 2007
[7] RHA: Rice husk ash, Chindaprasirt *et al.* 2008
[8] GPOFA: Ground palm oil fuel ash, coarse ground, Tangchirapat and Jaturapitakkul 2010
[9] GPOFA: Ground palm oil fuel ash, fine ground, Tangchirapat and Jaturapitakkul 2010
[10] GPOFA: Ground palm oil fuel ash, Sata *et al.* 2007
[11] POFA: Palm oil fuel ash, Tangchirapat *et al.* 2012
[12] POFA: Palm oil fuel ash, Chindaprasirt *et al.* 2008
[13] SCBA: Sugar cane bagasse ash, Cordeiro *et al.* 2012
[14] SCBA: Sugar cane bagasse ash, Ganesan *et al.* 2007
[15] SCBA: Sugar cane bagasse ash, Cordeiro *et al.* 2009
[16] W(S)A: Wood (sawdust) ash, Abdullahi 2006
[17] HCWA: High calcium wood ash, Chee and Mahyuddin 2012
* Denotes if the particular type of ash was used for strength (k) of for Rapid Chloride Permeability Test (RCPT) assessment

Bagasse-rice husk-wood ash (*BRWA*) (Horsakulthai *et al.* 2011) is a by-product obtained from biomass power plants that use bagasse (82.5%), rice husk (15%) and chop wood (2.5%) co-burning in producing steam for generating electricity to supply the sugar mills. It should be noted that most of the *BRWA* is disposed of as waste in landfill which causes environmental problems such as air pollution as well as groundwater quality problem owing to the leaching of metals from the ashes. In terms of chemical composition, the sum of SiO_2, Al_2O_3, and Fe_2O_3 was 82.7% and the LOI was 3.6% (< 10%) complying with ASTM C618 requirement as a natural pozzolan.

Palm oil fuel ash (*POFA*) is a by-product of the palm oil industry. It is a waste obtained from burning palm oil fibers, shells, and empty fruit bunches as fuel in producing steam to generate electricity for the palm oil extraction process. In general, it contains high amounts of silicon and aluminum oxides (in the amorphous state) and was recently accepted as a pozzolanic material (Tangchirapat and Jaturapitakkul 2010). According to the chemical composition of the types of *POFA* selected in this study (Tangchirapat and Jaturapitakkul 2010, Sata *et al.* 2007, Tangchirapat *et al.* 2012, Chindaprasirt *et al.* 2008), of an average SiO_2 composition from 55% to 65% and LOI in the region of 10%, it can be said that, although POFA is not a natural pozzolan, it may be classified as Class N (natural) pozzolan according to ASTM C618 2012.

Sugar Cane Bagasse Ash (*SCBA*) is a by-product of the industry involved with sugar cane and alcohol production. The bagasse is usually burned in boilers at temperatures varying from 700 to 900 °C. Preliminary investigations on SCBA have demonstrated that it presents the appropriate chemical composition for application as a pozzolan, mainly in regard to its high silica content and presence of amorphous silica (Cordeiro *et al.* 2009). However, it is important to note that the SiO_2 content (78.3%) covers amorphous and crystalline silica (from SCBA) and some sand contamination has been observed, identified by the presence of quartz and cristobalite phases in the diffraction patterns of SCBA. This high content of quartz is ultimately due to sand adhered to the sugar cane, which is harvested along with it. Even after washing the sugar cane, sand can represent as much as 2% in weight of the material that is processed (Cordeiro *et al.* 2009). After the loss of organic matter during bagasse burning, this proportion increases significantly. The presence of cristobalite, previously mentioned, can be associated to the high temperature in the boiler.

Wood ash (*WA*) is the inorganic and organic residue generated due to combustion of wood and wood products (chips, saw dust, bark, etc.). Typically wood burned for fuel at pulp/paper mills or at wood products industries, consist of saw dust, wood chips, bark, saw mill scraps, hard chips rejected from pulping and excess screenings sheaves (Abdullahi 2006). In a sense it can be related to fly ash since fly ash is obtained from coal, which is a fossilized wood. The chemical composition of the selected types of WA indicates very high LOI, high alkali content and very low SiO_2 values. Overall, these

particular types of WA do not satisfy the requirements prescribed in ASTM Standard C618 to be classified as a Class N pozzolan. It should also be noted that the high loss of ignition means that the wood ash contains appreciable amount of un-burnt carbon which reduces its pozzolanic activity. The un-burnt carbon is not pozzolanic and its presence serves as filler to the mixture.

4.2.2   Methodology followed for the evaluation of biomass ashes as cementitious materials

According to the chemical configuration of these types of ashes, the mix design (w/c ratio, cement content, SCM replacement level, aggregate size) used in each particular study and based on the compressive strength data available from the literature (noted as experimental), estimation of the compressive strength for a range of *k*-values, took place. Such calculations were possible using an analytical tool for the estimation of concrete strength and service life; EUCON; Papadakis and Efstathiou 2005. For each type of biomass ash used in this study, different sets of compressive strength data were estimated for a range of *k*-values (from the very low value of 0.2 to higher values of 1.7). Each set of strength data, was evaluated in terms of statistical proximity to the experimental strength values, based on the principles of the least squares method (Table 4.2, Figure 4.1). The *k*-value of the set of data that provided the best fit was assumed to be the efficiency factor (for 28 days compressive strength) of the biomass ash.

In addition, where data were available, the performance of biomass ashes in terms of chloride ion penetration, expressed as the total charge passed through biomass ash blended concrete specimens (measured according to ASTM C 1202), were evaluated. Based on the values of charge (Coulombs) passed through each individual biomass ash concrete investigated, with increasing SCM content, the difference (%) to control (no SCM addition) was calculated, as it is illustrated in Section 4.3.2 of this study.

Table 4.2   Regression analysis for the calculation of *k*-value of ashes based on the estimation of compressive strength (representative example for Ground Rice Husk Bark Ash, Sata *et al.* 2007).

SCM		Experimental compressive strength (MPa)	Calculated Compressive Strength (MPa)			
			k factor for 28 days compressive strength			
Type	(%)		1.0	1.2	1.4	1.6
GRHBA	0	78	80.1	80.1	80.1	80.1
	10	86	80.1	81.8	83.4	85.0
	20	88	80.3	83.6	86.7	89.9
	30	85	71.0	74.0	77.1	82.0
		SLSQ	294.5	162.4	75.3	**18.0**
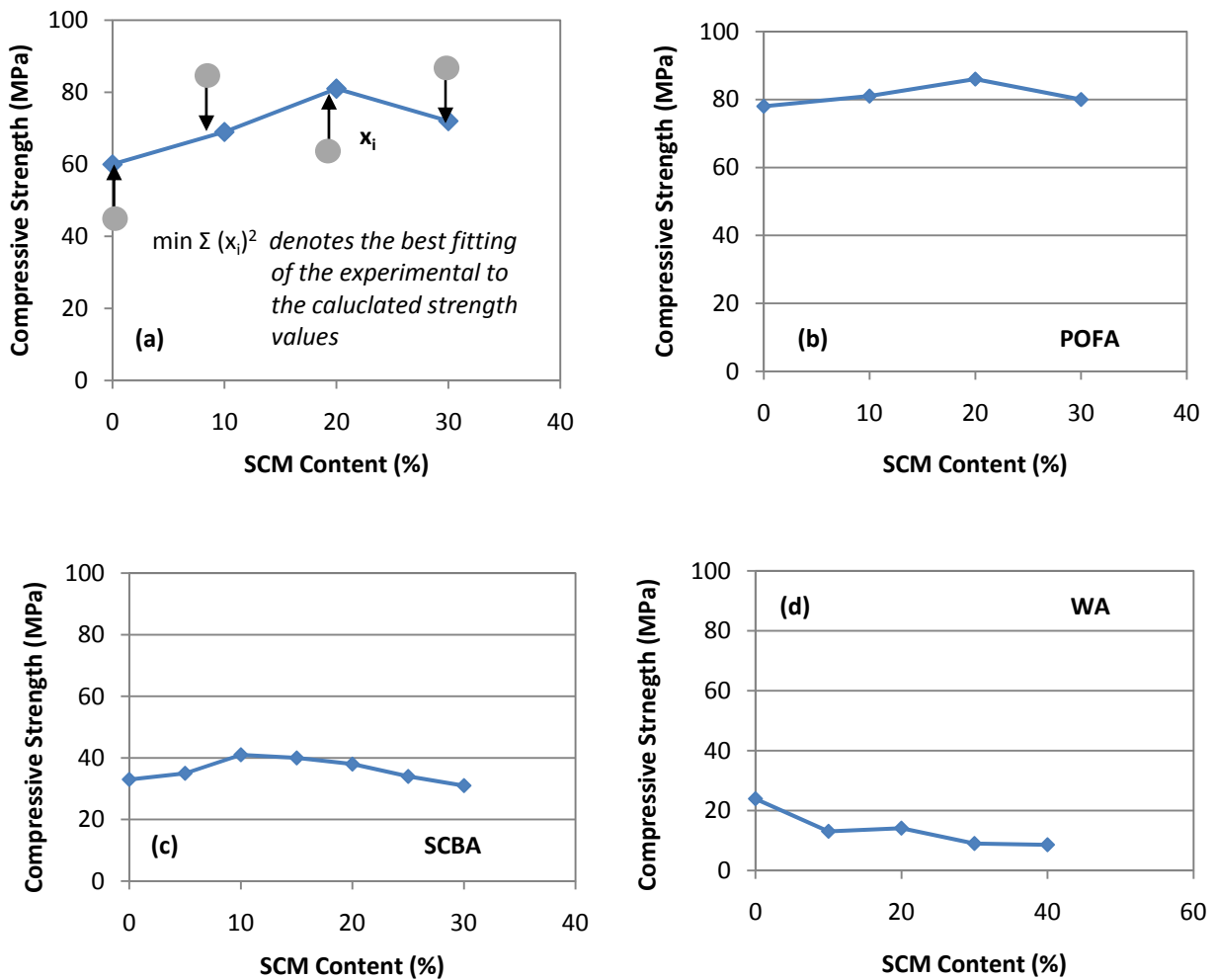
Figure 4.1   Estimation of k-factor using regression analysis, (a) schematic overview, and typical examples (b) POFA, Sata et al. 2007, (c) SCBA, Ganesan et al. 2007, and (d) WA, Abdullahi 2006.

4.3   Results of biomass ashes evaluation

In terms of compressive strength development it should be noted that, a common observation from the literature (as indicated in Figure 4.1) is that there is an optimum level of cement replacement by biomass ashes. After a certain percentage of biomass ash, the derived strength values are reducing (in some cases being higher than control). This can be attributed to the initial fast rate of the pozzolanic reaction, which at high replacement levels this rate drops at values bellow one and the filler effect becomes more pronounced.

Overall, in most of the RHA mixtures the high levels of amorphous silica and the fine particle size of RHA are the principle reasons for the excellent pozzolanic activity and the increase in compressive strength observed.

Utilisation of Palm oil fuel ashes (with SiO_2 content on average in the region of 65%, less than that of the RHA types of ashes) in the concrete mix contributed to the compressive strength, via a fast pozzolanic reaction, depending on the level of fineness of the POFA. The compressive strength of concrete with 20% POFA (Sata *et al.* 2009) was found to be higher than those of 10% and 30% (Figure 4.1b). At another study (Tangchirapat and Jaturapitakkul 2010) for the same percentage of POFA (20%) of the same chemical composition but of different level of fineness (of median size 19.9 μm and 10.1 μm) the one with the lower median size resulted in higher compressive strength (33 MPa, for d_{50} of 10.1 μm, compared to 27 MPa for d_{50} of 19.1 μm) at 28 days.

The same was noticed on SCBA mixes (Ganesan *et al.* 2007). Up to 20% replacement level the compressive strength was higher compared to control specimens, while at higher levels the strength was decreased.

As far as WA is concerned, results from the literature (Abdullahi 2006, Chee and Mahyuddin 2012) showed in general the increase in the levels of cement replacement resulted in a gradual decrease in the compressive strength. Despite the subsequent strength reduction per increasing level of WA incorporation, the mix containing 20% wood ash had higher strength than that containing 10% wood ash at 28 days. This was due to the fact that the silica provided by 10% wood ash was inadequate to react with the calcium hydroxide produced by the hydration of cement. Increase in wood ash content beyond 20% resulted in a reduction in strength. In this case the silica present in the mix was in excess of the amount required to combine with the calcium hydroxide from the hydrating cement. The excess silica had no pozzolanic value but only served as filler.

4.3.1 Efficiency factors

An overview of the calculated k-factors, per group category of the biomass ashes investigated, is illustrated in Figure 4.2 and given Table 4.3. A first observation is that the different origins and chemical configurations of the individual ashes resulted in different *k*-values. Overall, on average, a k-value of 1.38 was calculated for rice husk (and mixtures) ashes, while for palm oil fuel and sugar cane bagasse ashes the corresponding efficiency factors were found to be 1.2 and 0.5 (respectively). As it was expected wood contained ashes gave *k*-values bellow 0.2.
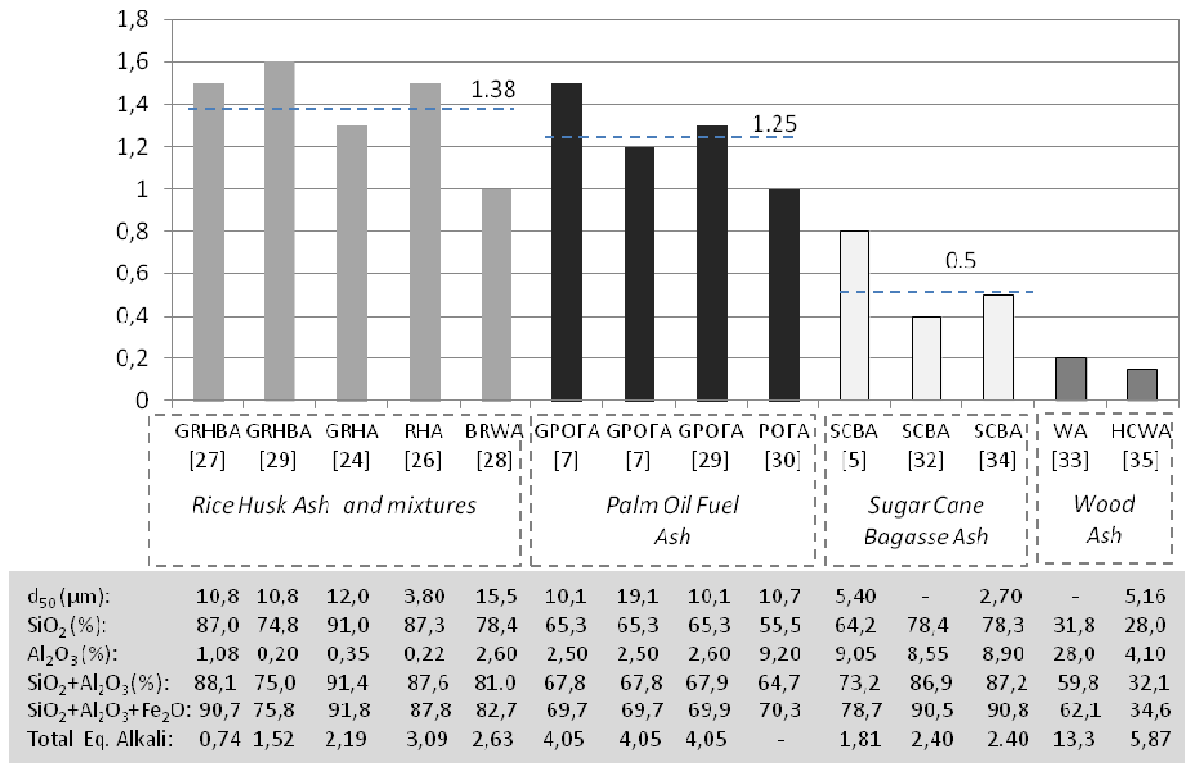
Figure 4.2   Estimation of k-values of various biomass ashes.

Table 4.3   k-values of ashes investigated in this study.

SCM Type	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	1+2 (%)	1+2+3 (%)	CaO (%)	SO$_3$ (%)	Na$_2$O$_3$ (%)	K$_2$O (%)	LOI (%)	d$_{50}$ (μm)	k
GRHBA	87.0	1.08	2.58	88.1	90.7	1.25	0.09	0.08	1.00	5.71	10.8	**1.5**
GRHBA	74.8	0.20	0.80	75.0	75.8	5.90	0.50	0.20	2.00	11.2	10.8	**1.6**
RHA	91.0	0.35	0.41	91.3	91.8	1.95	1.21	0.08	3.21	8.50	12.0	**1.3**
RHA	87.3	0.22	0.28	87.5	87.8	0.48	-	1.02	3.14	2.10	3.80	**1.5**
BRWA	78.4	2.60	1.70	81.0	82.7	7.40	1.10	0.20	3.70	3.60	15.5	**1.0**
GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	0.30	5.70	10.0	10.1	**1.5**
GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	0.30	5.70	10.0	19.1	**1.2**
GPOFA	65.3	2.60	2.00	67.9	69.9	6.40	0.50	0.30	5.70	10.1	10.1	**1.3**
POFA	55.5	9.20	5.60	64.7	70.3	12.4	2.30	-	-	7.90	10.7	**1.0**
SCBA	64.2	9.05	5.52	73.2	78.7	8.14	-	0.92	1.35	4.90	5.40	**0.8**
SCBA	78.3	8.55	3.61	86.9	90.5	2.15	-	0.12	3.46	0.42	-	**0.4**
SCBA	78.3	8.90	3.60	87.2	90.8	2.20	-	0.10	3.50	-	2.70	**0.5**
W(S)A	31.8	28.0	2.64	59.8	62.1	10.5	0.45	6.50	10.4	27.0	-	**0.2**
HCWA	28.0	4.10	2.50	32.1	34.6	39.0	1.00	1.00	7.40	7.22	5.16	**0.15**

In particular the following main observations can be made:

- RHA and mixtures (rich in rice husk ash) produced *k*-values of above 1.3, up to 1.6 (except BRWA, Horsakulthai *et al.* 2011, with a RHA participation of 15%, which gave a *k*-value of 1.0).

- The low level of fineness (expressed as d_{50}) from 3.8 μm to 10.8 μm, does not seem to have a profound effect on the derived k-factors, since RHA of similar compositions produced values of 1.5 to 1.6. However, for a median size of 12 μm, the derived efficiency factor was slightly lower (1.3).

- These inconsistencies with the level of fineness were also observed in the case of sugar cane bagasse ash (SCBA), but for similar (low) d_{50} values. A particular type of SCBA with a d_{50} of 2.70 μm, produced a *k*-value of 0.5 (Cordeiro *et al.* 2012), while a similar type of SCBA with larger d_{50} value of 5.4 μm, produced a *k*-value of 0.8 (Ganesan *et al.* 2007). This difference however can be attributed on the fact that the SCBA with the low k-value was rich in crystalline silica.

- Palm oil fuel ashes (POFA) with less SiO_2 content than RHA produced in certain cases similar k-factors (1.3; Sata *et al.* 2007, 1.5; Tangchirapat and Jaturapitakkul 2010).

- The level of fineness appears to have some effect on POFA mixtures (Tangchirapat and Jaturapitakkul 2010, Sata *et al.* 2007, Tangchirapat *et al.* 2012). For the same chemical composition of POFA reduction of the d_{50} from 19.1 μm to 10.1 μm (Tangchirapat and Jaturapitakkul 2010) was translated as an increase of the *k*-values (from 1.2 to 1.5). However, another type of POFA with a similar level of fineness to 10.1 μm (10.7 μm) (Tangchirapat *et al.* 2012) produced a *k*-value of 1.0 (much lower than 1.5).

4.3.2   Chloride penetration

As it was previously mentioned, where data were available, the performance of biomass ashes in terms of chloride ion penetration, (measured according to ASTM C 1202), was evaluated. The difference (%) to control (no SCM addition) in terms of charge passed per increasing SCM content is given in Table 4.4 and Fig. 4.3.

Overall, the charge passed was substantially reduced with incorporation of biomass ashes into the concrete mix. Cement replacement by rice husk ash drastically reduced the (per ASTM C1202) rapid chloride penetrability of concrete from a low (charge ranging from 1000 to 2000 C) to very low (charge ranging from 100 to 1000 C) ratings (per ASTM C1202). In general RHA was found to be more drastic in that sense, than SCBA and POFA. Incorporation of 20% RHA (Figure 4.3a) produced a reduction in the charge passed of more than 60% (and up to 90%), while at lower biomass ash quantities (10%) a steady reduction (for all RHA investigated) of 43% on average was noticed.

Table 4.4   Performance in RCPT in terms of reduction in electrical charge passed.

SCM (%)	SCBA [5]		SCBA [32]		RHA [25]		RHA [31]		RHA [26]		POFA [31]	
	(C)	**D(%)**	*(C)*	**D(%)**	*(C)*	**D(%)**	*(C)*	**D(%)**	*(C)*	**D(%)**	*(C)*	**D(%)**
0	*2780*	0	*1179*	0	*1161*	0	*7450*	0	*2870*	0	*7450*	0
5	*2045*	26.4	*783*	33.6	*1108*	4.57	-	-	*2200*	23.3	-	-
10	*1850*	33.5	*774*	34.4	*653*	43.8	-	-	*1500*	47.7	-	-
15	*1300*	53.3	*882*	25.2	*309*	73.4	-	-	*1250*	56.5	-	-
20	*1200*	56.8	-	-	*265*	77.2	*750*	89.9	*1000*	65.2	*1950*	73.8
25	*1050*	62.2	-	-	*213*	81.7	-	-	*850*	70.4	-	-
30	*2090*	24.8	-	-	*273*	76.5	-	-	*780*	72.8	-	-
35	-	-	-	-	-	-	-	-	*950*	66.9	-	-
40	-	-	-	-	-	-	*250*	96.6	-	-	*1000*	86.6

(C) Charge passed (in Coulombs), (D)   Difference to the control value (%)
charge ranging from 1000 to 2000 C: low permeability, while from 100 to 1000 C: very low permeability
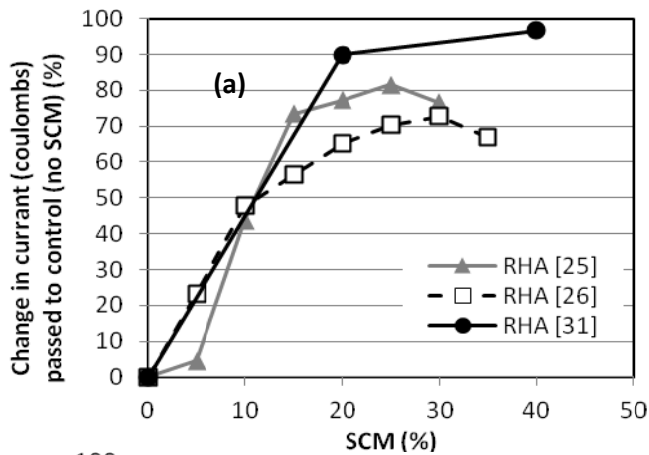
	RHA [25]	RHA [31]	RHA [26]
SiO$_2$ (%)	92.9	91.6	87.3
Al$_2$O$_3$ (%)	0.31	0.35	0.22
Fe$_2$O$_3$ (%)	0.26	0.40	0.28
CaO (%)	0.53	0.60	0.48
SO$_3$ (%)	-	-	-
LOI (%)	1.97	3.70	2.10
d$_{50}$ (μm)	-	7.41	3.80
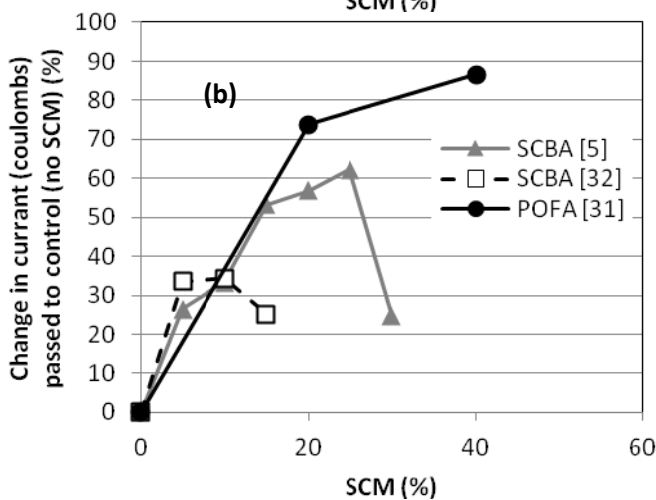
	SCBA [5]	SCBA [32]	POFA [31]
SiO$_2$ (%)	64.2	78.4	63.6
Al$_2$O$_3$ (%)	9.05	8.55	1.60
Fe$_2$O$_3$ (%)	5.52	3.61	1.40
CaO (%)	8.14	2.15	7.60
SO$_3$ (%)	-	-	0.20
LOI (%)	4.90	0.42	9.60
d$_{50}$ (μm)	5.40	-	7.20

Figure 4.3   Performance of representative biomass ashes in RCPT.

4.4 Discussion

Trying to identify the specific influence of the main characteristics of the biomass ashes on the efficiency factors, it can be noted that:

- overall RHAs, rich in SiO_2 content (> 85%), produced high k-values,
- wood containing ashes, with very low SiO_2 content (< 30%), produced the lowest k-values.

Hence, it appears that the influence of SiO_2 should be quite significant on the derived k-value of the ash. However, considering that SCBA with higher SiO_2 content than that of POFA produced smaller k-values than the latter type of ash, the influence of SiO_2 content is not straight forward.

In the literature (Papadakis *et al.* 2002, Papadakis and Tsimas 2002, Lothenbach *et al.* 2012) there is a consensus that the activity of SCMs, in general (including biomass ashes), is mainly attributed to the fact that they possess significant contents of active constituents (active silica) that combine with $Ca(OH)_2$ produced from cement hydration to form hydration products with binding properties. It is the active silica (non-crystalline silica glass, present in the amorphous and mostly vitreous part of the SCM), which is part of the total silica content of the SCM that is involved in the hydration reactions producing CSH to which the strengthening of cement is attributed. However, for the variety of biomass ashes investigated in this study, information on the active silica content was unavailable. On this note, benchmarking of the different types of ashes used in this project in terms of the influence of SiO_2 content and of the added influence of SiO_2 with the other primary oxides (Al_2O_3, Fe_2O_3), on the derived efficiency factors, is given in Table 4.5 and illustrated in Figure 4.4.

Although a trend, that with reducing SiO_2 content smaller derived k-values are derived, is slightly evident (Figure 4.4a), certain "abnormalities" (points 4, 5, 6 and 11 illustrated in Figure 4.4a and highlighted in Table 4.5a) distort this image.

A closer look reveals that ashes with high SiO_2 content and low (up to 2.6 %) Al_2O_3 and Fe_2O_3 contents produced higher than 1.0 k-values. On the other hand ashes with high Al_2O_3 (more than 8%) and Fe_2O_3 (above 2.6%) even if they are rich in SiO_2 (78%), they produced k-values bellow 0.8. The previously mentioned "abnormalities" refer to such types of ashes, namely sugar cane bagasse ashes; points 5 (Abdullahi 2006), 6 (Cordeiro *et al.* 2012), 11 (Ganesan *et al.* 2007) in Figure 4.4a.

Table 4.5 Biomass ash results categorized by primary oxide contents; [a] SiO$_2$ (%), [b] SiO$_2$+Al$_2$O$_3$ (%) and [c] SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ (%) contents.

	a/a	SCM Type	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	Si+Al (%)	Si+Al+Fe (%)	CaO (%)	SO$_3$ (%)	Eq. Alk. (%)	LOI (%)	d$_{50}$ (μm)	k
[a]	1	GRHA	91.0	0.35	0.41	91.4	91.8	1.95	1.21	2.19	8.50	12.0	1.3
	2	RHA	87.3	0.22	0.28	87.5	87.8	0.48	-	3.09	2.10	3.80	1.5
	3	GRHBA	87.0	1.08	2.58	88.1	90.7	1.25	0.09	0.74	5.71	10.8	1.5
	4	BRWA	78.4	2.60	1.70	81.0	82.7	7.40	1.10	2.63	3.60	15.5	1
	5	SCBA	78.3	8.55	3.61	86.9	90.5	2.15	-	2.40	0.42	-	0.4
	6	SCBA	78.3	8.90	3.60	87.2	90.8	8.14	-	1.81	4.90	5.40	0.5
	7	GRHBA	74.8	0.20	0.80	75.0	75.8	5.90	0.50	1.52	11.2	10.8	1.6
	8	GPOFA	65.3	2.60	2.00	67.9	69.9	6.40	0.50	4.05	10.1	10.1	1.3
	9	GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	10.1	1.5
	10	GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	19.1	1.2
	11	SCBA	64.1	9.05	5.52	73.2	78.7	8.14	-	1.81	4.90	5.40	0.8
	12	POFA	55.5	9.20	5.60	64.7	70.3	12.40	2.30	0.00	7.90	10.7	1
	13	WA	31.8	28.0	2.34	59.8	62.1	10.53	0.45	13.3	27.0	-	0.2
	14	HCWA	28.0	4.10	2.50	32.1	34.6	39.0	1.00	5.87	7.22	5.16	0.15
[b]	1	GRHA	91.0	0.35	0.41	91.4	91.8	1.95	1.21	2.19	8.50	12.0	1.3
	2	GRHBA	87.0	1.08	2.58	88.1	90.7	1.25	0.09	0.74	5.71	10.8	1.5
	3	RHA	87.3	0.22	0.28	87.5	87.8	0.48	-	3.09	2.10	3.80	1.5
	4	SCBA	78.3	8.90	3.60	87.2	90.8	8.14	-	1.81	4.90	5.40	0.5
	5	SCBA	78.3	8.55	3.61	86.9	90.5	2.15	-	2.40	0.42	-	0.4
	6	BRWA	78.4	2.60	1.70	81.0	82.7	7.40	1.10	2.63	3.60	15.5	1
	7	GRHBA	74.8	0.20	0.80	75.0	75.8	5.90	0.50	1.52	11.2	10.8	1.6
	8	SCBA	64.2	9.05	5.52	73.2	78.7	8.14	-	1.81	4.90	5.40	0.8
	9	GPOFA	65.3	2.60	2.00	67.9	69.9	6.40	0.50	4.05	10.1	10.1	1.3
	10	GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	10.1	1.5
	11	GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	19.1	1.2
	12	POFA	55.5	9.20	5.60	64.7	70.3	12.4	2.30	0.00	7.90	10.7	1
	13	WA	31.8	28.0	2.34	59.8	62.1	10.5	0.45	13.3	27.0	-	0.2
	14	HCWA	28.0	4.10	2.50	32.1	34.6	39.0	1.00	5.87	7.22	5.16	0.15
[c]	1	GRHA	91.0	0.35	0.41	91.8	91.4	1.95	1.21	2.19	8.50	12.0	1.3
	2	SCBA	78.3	8.90	3.60	90.8	87.2	8.14	-	1.81	4.90	5.40	0.5
	3	GRHBA	87.0	1.08	2.58	90.7	88.1	1.25	0.09	0.74	5.71	10.8	1.5
	4	SCBA	78.3	8.55	3.61	90.5	86.9	2.15	-	2.40	0.42	-	0.4
	5	RHA	87.3	0.22	0.28	87.8	87.5	0.48	-	3.09	2.10	3.80	1.5
	6	BRWA	78.4	2.60	1.70	82.7	81.0	7.40	1.10	2.63	3.60	15.5	1
	7	SCBA	64.2	9.05	5.52	78.7	73.2	8.14	-	1.81	4.90	5.40	0.8
	8	GRHBA	74.8	0.20	0.80	75.8	75.0	5.90	0.50	1.52	11.2	10.8	1.6
	9	POFA	55.5	9.20	5.60	70.3	64.7	12.4	2.30	0.00	7.90	10.7	1
	10	GPOFA	65.3	2.60	2.00	69.9	67.9	6.40	0.50	4.05	10.1	10.1	1.3
	11	GPOFA	65.3	2.50	1.90	69.7	67.8	6.40	0.40	4.05	10.0	10.1	1.5
	12	GPOFA	65.3	2.50	1.90	69.7	67.8	6.40	0.40	4.05	10.0	19.1	1.2
	13	WA	31.8	28.0	2.34	62.1	59.8	10.5	0.45	13.33	27.0	-	0.2
	14	HCWA	28.0	4.10	2.50	34.6	32.1	39.0	1.00	5.87	7.22	5.16	0.15
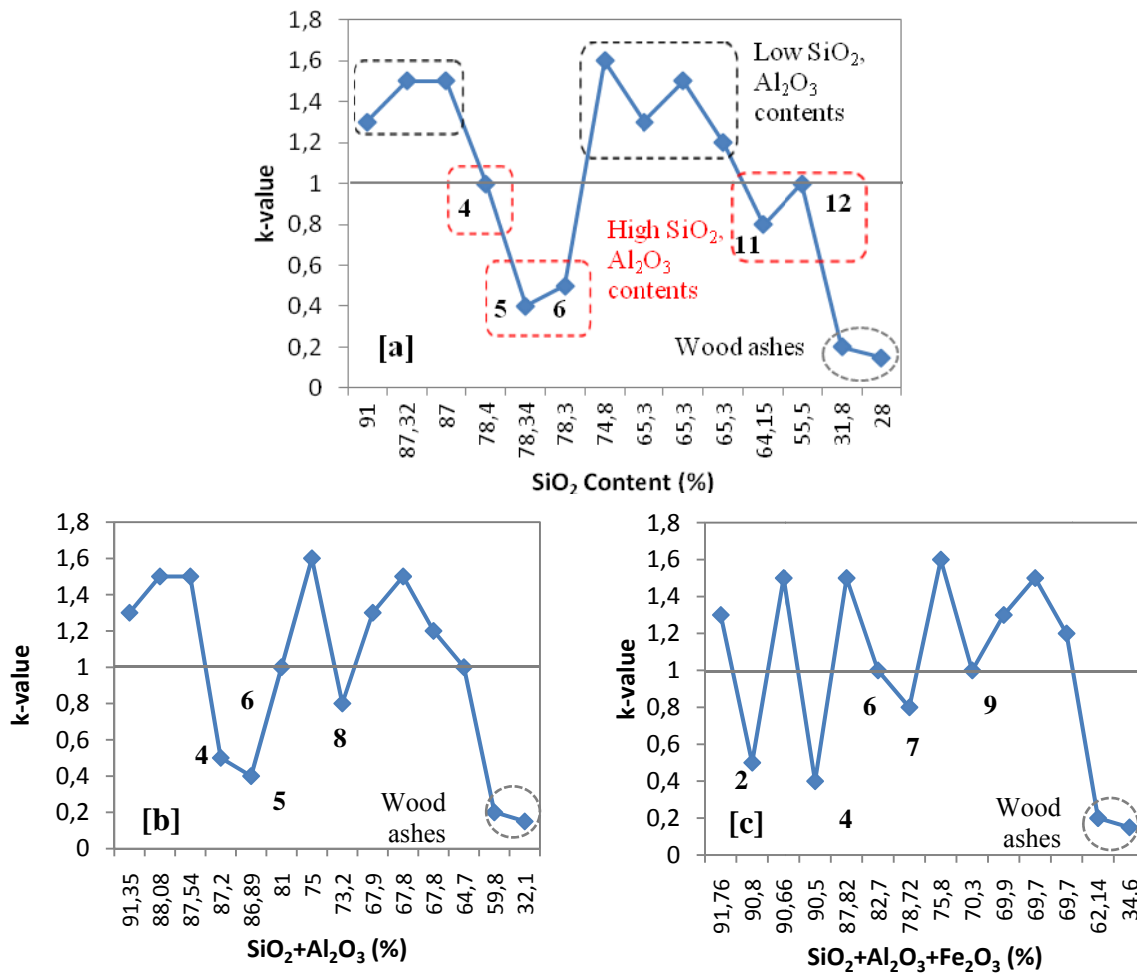
Figure 4.4 Effect of primary oxide contents on k-values of biomass ashes; [a] SiO_2 (%), [b] $SiO_2+Al_2O_3$ (%) and [c] $SiO_2+Al_2O_3+Fe_2O_3$ (%) content.

In addition to the above, two further points strike out. A type of POFA (Tangchirapat *et al.* 2012) (point 12) with high Al_2O_3 and Fe_2O_3 contents but also rich in CaO (12.4%) and a mixture type of ash, BRWA (Horsakulthai et al. 2011) (point 4) containing a very small portion (15%) of rice husk wood ash, being low in Al_2O_3 and Fe_2O_3 contents but high in CaO (7.4%).

Hence the influence of the level of SiO_2 in the ash does carry certain validity on the derived value of the efficiency factor, but is also affected by the composition of the ash in other oxides. On that note, the influence of SiO_2 in connection to the other major oxides (Al_2O_3 and Fe_2O_3) is examined. By investigating the combined effect of $SiO_2+Al_2O_3$ content, a similar behavior is observed (Table 4.5bc, Figure 4.4b, c). The same trend/mishaps is observed as in the case of the effect of SiO_2 content, with the same types of ashes and their particularities as previously explained (in primary oxides and CaO

composition) deviating to a great extend. Such a deviation becomes even clearer when the combined effect of all three major oxides on the derived k-values is investigated (Table 4.5c, Figure 4.4c).

A common observation of all of the above mentioned ash classifications (in terms of their primary oxide contents) is that certain types of rice husk ash by producing high *k*-values, appear at the top of these classifications, while, wood containing type of ashes (WA; Abdullahi 2006, HCWA; Chee and Mahyuddin 2012), with very low derived efficiency factors (< 0.2), appear at the bottom. This is not surprising since wood ashes, usually have very low contents in SiO_2 and contain appreciable amounts of un-burnt carbon (up to 27% in a particular WA, Abdullahi 2006, investigated in this study) which reduces their pozzolanic activity to a great extend. Unburned carbon is not pozzolanic and its presence serves as filler to the mixture causing however problems of volume stability. High unburned carbon contents, the main form of LOI (loss on ignition) in the ash, are known to be responsible for strength development and durability associated problems (increased water demand, increased permeability; Hwang *et al.* 2011, Cordeiro *et al.* 2012, Wang and Baxter 2007).

It should be noted at this stage, that when the ash is produced in industrial combustion systems (as the majority of the ashes investigated in this study), the temperature of combustion, the cleanliness of the biomass fuel and the technology used can have profound effects on the characteristics of the ash, especially on the unburned carbon content. Controlled burning at 800 °C, through a fluidized bed combustion process resulted in considerably higher values of LOI, compared to burning at 1300 °C (Sata *et al.* 2007). However, it has also been reported that smaller LOI values (or residual carbon contents) of up to 12%, exhibited by every type of biomass ash investigated in this study, except wood ash, did not have any detrimental effect on the strength and microstructure of cement and concrete (Hornain *et al.* 1992).

Overall, at this point, it can be concluded that upon a certain percentage in Al_2O_3, Fe_2O_3 and CaO contents, high SiO_2 content translates into a high *k*-value. However, at high compositions of CaO (even for low Al_2O_3, Fe_2O_3 contents) and/or at high contents of Al_2O_3, Fe_2O_3, the derived k-values are not "linear" with that high SiO_2 content. The way Al_2O_3, Fe_2O_3 and CaO contents influence the level of the derived k-value, (even for a high contained percentage of SiO_2 in the ash) is evident into the following Figure 4.5.

On the range of biomass ashes investigated in this study, of similar particle median size (d_{50}) and LOI, concentration in Al_2O_3 of more than 4.1% produced efficiency factors bellow 1.0, even for high SiO_2 content (more than 78%), as it illustrated at points 1 (Cordeiro *et al.* 2009) and 2 (Cordeiro *et al.* 2012) in Figure 4.5a. In terms of Fe_2O_3 (Figure 4.5b) and CaO (Figure 4.5c) contents, concentration of more than 3.0 % and 8.0 % respectively, produced efficiency factors well bellow 1.0. Overall, based on their

combined influence, it appears that as their percentages in the ash increase, the derived k-values drop bellow 1.0, well even bellow 0.5 (Figure 4.5d).
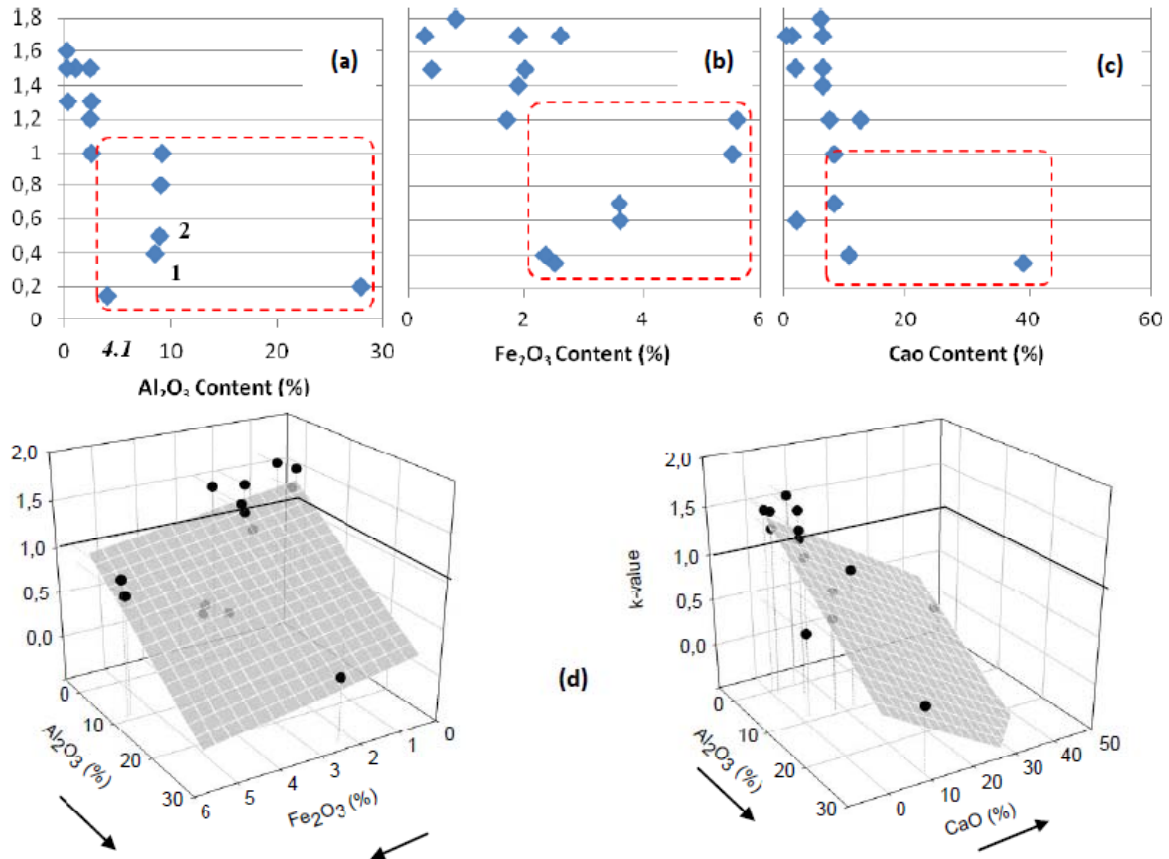
Figure 4.5   Effect of high quantities of Al₂O₃ (%) [a], Fe₂O₃ (%) [b] and CaO (%) [c] contents on k-values of ashes.

In terms of the influence of CaO results are contradictory. In theory, high CaO contents in the ash are expected to contribute to hydraulic activity (Rajamma 2011). The pozzolanic activity of the ash in a cement matrix enhances the formation of C-S-H gel, through the reaction of amorphous silica content of the ash with the free lime from cement hydration. On that note, high CaO contents have been found to further aid this particular process by reacting with the SiO_2 content of the ash (Ganesan *et al.* 2007). However, it has been reported that high carbon contents led to increased water demand of the concrete mix (Hwang *et al.* 2011, Sata *et al.* 2007).

Although, relatively high alumina contents (and iron oxide) in cement in the form of C_3A (3· CaO· Al_2O_3) or C_4AF (4· CaO· Al_2O_3· Fe_2O_3) phases, are known for their small contribution to early

strength development, their influence in the chloride binding capacity of the cement mix is crucial. High alumina contents can increase cement's potential for Friedel's salt production. The latter is formed as a result of the chloride binding by cementitious components (C_3A, C_4AF phases). This process is beneficial, as far as the permeability of chlorides is concerned, since formation of Friedel's salt results in a less porous structure, hence to reduced "transport" of chlorides into the concrete mix.

Such a less porous structure, was observed on a variety of the biomass ashes (RHA, POFA and in some SCBA) investigated in this study, based on the change of the reduction of chloride permeability from "low" to "very low" rating (according to ASTM C1202), as it was discussed in the previous section. Rapid Chloride Permeability Test (RCPT) indicated that the total charge passed on biomass ash concrete samples, was considerably reduced (compared to control samples), up to almost 90% (as it was indicated in Figure 4.3) for a 20% replacement by RHA. Considerable reductions were also noticed for other types of biomass ashes (73.8 % for 20% POFA incorporation and 56.8 % for SCBA).

In general, the transport of chloride ions (and the consequent electrochemical processes) through biomass ash blended concretes depends on the pore structure of the concrete, while the electrical conduction depends on both pore structure characteristics and electrical conductivity of the pore solution (Ganesan *et al.* 2008). Overall, the finer particles of ashes develop discontinuous and tortuous pore in concrete structure and the pores present in the concrete are completely filled up by finer particles.

Since the total charge passed through the concrete depends on the electrical conductance, low unburnt carbon content present in some types of biomass ashes is known to contribute to the significant reduction in the electrical charge passed. In general, a reduction in the unburnt carbon content may be beneficial from the chloride permeability point of view. For example, when rice husk ash which has a lower loss on ignition value compared to OPC is used to partially replace OPC, resistance to chloride permeation is substantially improved. This may be probably due to a decrease in electrical conductivity of concrete due to lowering of unburnt carbon content in RHA, in addition to pore structure refinement and conductivity of pore solution. Such an observation is further reinforced considering the substantial reductions in charge passed achieved when RHA was utilized (Figure 4.3) with low LOI values from 1.97% to 3.7%.

Overall, the chloride-ion penetration results suggest pore refinement due to the pozzolanic reaction of ultrafine biomass ash and demonstrate the significant potential of these types of ashes as mineral admixtures in concrete, as long as an appropriate grinding strategy is used and product fineness is achieved.

Chapter 5. Utilization of rice husk ash in the building sector – Technoeconomical analysis and environmental benefits

5.1 Introduction

5.1.1 General

Rice husk ash (RHA) is the solid-state residue of the incineration of the rice husk, a process used in the rice industry for heat, steam and/or electrical power production. The potential uses of this by-product include materials of high-added value like cement/concrete-production enhancing materials (pozzolanic materials), zeolites, waterglass, etc. In the previous Chapter 4 it was observed that RHA can act as an efficient pozzolanic material (and supplementary cementing material - SCM) provided its amorphous and fine state and offering thus high environmental benefits to the construction industry.

RHA has shown to contain significant amount of reactive silica that could contribute chemically to the development of pozzolanic reactions. In many cases – depending on the nature of husks and burning/cooling conditions – the total silica of RHA exceeds 90% with most of it being non-crystalline, thus reactive under alkaline conditions (Antiohos *et al.* 2014). Pozzolanic activity of RHA depends on silica content, silica crystallization phase, and size and surface area of ash particles. Ideally, ash must contain limited amount of unburnt carbon. RHA that has amorphous silica content and large surface area can be produced by combustion of rice husk at controlled temperature (Mehta 1989) and these factors are mainly responsible for its high reactivity (Mehta 1994, Sousa-Coutinho, 2003).

Reactivity of RHA is attributed to its high content of non-crystalline silica, and to its very large surface area governed by the cellular structure of the particles as well (Mehta 1994, Zhang and Malhotra 1996, Chandra 1997, Sousa-Coutinho 2003, Saraswathy 2007). When pozzolanic materials are added to cement, the silica (SiO_2) present in these materials reacts with free lime released during the hydration of cement and forms additional calcium silicate hydrates (C-S-H) as new hydration products which improve the mechanical properties of concrete formulation (Ganesan and Thangavel 2007).

Despite the fact that a lot of work has been done on treated RHA, results on the direct use of untreated RHA are scarce in the literature and are usually limited to strength contribution and not durability aspects. Feng *et al.* (2004), for example, examined the pozzolanic properties of both untreated and treated RHA but did not attempt to assess their behavior in terms of durability. Sensale (2010) analyzed the effect of two types of RHA (amorphous and partially crystalline optimized by dry-milling) on durability of cementitious materials by proper testing. Other relevant studies (Gastaldini *et al.* 2009, Ramezanianpour *et al.* 2009) have also examined the influence of untreated RHA in certain durability properties; however, more investigation has to be conducted concerning its valorization in cement-based mortars and concrete systems and especially properties like resistivity and resistance to carbonation.

Especially, RHA for building applications has great technical & environmental benefits, as was shown during PYRICE project 2008, PYRICE II project 2012:

- Using RHA to replace cement and aggregates in building applications, components of strength equal to a reference mixture can be obtained. At the same time, a similar durability in general is achieved, plus significant ecological benefits, due to industrial by-products use (reduction of pollution from RHA arbitrary disposal) and decrease in the cement quantity (energy saving and CO_2-emission reduction). As the k-value for treated RHA is estimated around 1 (equal to Portland cement) or higher (see Chapter 4 as well), it means that RHA can substitute equally cement, and by taking into account that 1 t of cement production emits 1 t CO_2, every 1 t of RHA used in building applications almost save 1 t of CO_2 emissions.

- Using RHA to replace only aggregates, elements of significantly higher durability and strength can be produced increasing slightly the production cost. However, due to increase in durability, a significant decrease in maintenance and repair costs is expected. To this, significant ecological benefits should be added, due to use of industrial by-products and building lifetime lengthening.

5.1.2 Present study

The target products, i.e., the RHA-derivatives for building applications at an order of *increasing price* have as follows:

1. *Production of tundish powder / insulator* for steel & construction industry
2. *Production of pozzolanic material* for construction industry

The *first choice (insulator / tundish powder production)* offers a decent market price, and it requires a minimum of RHA production modifications in order to fulfil the quality requirements for steel industry. These are carbon content less than 5%, a high amorphous silica proportion (more than 80%), and a particular grain size distribution upon request.

RHA is used by the steel industry in the production of high quality flat steel. Flat steel is a plate product or a hot rolled strip product, typically used for automotive body panels and domestic 'white goods' products. RHA is an excellent insulator and it can be also used for construction – isolation applications, having low thermal conductivity, high melting point, low bulk density and high porosity. It is this insulating property that makes it an excellent '*tundish powder*'. These are powders that are used to insulate the tundish, prevent rapid cooling of the steel and ensure uniform solidification in the continuous casting process.

Steel & construction market for RHA uses as tundish powder / insulator:
- The market within the steel industry is well established.
- However there are constraints to the expansion of this market due to health issues associated with using RHA. Crystalline ash, the form preferred by the steel industry, is carcinogenic and the use of RHA is banned in some European countries. This trend is likely to increase.
- There is more scope for development in Asian and Eastern markets, but the future size of the market is not certain.
- Some companies are pelletising RHA, and state that this overcomes the health issues. There is controversy over whether this is the case, but some steel manufacturers have converted to pellets.

The *second choice (pozzolanic material production)* offers a relatively higher market price. The fixed and operational costs are rather low, the quality of the product can be easily ensured, and there are plenty of

customers in Greece and in Europe to adsorb the production. As it does not require high technology and intensive infrastructure, it could easily be reproduced from other competitors threatening the future sales.

Cement & construction market for RHA uses as pozzolanic material:
- The cement markets are not as well developed as steel, but there is great potential for the use of RHA in this area.
- It is currently not being used to any extent, except in the USA. Two main issues appear to be limiting its use: lack of awareness of the potential for RHA and the quality of the product itself.
- The cement industry requires amorphous ash, so there are none of the health issues associated with crystalline ash.
- The cement industry has to produce a consistent, high quality and standard product. This in turn requires RHA from a controlled combustion environment, to ensure a consistent standard ash. Producing RHA of the correct quality may cost more than producing normal ash due to boiler modifications etc.
- In addition to the use of the ash, it may be possible to generate Certified Emission Reductions (CER-carbon credits) when substituting for Portland cement. Portland cement requires enormous heating in its manufacture and avoiding the energy (derived from fossil fuels) and thus carbon emitted from its manufacture could generate an additional income stream for the producers of RHA.

RHA can also replace silica fume in high strength concrete or repair mortars: Silica fume or micro silica is the most commonly used mineral admixture in high strength concrete. The major characteristics of RHA are its high water demand and coarseness compared with condensed silica fume. To solve these problems RHA *needs to be ground finely into particles of 8-10 μm* and a superplasticizer added to reduce water requirement.

The present Chapter deals with the elaboration of a technical and financial study and a preliminary design for the industrial production of the RHA-derivatives for building applications, including an environmental analysis. A conceptual design is first applied to find the best process flowsheet and estimate the optimum design conditions: Having the appropriate methods that should be followed for the production of RHA-derivatives, *an optimum, technical and economical, design of the processes at industrial level* is carried out. The target is a technical acceptable solution at the possible lowest fixed, operational and environmental cost. This goal is succeeded by applying a *conceptual design* to find the best process flowsheet (i.e., to select the process units and the interconnections among these units) and estimate the optimum design conditions. After definition of the operational parameters, the process flowchart is

constructed via a *hierarchy of design decisions,* namely structure of input-output, recycling, separation and thermal integration (saving energy).

An assessment for the following techno-economical characteristics is further performed: origin, quantity and characterization of the raw materials, proposed treatment process to produce high marketable products, fixed cost, required personnel, operational cost, product cost, market (supply and demand, competition), sale price, profit, financing possibilities, lifetime, etc. The limitations that may arise are examined, such as the registration of these new materials according to EU and national regulations. Knowing the above components, the rate of return on investment is estimated and the first conclusions for the undertaking of this investment are drawn.

Risk assessment analyses (partial and summarized) take place and the relative elasticity analysis for certain major cost-effecting parameters is carried out. Greater degree of detail is also provided for elements of the current study such as: buildings, health and safety, environmental protection etc. Detailed design of the equipment (main and supplementary) is provided as well. Thorough imprint of the organization chart and the personnel of the unit (and thus assessment of the necessity of stuff), along with all other cost-effecting production factors (maintenance, spare parts, consumption), reserves (raw and supplementary), provisions and general expenses (administrative, customer support and sales) are essential to the study. This analytical form of technical/economical study would provide:

- precise demands for capital for a fixed investment
- provisions for operational capitals
- provisions for revenue

In the following sections, the appropriate components that compose the technoeconomical study are presented for each one of the above targeted products, converging to final conclusions & suggestions for a porential investment.

5.2   RHA derivatives for construction – Production processes

5.2.1   Rice and RHA production

Very few cereals hold the same importance in human nutrition world wide, as rice. 60% of earth's population has a rice-based nutrition. Rice is a primary source of food for billions of people, and ranks

second to cow milk in terms of production value and third after sugar cane and maize in terms of production quantity, with the wheat ranked forth (FAO Statistical Database 2007). Globally, approximately 600 million tonnes of **rice paddy** is produced each year. The annual production of paddy rice (*Oryza sativa*) globally was 657,413,530 tonnes in 2007. Of this, 95% was produced by 20 countries, as shown in Table 5.1. World rice production is expected to peak in 2008, however the increased demand and reduction of exports will be maintaining rice highly priced in short-run al least.

Table 5.1   Rice paddy, in the 20 highest producing countries, FAO 2007.

Rank	Area	Production (Int $1000)	Production (tonnes)
1	China	35,526,760	187,397,460
2	India	29,968,800	144,570,000
3	Indonesia	11,845,150	57,157,436
4	Bangladesh	7,981,474	43,057,000
5	Viet Nam	7,334,530	35,942,700
6	Thailand	6,357,229	32,099,401
7	Myanmar	6,224,919	31,450,000
8	Philippines	3,229,486	16,240,194
9	Brazil	2,309,714	11,060,700
10	Japan	2,310,732	10,893,000
11	United States of America	1,882,144	8,999,230
12	Pakistan	1,709,320	8,345,100
13	Egypt	1,392,410	6,876,830
14	Cambodia	1,375,592	6,727,000
15	Korea, Republic of	1,276,292	6,038,000
16	Nepal	767,014	3,680,839
17	Nigeria	652,545	3,186,000
18	Sri Lanka	645,100	3,131,000
19	Madagascar	724,660	3,000,000
20	Iran, Islamic Republic of	471,135	2,800,000
	Rest of the World	7,008,994	34,761,640
	Total (World)	130,994,000	657,413,530
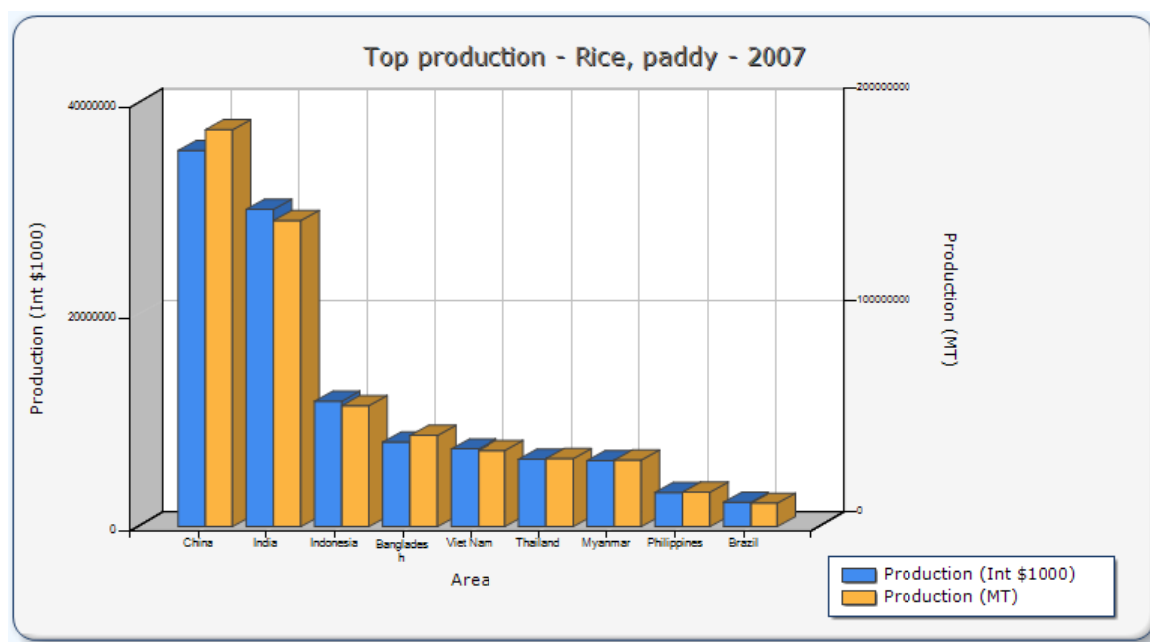
Figure 5.1 *Chart showing the 9 highest rice paddy producing countries in 2007, FAO 2007.*

Production of rice is dominated by Asia, where rice is the only food crop that can be grown during the rainy season in the waterlogged tropical areas. Most paddy is produced by China (28.5%) followed by India (22%). Globally, rice production is increasing, with an increase of 10% from 1992 – 2002, and 13% from 2002-2007.

In **Greece**, the rice paddy production, imports and rice milled exports are given in Table 5.2 (FAO 2007). A steady increase on rice paddy production is observed during the last years.

Table 5.2   Rice paddy production, imports and rice milled exports, in Greece, FAO 2007.

	2005	**2006**	**2007**	**2008**
Production of rice paddy, tonnes	158,991	179,193	184,243	208,800
Area harvested, Ha	22,281	23,236	25,000	31,000
Rice paddy imports, tonnes		20,163	9,404	
Rice milled exports, tonnes	53,014	67,785	69,061	

Yields are affected by several factors, including the agronomy of the crop. This is influenced by the physical and cultural environments and scale under which the rice is grown. International co-ordination and co-operation in technological advances of rice production is providing alternatives to the limitations of cultural practices, by the use of chemical fertilisers, insecticides, pesticides and introduction of new varieties. Rice production is often set back by the weather, monsoons and droughts, but the effects of this are increasingly being limited by irrigation and water control systems.

On average 20% of the rice paddy is husk (Beagle 1978), giving an annual total production of approximately 120 million tonnes. Rice husks are one of the largest readily available but most under-utilised biomass resources, being an ideal fuel for electricity generation and heat or steam production. The calorific value varies with rice variety, moisture and bran content but a typical value for husks with 8-10% moisture content and essentially zero bran is 15 MJ/kg. The treatment of rice husk as a 'resource' for energy production is a departure from the perception that husks present disposal problems. The concept of generating energy from rice husk has great potential, particularly in those countries that are primarily dependent on imported oil for their energy needs. For these countries, the use of locally available biomass, including rice husks is of crucial importance.

5.2.2   RHA derivatives

Rice husk is unusually high in ash compared to other biomass fuels – around 18-20% (Velupillai *et al.* 1997). **Assuming a husk to paddy ratio of 20%, and an ash to husk ratio of 18%,** *the total global ash production could be as high as 23,700,000 tonnes per year.* **The potential rice husk ash production in Greece is thus estimated as** *8,000 tonnes per year***.**

The ash is 92 to 95% silica (SiO_2), highly porous and lightweight, with a very high external surface area. Its absorbent and insulating properties are useful to many industrial applications, and the ash has been the subject of many research studies. If a long term sustainable market and price for rice husk ash can be established, then the viability of rice husk power or co-generation plants are substantially improved. A 3 MW power plant would require 31,000 tonnes of rice husk per year, if operating at a 90% capacity factor. This would result in 5580 tonnes of ash per year. Revenue from selling the ash for beneficial use would decrease the pay-back period for the capital needed to build the project. Many more plants in the 2 - 5 MW range can become commercially viable around the world and this biomass resource can be utilized to a much greater extent than at present.

Rice husk ash has many applications due to its various properties. It is an **excellent insulator**, so has applications in industrial processes such as steel foundries, and in the manufacture of insulation for houses and refractory bricks. It is an **active pozzolan** and has several applications in the cement and concrete industry. It is also highly absorbent, and is used to absorb oil on hard surfaces and potentially to filter arsenic from water. More recently, studies have been carried out to purify it and use it in place of silica in a range of industrial uses, including **silicon chip manufacture**.

RHA is a general term describing all types of ash produced from burning rice husks. In practice, the type of ash varies considerably according to the burning technique. Two forms predominate in combustion and gasification. The silica in the ash undergoes structural transformations depending on the temperature regime that undergoes during combustion. At 550°C – 800°C amorphous silica is formed and at greater temperatures, crystalline silica is formed. These types of silica have different properties and it is important to produce ash of the correct specification for the particular end use. There are health issues associated with the use of crystalline ash, inhalation of which can lead to a number of diseases, the most common being silicosis. This affects the potential markets for this type of ash.

The principles of the conceptual design have been applied for the preliminary design of RHA conversion to insulation or pozzolanic materials; the main conclusions are given as follows:

➢ **For the production of tundish powder / insulation material low carbon content (LOI), low crystalline content and stable quality are required.** The most commonly used boilers are based on *fixed grate technologies*, which tend to produce ash with high carbon content, high LOI content and high proportions of crystalline to amorphous ash. Several adjustments on operational parameters (temperature, feed, residence time) are required in order to meet the above specifications. *The values of these parameters, sufficient to produce RHA of the required specifications, can be found from the pilot plant runs.* Suspension fired boilers generally produce more amorphous ash than stoker fired boilers despite the fact that they may operate at higher temperatures. This is because the operating time at high temperatures for suspension fired boilers is comparatively short. *Commonly, in the production of highly amorphous ash, low temperatures and fairly long "burn-times" are used.*

➢ In the case of RHA treatment in order to produce an upgraded material with pozzolanic properties, only **a mill is practically required**. Thus, in additional to the conceptual design, a market

research was also performed in order to identify a suitable mill, able to meet the potential customers' requirements (mainly high fineness). Better burning conditions and/or additional burning in order to get a whitish product are also required.

5.2.3 Flowchart for insulation materials production

Steel industry has a great potential for using RHA mostly as an insulation material or tundish powder. Similar applications could be found in other industries and production processes, such as construction of insulation panels, application of insulation blocks, etc. Thus, commercially, it is important to determine and control the type and quality of rice husk ash produced in order to meet the regulations for the specific uses. These can vary depending upon the different combustion techniques used. For example, stoker fired boilers tend to produce higher quantities of crystalline ash, whereas similar boilers with suspension firing produce more amorphous ash. The additional revenue stream provided by the sale of RHA may be the key to an energy projects' viability. If this is the case the appropriate technology should be chosen to produce ash of the required type and quality for the target RHA market.

The high ash content of rice husks and the characteristics of the ash impose restrictions on the design of the combustion systems. For example, the ash removal system must be able to remove the ash without affecting the combustion characteristics of the furnace (especially if the ash produced is mostly bottom ash). The temperatures must be controlled such that the ash melting temperature of approximately 1440ºC is not exceeded and care must be taken that entrained ash does not erode components of the boiler tubes and heat exchangers.

For the established market of the steel industry and the emerging market in the cement industry sufficient data is available on the physical and chemical requirements as regards the upgraded RHA (PYRICE project 2012). In Chapter 4, information has been provided on the characteristics of, and potential uses for RHA.

In summary, depending on the combustion method chosen, RHA can vary from having a negative value, where costs have to be incurred to dispose of it, to having various positive values depending on its quality and the market for it beneficial use. The main characteristics that determine the potential value of RHA are:

- residual carbon content,

- significant quantity of crystalline phases of silica dioxide present
- mainly amorphous silica with little or no crystalline phases

Combustion of rice husks, typically in stoker fired boilers, where the ash experiences sustained temperature above 750°C leads to a significant quantity of crystalline silica in the resultant ash. The steel market (insulation materials) is preferred for this type of ash. However, the most important characteristics for insulation applications is carbon content (connected with LOI as explained above) and fineness. These characteristics may vary depending on application.

In this case no specific requirements were put for an RHA of high crystalline content. This has to be related with the fact that the crystalline content is connected with health issues (silicosis) and thus finally is not anymore a property that is required. On the contrary, RHA with higher percentage on amorphous phase should be produced.

According to the above specifications put by a potential customer and the RHA production characteristics presented in previous chapters, the following preliminary design directions can be concluded:

- Indistinct and vague details are often given for boiler descriptions and RHA analyses. In such cases the 'value' of RHA analyses in a commercial sense is minimal.
- The change from amorphous to crystalline ash occurs at approximately 800°C, although the process is often 'incomplete' until 900°C is achieved.
- Generally, lighter coloured ash has achieved a more complete carbon burnout.
- All combustion processes devised to burn rice husks remain below 1440°C, which is the RHA melting temperature.
- The chemical and physical properties of the ash may be influenced by the soil chemistry, paddy variety and fertiliser use.
- Suspension fired boilers generally produce more amorphous ash than stoker fired boilers despite the fact that they may operate at higher temperatures. This is because the operating time at high temperatures for suspension fired boilers is comparatively short.
- Commonly, in the production of highly amorphous ash, low temperatures and fairly long 'burn-times' are used.
- Fly ash is a fine material and is of higher marketable value since it requires less grinding than the generally coarser bottom ash.

- Fixed grate technologies tend to produce ash with higher carbon content, higher LOI and higher proportions of crystalline to amorphous ash.
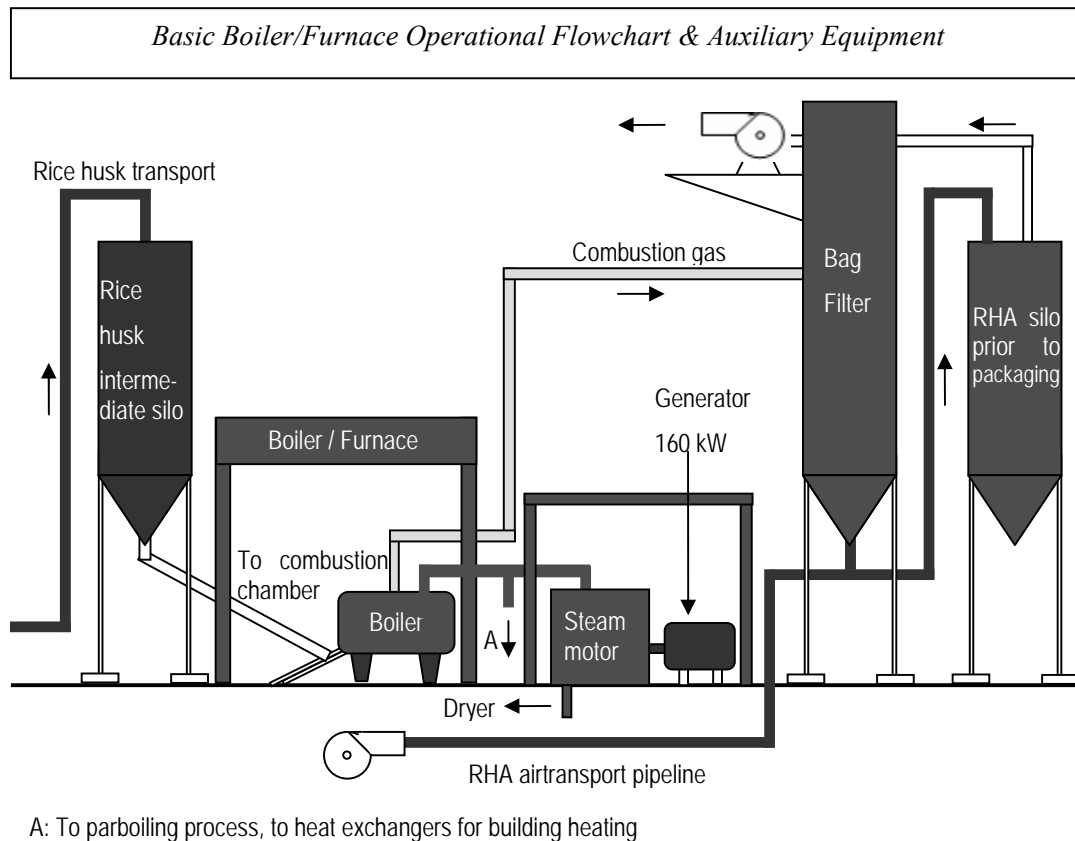
Figure 5.2   Simplified flowsheet for RHA production as an insulation material (PYRICE 2012).

The Greek rice industry cooperating in this research has two conventional moving grate combustors in its factories, see above general flowchart. These furnace/boiler systems have different adjustments to operational pressure and temperatures to match parboiling production demands. The main process performed is the incineration of rice husks produced from rice milling (20% w/w). The main purpose of the incineration is the biomass exploitation for heat production that would cover the excessive energy demands in both plants. The rice parboiling process is in great demand for heat (steam and drying) that needs to be covered by the incineration process and there is also great demand for the facilities heating. To further expand the process the company has developed an **energy saving strategy** in a twofold manner:

- the production of high added value materials from RHA, as well as,

- the production of electricity (use of steam).

The combustion is performed in a moving grate furnace that results to high crystalline silica content, large ash particle size and high carbon content. Since there was no original plan for RHA exploitation, this type of combustion was found to be more affordable (economically) and with higher productivity than other types of furnaces, but also with serious disadvantages in terms of RHA quality properties. The RHA properties have to be refined in order to meet customer specifications (for all types of RHA products).

5.2.4   Flowchart for pozzolanic materials production

Having the appropriate methods that should be followed for the conversion of RHA from a waste material to a useful by-product with important pozzolanic properties, *an optimum, technical and economical, design of the process* at industrial level was carried out. After definition of the operational parameters, the process flowchart is constructed including input-output, recycling, separation and thermal integration. The target is a technical acceptable solution at the possible lowest fixed and operational cost.

Production method: As the most critical unit process it could be suggested the conversion of the raw RHA (**RR**) to upgraded RHA (**UR**) that meets the customer requirements, i.e., fineness level. Thus, this process can be represented by the following "reaction":

$$\textit{Raw RHA (RR)} \;\rightarrow\; \textit{Upgraded RHA (UR)} + \textit{Improper RHA (IR)} \tag{5.1}$$
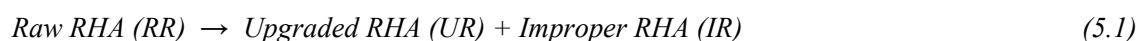
In the above reaction, the production of an improper RHA (**IR**) has been also anticipated, in other words this RHA that does not fulfil the requirements and in general its treatment is non-economically viable. The process described by Eq. (5.1) takes place in a mill. Due to low content in free CaO no partial hydration of raw RHA is required and thus the milling process does not include water (dry process) for hydration of free CaO to $Ca(OH)_2$ (for expansion prevention). Thus no water is drained into the mill, no further heating is therefore needed at 110 $^{\circ}$C for water vaporization, as it is necessary on other fly ashes treatment, e.g., high-calcium fly ashes from lignite combustion.

The temperature at which the above process takes place is that of the surrounding environment increased by any adiabatic elevation, due to heat release during milling. Subjects of pressure and catalyst do not

interfere in the present process. The process kinetics is actually defined from the residence time in the mill in order to achieve the required fineness.

The whole production process can be divided into the following *three stages*:

1.   Homogenization of the raw material (RR)
2.   Milling of RR to final product (UR)
3.   Homogenization of the final product and storage for disposal

Production rate: An initial capacity of 1000 t UR /y is considered as the basic scenario. This amount can be obtained easily by the present production rate of RHA in factories of the Greek rice industry. Later on a sensitivity analysis on the influence of unit capacity to cost-benefit characteristics will be performed.

Product specifications: The specifications are according to customer requirements or to the European Standard EN-450 for use of fly ashes into concrete. These in the most of the cases are:

-   homogeneity
-   fineness: retained in 45μm sieve < 40% bw.
-   free CaO < 1 or 2.5%
-   sulphates SO_3 < 3%
-   loss on ignition < 5%

As the production rate is estimated at about 1000 t/yr, with a solid-treatment character *the batch operation* is selected instead the continuous one. It means that the specific plant for RHA treatment will operate only for one (1) eight-hour shifts per day.

The final flowsheet, taking into account all appropriate hierarchical procedure, the specific characteristics, and the common engineering design principles, is given in Fig. 5.3.

FLOWCHART OF RHA TREATMENT FOR BUILDING APPLICATIONS
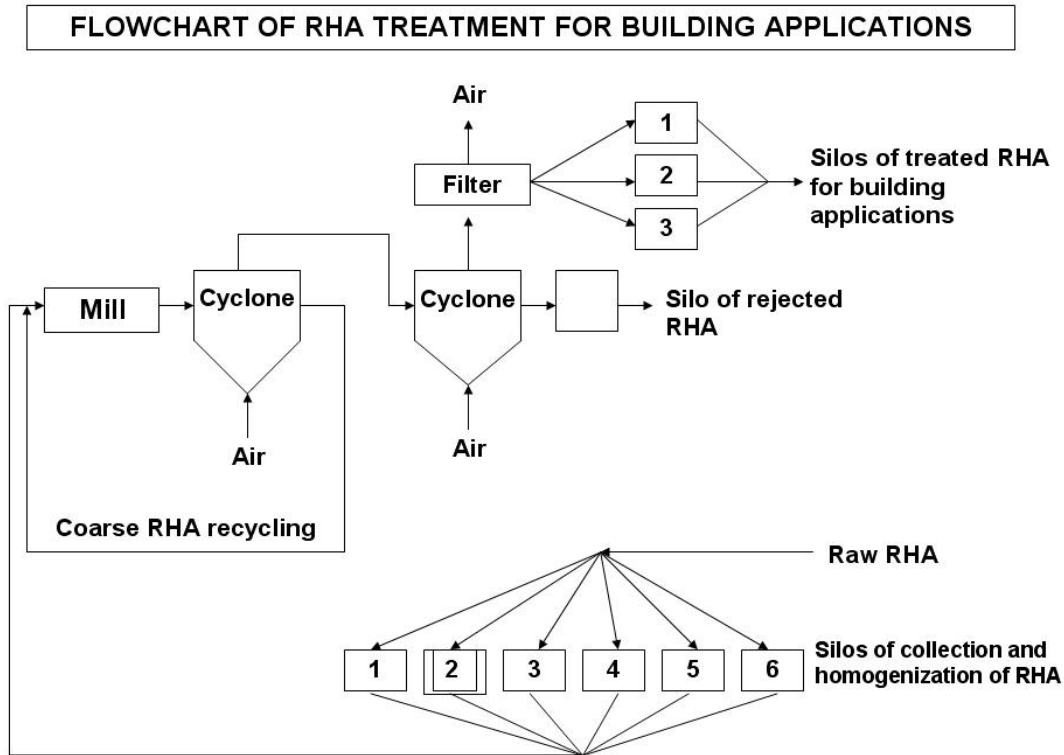
Figure 5.3   Suggested flowsheet for pozzolanic material production from RHA (PYRICE 2008, 2012).

5.2.5   Raw materials

RHA can be produced from rice husks by a number of thermal processes. Commercially, it is important to determine and control the type and quality of rice husk ash produced. These can vary depending upon the different combustion techniques used. For example, stoker fired boilers tend to produce higher quantities of crystalline ash, whereas similar boilers with suspension firing produce more amorphous ash. The additional revenue stream provided by the sale of RHA may be the key to an energy projects' viability. If this is the case the appropriate technology should be chosen to produce ash of the required type and quality for the target RHA market. For example, the colour of the ash is important for some cement markets where the ash influences the colour of the final cementitious product, as well as being a major indicator of the samples' residual carbon.

The high ash content of rice husks and the characteristics of the ash impose restrictions on the design of the combustion systems. For example, the ash removal system must be able to remove the ash without

affecting the combustion characteristics of the furnace (especially if the ash produced is mostly bottom ash).

Typically, the ash will contain some unburnt components as well as inert components of the husks. The unburnt component is predominantly carbon. It is typically measured by reheating a sample of the ash in an oven. The difference in mass of the sample before and after heating is referred to as the 'Loss on Ignition' (LOI). The LOI value is normally the same as the carbon content of the ash. The carbon content of RHA varies according to the combustion process. RHA analyses from a literature search and from analyses performed on RHA material for this study indicate carbon (or LOI) values ranging from 1% to 35%. Typically, commercial RHA combustion appears to result in RHA with 5-7% maximum carbon.

The colour of the ash generally reflects the completeness of the combustion process as well as the structural composition of the ash. Generally, darker ashes exhibit higher carbon content (with the exception of those that may be darker due to soil chemistry/region. Lighter ashes have achieved higher carbon burnout, whilst those showing a pinkish tinge have higher crystalline (tridymite or cristobalite) content.

The main factors in the various combustion and gasification processes that determine the type of ash produced are time, temperature and turbulence. These effect all chemical changes that occur in the combustion process including the way the ash morphology is altered.

A summary from the literature given RHA analyses is shown Table 5.3.

Chemical analyses of RHA samples from the Greek rice industry, Table 5.4, have shown a high percentage of active (amorphous) silica, about 70% in the sample. This amorphous SiO_2 *is the basic component* that is of interest and all the above advanced potential applications are based on. Optimization in RHA production has to be sought for maximum production of active SiO_2 and then investigation is required for further exploitation of the RHA.

A disadvantage of the above RHA, is the rather high loss on ignition, that is mostly owed to unburnt carbon, and varies between 5-10%. The presence of carbon complicates some of the above applications and some ways for its limitation under 5% must be sought. Thus, from the above initial RHA analyses, and by studying the international literature, it seems that the present RHA, under specified production conditions, can be converted into advanced and high-added value materials, and in any case the

technology risks are limited. Still remain the production and economic risks due to relevant ignorance of pilot production and deep market characteristics (main objectives of the present proposal). Certainly, the production of each RHA-derivative, demands new establishments and buildings as well as specialized equipment of high operational costs, but this is also part of the current investigation.

Table 5.3   Ranges on RHA analysis from various literature sources (PYRICE 2008, 2012).

Property, analysis	
pH	8-11
SiO_2 (Total, %)	62-98
SiO_2 (Amorphous, %)	0.2-98
SiO_2 (Crystalline, %)	0.5-98
Al_2O_3 (%)	0.01-1
Fe_2O_3 (%)	0-2.8
CaO (%)	0.1-1.3
MgO (%)	0-2
P_2O_5 (%)	0-2.7
Na_2O (%)	0-1.6
K_2O (%)	0.1-2.5
TiO_2 (%)	0-0.03
Cl	0.01-0.04
LOI (%)	1.5-5.5
Carbon (%)	2.7-6.4

Table 5.4   Ranges on Greek RHA analyses (PYRICE 2008, 2012).

Property, analysis	
pH	7.9-10.2
SiO_2 (Total, %)	73-89
SiO_2 (Amorphous, %)	63-70
Activity ratio (amorphous/total SiO_2)	71-93
Al_2O_3 (%)	0.13-0.22
Fe_2O_3 (%)	0.28-0.70
CaO (%)	0.67-2.25
MgO (%)	0.26-0.36
Na_2O (%)	0.15-0.47
K_2O (%)	0.62-1.96
LOI (%)	4-17
Carbon (%)	5-10

5.3   Equipment, plant site and restrictions

5.3.1   Equipment for RHA conversion to pozzolanic material

Based on the flowchart, Fig. 5.3, it is possible to identify the main and auxiliary equipment required. In this way, the type is determined as well as the size of equipment is estimated, i.e., type and size of mill, cyclones and silos, transport equipment and compressors. At the same time indications are provided for construction materials of this equipment in order to meet their working conditions. The requirements for the auxiliary equipment are recorded (storage, transport, possible controls, etc.) as well as the necessary quantities of energy (electricity, fuel and compressed air) and water. Of course at this stage it should be considered if all or part of the required main and auxiliary equipment exists and is probably available. Following, the basic units of equipment will be examined: the homogeneity system and the mill, based on literature data.

a.   Collection & RHA homogenization

The most serious problem that needs to be addressed in order to use RHA, is the great fluctuation in RHA's composition. This property characterizes more or less, nearly all ashes that are produced from biomass, coal or lignite. To tackle this problem, production must contribute to the effort of homogenizing rice husk that will be burned. This effort is essential anyway, for better energy exploitation of fuel. In this context, the following are proposed:

✓   *Strict quality control of raw and treated RHA*. For this purpose, close cooperation between production and RHA exploitation unit is required to ensure, as much as possible, consistent quality of rice husk and consequently consistent quality of RHA.

✓   *High degree of homogenization of the raw ash* before its supply to the grinder. In order to address the problems of homogeneity while operating the grinder for the processing of ash, a system of continuous monitoring of raw ash should be organized. Continuous sampling should take place through a special device that can be adjusted to the supply lines of the silos. These samples should be checked for their sulphates (SO_3) and the very high levels of free CaO, while forming an opinion about the exact quality of the ash that the next few hours will go through grinding. Samples that do not meet up, for various reasons, the highest levels of standard values (e.g., 3% for sulphate or 2.5% for free CaO) should be **discarded**.

✓ *High degree of homogenization of treated ash for sale.* The ash can been stored in different silos in layers, so that the final product that will result from each silo will be as homogeneous as possible.

Similarly, for this project and in order to ensure product homogeneity, **a series of six (6) silos for storing raw material and a series of three (3) silos for storing the final product are proposed**. The raw material for processing will result from all six silos containing raw material and the final product for distribution will result from all the three silos containing the final product.

b. *The grinding mill*

The RHA grinding mill is considered to be a critical process. The study for the grinding plant of Greek Public Electricity Corporation (DEI) at Ptolemais as well as the organization and the equipment of the chemical laboratory for quality control of the ash were all part of the contact work for the construction of the dam by the consortium AEGEK - HIDROGRANJA - ASI RCC under the supervision of DEI. The unit consists of a closed-circuit grinding mill with additional supplementary equipment. The mill has three apartments and the nominal capacity is 16.7-23.0 t / h for the projected product fineness. Note that the mill was tested on productions 30t / h at which it responded with the subsequent modification of fineness provided that a large reduction of free CaO is not required. Its dimensions are (diameter x length) 2.6x12m and operates with a degree of filling 30% which is covered by grinding bodies with dimensions 30 and 40 mm (total weight 42 t) and the material that has a bulk density of 860 kg/m^3. The movement of the mill is achieved by an engine with power 720 kW.

For the present study, a similar grinding mill is suggested to be examined of proportional capacity.

Having however performed an extended literature survey and experimental investigation vibration-type of milling systems is suggested. In the Fig. 5.4 images of vibratory grinding mills are given.

Figure 5.4 Vibratory grinding mills for RHA efficient milling to sub-micron level; commercially available by Bulton (left) AMKCO (right).

5.3.2 Plant site

The choice of the plant site has a definite influence on the project success. The main criteria for the selection of the plant site are to minimize the cost of production, transport and storage. If the under design unit has been decided to be an expansion of an existing industrial site, then the design needs to be compatible with any existing facilities. As such are considered to be supplies of fuel, steam, cooling water and other sub-cooling means, the electricity supply as well as the waste treatment facility. If the unit is to be constructed in a new independent site then the choice of the location should be made after considering a number of factors:

Land cost. The cost for purchasing land or renting premises in some cases contributes significantly to the definition of the overall fixed costs.

Purchase of raw materials. Placing the plant near the source of raw materials means reduction in the costs of transport and storage. The same is true in the case of auxiliary materials, fuel, packaging materials, etc., depending on the type and characteristics of the business.

Product purchase. It is preferable to install the plant near the main markets mainly because it reduces the distribution cost. It is common to have plants that produce intermediate products elsewhere for specific reasons and plants that produce the final products to be close to major urban centers.

Infrastructures of *area.* The candidate area should gather a number of characteristics for accommodating the plant. These are mainly: an industrial zone, capable workforce of different education and experience, accommodation for staff, training opportunities, leisure and health care facilities, energy and water supplies, waste treatment facilities, appropriate suppliers of materials and services, and good transportation network. The existence of a port or highway connections are also key elements.

Characteristics of environment. The climate has relatively little effect on the choice, but the cost of heating, cooling or insulation to maintain stable conditions in the production and storage area, the cost of corrosion protection in coastal areas or wetlands and any transportation exclusion of the factory by bad weather should be considered. Another issue that should also be considered is whether the land is suitable for the construction of industrial buildings and take into account the seismic characteristics of the area.

Investment incentives and tax exemptions. Clearly the establishment of the plant must be within the areas that are foreseen by the law depending on the type of industry. Greece is divided into categories of industrial areas, which vary depending on the location and incentives that encourage or discourage are provided. The incentives that are usually provided in order to invest in areas where industrial development is sought (mainly remote and economically problematic regions) are grants, interest subsidies, tax exemptions and increased depreciation, which are often quite powerful in selecting the final location of the unit.

Based on the above analysis and because the raw material is obtained exclusively from the Greek rice industry, it is expected that the *site plant for RHA treatment and the production of added value materials will be at close distance from the factories*. The proximity allows direct supply of raw ash through pneumatic system. Furthermore, the communication between technical staff of both companies is an important issue for the development of the production (benefits: reduction of transport, quality control and production level, management benefits, etc.). Also, the criteria which include development incentives and tax exemptions are considered as very important for the selection of an alternative location for this investment. There are areas with good access to key raw materials and product markets, where important support is provided for the assets (and operating) costs of around 45%. For example, the *industrial areas*

of Astakos and Sindos concentrate enough of these positive attributes so as to qualify as an alternative location for the site plant.

5.3.3 Restrictions

a. Patents and legal restrictions

This issue is not a direct part of technoeconomical analysis, but it is possible to exclude certain processes or products. If relevant patents exist then these must be identified and loyalties must be paid. No similar techniques were patented for pozzolanic material production from RHA; leaving thus space for potential patenting from the present work.

The resulting product (RHA for structural applications) is according to the European Standards EN 450. Through EN-450, the technical specifications of the material are provided, as well as the frequency and the process control, compliance criteria and other features that ensure the desired quality. This means that through EN-450, the legal constraints arising from the use of the product are covered. It should be noted that Greek standards are expected, which are considered less "stricted" than EN-450. Thus, RHA complies with these standards since it already complies with European EN-450.

Additionally, the producer may adopt a quality system such as ISO 9000, which increase*s* overall the reliability of the manufactured products.

b. Operating limitations, security and environmental protection

In many cases the design should be done with certain constraints that are either associated with the proper operation of the facility or with safety issues and environmental protection. With regard to operating limitations, for example, the operating conditions under which some materials can polymerized and create deposition heat exchange surfaces, or to other units of the process need to be known. Other materials can form carbon deposits and deactivate the catalyst. Also, materials with high toxicity and high corrosivity can affect the design proposal. Therefore the engineer designer must take into account these operating limitations and plan within acceptable limits.

Also the security issues which introduce similar restrictions are very important. It should be noted that an engineer not only plans properly and economically, but above all in a safe way. The safety is connected

with the avoidance of accidents that cause injuries to personnel or the environment. Clearly, conditions of operation within the limits of a mixture's ignition should be avoided. Similarly, the designer must avoid negative impact on the environment, and various emissions of the process (gaseous emissions, liquid and solid wastes, noise and thermal pollution) must be within the predefined limits. Specifically:

c.   *Health & safety at work*

When engineers design a unit, a main issue is the creation of a perfectly healthy work environment that minimizes the risk of accidents during work. During the production of RHA, the silica in the ash undergoes structural transformations depending on the conditions (time, temperature etc.) of combustion. At 550°C – 800°C **amorphous ash** is formed and at temperatures greater than this, **crystalline ash** is formed. These types of silica have different properties and it is important to produce ash of the correct specification for the particular end-use. There are health issues associated with the use of crystalline ash, inhalation of which can lead to a number of diseases, the most common being silicosis. Amorphous ash does not contain the more harmful forms of silica, but can be a respiratory hazard, particularly if finely ground. In this case, *almost 100% of RHA produced is in amorphous state and not in crystalline.*

Exposure Limits

The UK Health and Safety Executive (HSE) has assigned a maximum exposure limit of $0.3mg/m^3$ for **crystalline silica**, expressed as an eight hour time weighted average [1]. The USA Permissible Exposure Limit (PEL) is $10mg/m^3$ divided by the % SiO_2 + 2. The UK HSE does not have regulations relating specifically to RHA, and state that the rules for silica should be followed. The UK HSE advises that samples should be taken if dust levels are expected, and that they should be regarded as significant if they are above $0.1mg/m^3$. In this case dust control levels should be implemented.

Occupational Safety & Safety Administration (OSHA) has an established PEL, which is the maximum amount of **amorphous silica** to which a worker *can be exposed* as *the percentage of* amorphous silica in the dust rises. The term SiO_2 refers to the percentage of amorphous silica in the sample. When the amorphous silica content is at or below 5.33% the total dust (Particulates Not Otherwise Regulated) PEL of $15 mg/m^3$ should be used.

The project PYRICE II (2012) aimed to the complete RHA management by capturing and converting the produced RHA to useful products. In addition to this complete solution a **Specific Programme for Capturing and Controlling Dust** at source was recommended to control dust exposure, including:

- ✓ *Dust control programme* which includes measures that ensure that workers are not exposed to dust. There a number of simple control measures that can be taken. More specifically reducing employee exposure to dust can be accomplished by three major steps: prevention, control systems, dilution or isolation.
- ✓ *Training and information to workers*
- ✓ *Equipment maintenance programme.*
- ✓ *Personal protection & first aid.*
- ✓ *Personal hygiene facilities, eating & clothing*
- ✓ *Record keeping.*
- ✓ *Regulated areas/warning signs.*

d. *Environmental protection*

When designing a unit in Chemical Industry, the main principle that is followed is that the environment should not be affected (in a negative way) in any way. For this reason it is required by the law to create an Environmental Impact Assessment (EIA). Thus the designer engineer should identify all possible sources of pollution that the unit can create and exclude them. Such pollution can be:

- ✓ Chemical (emission of hazardous or odour gases, liquid waste containing substances that alter the physiology of the recipient, creation of solid waste which are difficult for disposal)
- ✓ Thermal (disposal of high temperature water to the environment)
- ✓ Sound (noise emission)
- ✓ Aesthetic (no architectural adaption of the unit to the environment).

Gas emissions, dust and noise are issues that the engineer must deal with when designing a unit (absorption towers, filters, insulation, etc.). All waste will either be processed within the factory or will be directed to a common treatment plant that is shared with other factories (e.g. in an industrial area). Regarding the permitted levels of gaseous and liquid waste, general and local regulations exist, the quote of which is beyond the limits of this study.

5.4 Organizational structure, fixed and operational cost

5.4.1 Organizational structure and personnel

From the analysis in section 5.2, it is clear that the process should be designed as ***batch operation***, primarily because of capacity (production rate). So the proposed operation for the case of RHA conversion to insulation and/or pozzolanic material is **one shift daily (8h),** *5 days per week, 47 weeks per* year (5 weeks closing of factory for maintenance). Total production days: 235 per year. This particular production could be either a separate branch on Greek rice industry's activities or a separate subsidiary company of the Greek rice industry with objective to carry out these particular businesses.

In the latter case, a separate Direction Scheme is required. It is suggested a commercial company of Ltd or SA. The company's direction will be performed by a 5-member Board of Directors (President and four members), in cooperation with the General Manager of the plant.

The following organizational scheme is suggested:

1. Plant Management
- Board of Directors
- General Manager

2. Administrative & Financial Services
- Secretariat
- Supplies - Personnel
- Accounting

3. Production Department
- Unit of RHA treatment and homogenization
- Unit of packing and loading - Storages
- Maintenance unit

4. Quality Control
- Sampling
- Analyses

5.   Sales Department

- Sales

- Marketing / After sales support

The distribution of personnel in the above departments/ services is as follows:

1.   Plant Management (1+5)

   1 General Manager

   (plus 5 members of Board of Directors)

2.   Administrative & Financial Services (2)

   1 Administrative employee (Secretariat - Supplies - Personnel)

   1 Accountant

3.   Production Department (4)

   1 Operator for panel & loading (Unit of RHA treatment and homogenization)

   1 Worker (Unit of packing and loading - Storages)

   1 Driver (Products transportation)

   1 Technician (Maintenance unit)

4.   Quality control (1)

   1 laboratory chemist

5.   Sales Department (1)

   1 Employee for sales & marketing

Apart the BoD, total 9 persons are required of which:

- ✓   1 General Manager

- ✓   4 Executives-Administrative Officers - Scientists

- ✓   2 Operators-Technicians

- ✓   2 Workers-Drivers

5.4.2   Calculation of fixed costs and initial working capital

The purpose of this section is to provide the investors an understanding of the expenses that will occur and to estimate the financial viability of the project. The idea is to use this unit both for insulation materials production (having already a rice husk burner) as well as for the production of pozzolanic materials; it is thus an advanced unit that involves a milling line. An average capacity of the unit is considered to be: **1000 t/y**. We also consider as a **batch process: one shift (8h) per day**, 5 days a week, 47 weeks a year (5 weeks the factory shuts down for maintenance). Total production days: 235 per year.

The creation of an industrial plant requires expenditures for studies' elaboration, purchase of land and its configuration, purchase and installation of equipment, interfaces, components, etc. The total cost that is required from the stage of capturing the idea until the realization of a production unit, just before the start of its normal operation, is actually the *establishment capital*. This is divided into the fixed capital and the initial working capital. The *fixed capital* refers to costs for the acquisition or construction of equipment and their installation. The *initial working capital* refers to costs that are required in order for the production to achieve a level of normal operation. Usually, from this point and then *only operating costs* and *revenues* from the sale of products exist.

The *fixed capital, C (or fixed costs)* is divided into components, which are summarized below (cost of studies and establishment are included). All values are referred to real values after market research and gathering quotation from various suppliers. The currency used in all values is the **euro (€).**

Installations and machinery

Electromechanical equipment - mill – depreciation in 10 years	75,000
Installations – piping, 13% of basic equipment (10 years)	10,000
Equipment for quality control laboratory (10 years)	28,000
15 homogenization silos - storage, 50 t each (10 years)	82,500
Packing-loading unit (10 years)	28,000
1 loading machine, clark (10 years)	10,000
Subtotal	*233,500*

Buildings & land

Offices, laboratory, storage & buildings for equipment	47,000
Fencing	-

Land property (own property)	-
Subtotal (depreciation in 25 years for everything- out of land property)	*47,000*

Total	*280,500*
10% unpredictably	28,050
Total fixed cost, C	*308,550*

The *initial working capital* refers to the following expenses:

- *Test operation*: The cost for using staff at the stage of test operation.
- *Raw materials*: The cost of raw and auxiliary materials required from the start of production until the generation of revenue from their sale.
- *Labor and administrative costs*: Includes wages and salaries for the period mentioned above.
- *Disposal of products*: The storage, advertising (and sometimes transport) costs required for the products to reach the buyers.

The initial working capital as mentioned, is required to cover operating expenses for the period between the start of production until the generation of revenue from product sales (we assume a six month period). It covers the cost of raw and auxiliary materials, wages and salaries, the cost of the product delivery as well as the test operation cost. In order to estimate the initial working capital the individual components outlined above need to be assessed. However, this is not possible at least not until the design has proceeded satisfactorily. To overcome this problem, the *initial working capital*, *IC*, is calculated approximately as a percentage of fixed capital, C:

$$IC = (0.05\text{-}0.30)\ C \tag{5.2}$$

Usually a factor equal to 0.18 is taken into account. Estimations are in euro (€):

Initial working capital, IC	*55,540*

► Thus, the <u>*establishment capital*</u> is estimated as follows:

= total fixed cost + initial working capital

$$= \quad 308,550 + 55,540$$

$$= \quad 364,000 \; \text{€}$$

In the case that an establishment or fixed cost is sought for another smaller or higher production rate (capacity) then the simple method of proportionality could be used. This method reliable for first approximations is based in the following equation:

$$C_2 = C_1 \left(Q_2 / Q_1 \right)^n \tag{5.3}$$

where, Q_1, Q_2 : capacities (t/y), C_1 : fixed (or establishment) capital for capacity Q_1, C_2: fixed (or establishment) capital for capacity Q_2, and n a statistical parameter. The exponent n varies depending on the kind of the investment, according to historical data. For chemical industry parameter n equals usually to 2/3; that is the reason for calling this method as "*method of 2/3*".

5.4.3 Calculation of the operational cost

Revenues from sales, R (€/y, i.e. € per year) may be assessed upon market research, which will determine both the price and quality of products that the customer wants. For the purpose of basic calculations, the price can be determined from literature and from similar undertakings abroad or from direct information from the potential customers and market (see section 5.5). For the present case the revenues are:

Revenues, R (420 €/t * 1000 t/y) 420,000

The *operational cost*, OC (€/y) includes a number of elements which are provided in Table 5.5. The same table estimates approximately operating cost elements with the use of factors. It should be noted that in literature, numerous factors for all cost elements with significant differences exist, thus creating considerable uncertainty in calculations. For this reason, their widespread use is avoided. The factors in Table 5.5 are average values from literature which have been modified according to cases which have been applied in Greece. In order to calculate the operational cost it is essential to first determine (at least) the mass and energy balances.

Table 5.5   Operational cost elements.

	Description	Calculation methodology
1.	Raw & auxiliary materials	Calculation from mass balances
2.	Energy	Calculation from energy balances
3.	Manpower	Calculation
4.	Labor costs	0.05C*
5.	Administrative expenses	0.50 of element 3
6.	Insurance	0.01C*
7.	Depreciations	0.10C*
8.	Interests	Calculation
9.	General expenses	0.03R**
10.	Taxes	Calculation

* C : fixed cost, **R : revenues

Regarding the elements of the operational cost, one can observe the following. All values are referred to real values after market research and gathering quotation from suppliers. <u>All values are in €/y.</u>

Raw and auxiliary materials: Refers to all necessary materials (raw - auxiliary materials, intermediate products) from the processing of which products will result. The calculation of this element is easy with the use of balances and cost of materials. RHA has a potential for selling at a lowest price of 70€/t, thus it has to be charged to the operational costs as price for raw material

Untreated RHA, AR (70 €/t * 1000 t/y)   70,000

Energy: Includes solely the power which together with raw - auxiliary materials are the variable expenses of the operational cost, while the remaining elements in Table 5.5, are the semi-elastic or constant (inelastic) expenses. The variable expenses vary depending on the operational capacity of the plant (production rate), while the constant expenses are independent from it. We assume industrial use of medium voltage power (B1B and B2B) from the Public Power Corporation (DEI).

Mill power (234 kWh/t * 0.1€/kWh * 1000 t/y)   23,400

Power balance (33 kWh/t * 0.1€/kWh * 1000 t/y)	3,300
Total	*26,700*

Labor costs: Refers to the staff which works exclusively in the production. The calculation of the manpower is relatively easy and requires little experience. The number and the salaries of workers depend on the particular characteristics of the country (e.g., institutional framework, productivity). These are calculated based on average values which also contain insurance. They are calculated directly as there is the relevant info, see section 5.4.1.

4 technicians - workers * 1,400 (average) €/month * 14 months:	78,400

Maintenance: Includes all expenses for regular maintenance, and repairing of damages. The cost of maintenance is assumed to be equal to 5% of fixed capital.

Maintenance (0.05 * 233,500):	11,670

Administrative expenses: This element includes the expenses incurred for the support of production (administrative staff, offices, sales network, etc.) and is typically considered to be equal to 50-60% of the labor cost, however in this case it is calculated directly as there is the relevant info, see section 5.4.1.

1 director * 2,000 €/month * 14 months	28,000
1 chemist- R&D consultant * 1,400 €/month * 14 months	19,600
3 administrative staff * 1,400 (average) €/month * 14 months	58,800
Compensation for President and BoD members *- €/m x14 months	-
Total:	*106,400*

Insurance fees: Refer to the plant site and the products. Is it possible to assess its value from market information, but also it may accurately be calculated as 1% of fixed capital.

Insurance (0.01 * 233,500):	2,330

Depreciation: Expresses in an accounting manner, the return of the fixed capital. There are different methods of calculation, among which the simplest is *the linear depreciation*. The depreciation periods vary for the different assets, and are regulated in a legislative way. With the (realistic) assumption that the lifetime of a chemical industry is 10 years and with the use of the straight-line method, a 10% annual depreciation of the fixed capital is calculated. Here, we have defined the depreciation years during the calculation of fixed capital. We consider linear depreciation with zero residual value.

Depreciation (0.10 * 233,500+0.04 * 47,000):   25,230

Interests: Refers to the interest of the initial working capital and to the interest of loans for the purchase of equipment. The calculation is easy if the initial working capital and the rate of interest for various types of loans is known. At this point the interest is not calculated.

General costs: These are the costs for research and development (R&D), sales promotion and royalty payments for use of technology or product label. General costs vary considerably depending on the product and the business policy. Approximately, the general costs may be considered to represent 3% of revenues.

General costs (0.03 * 420 €/t * 1000 t/y):   12,600

Taxes: The tax rate is regulated legislatively in each country. In Greece, the tax rate is approximately 30-40% (although there are slight differences depending on the type of business). The tax is calculated on the amount obtained when deducting the operational costs excluding taxes from the income. Taxes (T) can be calculated as follows:

$$T = 0.30 \ (R - OC') \tag{5.4}$$

where, R : revenues, OC′: operational cost (excluding taxes), i.e., the sum of 1-9 components of the Table 5.5.

According to above estimations, the total operational cost, excluding taxes can be calculated as follows:

Table 5.6   Operational cost details for production of pozzolanic materials

	Cost description	*€/y*
1.	Raw and auxiliary materials	70,000
2.	Energy	26,700
3.	Labor costs	78,400
4.	Maintenance	11,670
5.	Administrative expenses	106,400
6.	Insurance fees	2,330
7.	Depreciation	25,230
8.	Interests	-
9.	General costs	12,600
	Operational cost (no taxes), OC′	*333,340*

5.5   Market, competition and sales

The steel and cement industries are identified as having the most potential for an adequate value, large market; issues discussed earlier in section 5.2.

Prices for RHA being sold to the steel industry are commercially sensitive and thus hard to determine. N.P.Singhania in India is selling RHA at US$150/t, delivery at Calcutta port, India. Other estimates of RHA on the world market are approximately $200 per tonne of ash, although it has been said that Thai RHA is worth US$300-400/t.

The cement markets are not as well developed as steel, but there is great potential for the use of RHA in this area. It is currently not being used to any extent, except in the USA. Two main issues appear to be limiting its use: lack of awareness of the potential for RHA and the quality of the product itself. The cement industry requires amorphous ash, so there are none of the health issues associated with crystalline ash. The cement industry has to produce a consistent, high quality and standard product. This in turn

requires RHA from a controlled combustion environment, to ensure a consistent standard ash. Producing RHA of the correct quality may cost more than producing normal ash due to boiler modifications etc. In addition to the use of the ash, it may be possible to generate Certified Emission Reductions (carbon credits) when substituting for Portland cement. Portland cement requires enormous heating in its manufacture and avoiding the energy (derived from fossil fuels) and thus carbon emitted from its manufacture could generate an additional income stream for the producers of RHA.

In the already opened market for building applications, RHA can substitute for **silica fume**, exhibiting similar properties, in various applications as highly pozzolanic material: specific types of concrete, shotcrete, self-compacted concrete, high-strength, high-performance concrete, repair mortars, etc. The market price of silica fume of 500 €/t is very attractive. The production of lightweight construction materials and insulation from RHA has potential, but current use is not widespread and there is limited knowledge of the methods used. Further research may develop this commercially, but not in the short term.

The cement industry has to produce a consistent, high quality and standard product. This in turn requires RHA from a controlled combustion environment, to ensure a consistent standard ash. Ash of a consistent quality is not readily available and is therefore not used by the cement industry. There are many other cheaper and more abundant pozzolans available. A waste product from coal fired power stations is pulverised fly ash (PFA). It is abundant and cheap and is therefore often used as an admixture in high strength concrete. Ground granulated blast furnace slag produced from iron smelters is also highly pozzolanic and available. **However, for high strength and quality, silica fume is preferred, for which RHA is a potential substitute – and therefore a focused market research on silica fume is required.**

The Europe and world producers are presented in the previous chapter; however the World Leader Producer of silica fume is **Elkem Materials** in Norway (see *http://www.materials.elkem.com/*). Elkem Materials is the globally dominating microsilica supplier and a leader in the marketing and implementation of Elkem Microsilica and its application technology worldwide. Elkem Microsilica is one of the principle products supplied by Elkem Materials. It finds a wide range of applications in high-strength concrete, other building materials such as roof tiles and facade cladding, and fire-proof products for heavy industry. Microsilica is also used for sealing tunnels and drilling oil-wells. This product comprises microscopic particles collected by filters downstream from the smelting process in silicon and ferrosilicon plants. Adding it to concrete and other materials increases their density and wear resistance, which extends the life of structures. Microsilica has been delivered by Elkem to a number of major

projects in Norway and internationally, including the Øresund/Great Belt connection. Elkem Materials also produces Ceramite, a fire-proof material which is particularly heat-resistant and hard-wearing. Treatment technology has been supplied by Elkem to industries world-wide for many years, and the company is currently involved with major filtration projects in China. Elkem Materials has a global distribution network, represented by our sales offices, distributors and agents.

No silica fume is produced in Greece; there is only importation of the material from the distribution network of Elkem Materials. The market price for silica fume in Greece is 500 €/t.

Market opportunities for RHA as a pozzolanic material:

1. Addition to cement
   a. adding RHA as pozzolanic material: up to 30%
   b. incorporating RHA in the low energy cement production, like belitics and other types.

2. Addition to concrete & mortars
Production of several concrete types as a direct reactive addition – as a fourth component in the mixture of raw materials of ready mixed concrete. Its potential use is particularly important and economically attractive in:
   ➢ High strength concrete (HSC)
   ➢ Shotcrete (Gunite)
   ➢ Self-compacted concrete (SCC)
   ➢ Repair mortars

Success key:
There is already a very good material on the market with exceptional properties: silica fume (Elkem Materials, 500 €/t). **The aim is to make RHA similar to (or replace) silica fume (SF or microsilica).**

RHA costs about - 40 €/t for handling and safe disposal. For the case of insulation and pozzolanic materials production the following product prices are foreseen:
   - According to real market and sales from the **pilot production of tundish powder or insulators for steel industry from the Greek rice industry's market prices of 70-140 €/t** can be achieved (**Solution A**: Development of upgraded and standardized RHA as insulator /tundish powder for steel industries, insulation panel constructors, etc.).

- According to real market and contacts with potential customers (successful test from ISOMAT SA: behavior 5-20% better than commercial silica fume) the price range for pozzolanic materials derived from RHA is 300-420 €/t, depending on quality (fineness, color) (**Solution B**: Development of upgraded and standardized RHA as pozzolanic material for mortar and concrete industries, constructors, etc.). As the market price for silica fume in Greece is 500 €/tonne **a feasible, good price to use as a scenario basis in the present technoeconomical analysis is 420 €/t for RHA as pozzolanic material for building applications.**

5.6   Cost-benefit analysis and evaluation

5.6.1   Expected profit

An approximate estimation of the expected profit (per unit or per year) is calculated, as well as the return on investment is evaluated, based on all the above data, as this is basic criterion for the actual implementation of the investment. Based on the analysis performed in sections 5.4 and 5.5, the following results are drawn regarding production of 1000 tonnes per year of pozzolanic material (almost 100% conversion of RHA to pozzolan):

Table 5.7   Economical outcome of the investment for pozzolanic material production.

Economical parameter	Results for a capacity 1000 t/y
Total fixed cost, C (€)	308,550
Initial working capital, IC (€)	55,540
Operational cost (no tax), OC´ (€/y)	333,340
Revenues, R (€/y)	420€/t * 1000 t/y= 420,000
Taxes, [T = 0.3(R – OC´)] (€/y)	26,000
Net profit, (K = R-OC'-T) (€/y)	60,660
Return on investment, i_r (%)	**16.7**
Payout period, τ (years)	**6.0**

5.6.2   Evaluation of the investment

Sometimes it is necessary to choose among different alternatives for an investment project, or even to rank various investment programs in order to determine the priority for their implementation. Depending on the investor, the selection and assessment criteria differ. When the investor comes from the public sector in addition to economic criteria, social criteria are also examined, whereas when the investors are from the private sector economic criteria are examined.

The investment decision is a critical process due to the fact that the values of certain factors need to be assessed, such as:

Plant capacity. The capacity depends greatly on the demand of the product. So if the capacity is greater than the demand, the fixed cost increases and the need to operate at lower capacity becomes obvious. Similar problems occur when the capacity is less than the demand of product.

Implementation time. The timing of the investment is crucial and there are cases that it affects its viability. For instance, if there is increased demand for a product, then the proper conditions for implementing the relevant project are set. However, if investment fails to be implemented on time then it is possible that the corresponding demand will be satisfied through the availability of another product or the consumer preferences might change. Finally, problems may arise in the opposite case (immediate implementation of investment) as well, as the product demand may be a temporary phenomenon.

Despite the uncertainty that accompanies an investment decision, it is possible to measure the economic efficiency based on the assumptions that have been made (capacity, product's price, etc.). The criteria or methods that are presented below give the opportunity to an investor or sponsor to determine the efficiency of the under evaluation project and compare it with other standards or alternative investments. From the existing methods of economic evaluation of investments, the most common will be used: the method of *return on investment rate* and *pay back period*.

a.   Return on investment

The return on investment is defined as follows:

$$i_r = K / (C + IC) \tag{5.5}$$

where, K: the annual net profit (revenues - total operational costs), C: total fixed cost of investment, and IC: the initial working capital. Obviously among two or more alternative investment plans, the one with the greater i_r will be selected. When considering a single investment plan then i_r should be greater than a minimum acceptable rate of return which is set by the company. This method ignores *the value change of money as a function of time*.

Based on the estimated data, the i_r for this investment is calculated and presented in Table 5.7.

b. Payout period

With this method, the time needed to recover the establishment capital is determined from the generated revenues during the operation of the facility. Quite simply, the payout period, τ, is evaluated as follows:

$$\tau = (C + IC) / K \tag{5.6}$$

Among two or more alternative investment plans, the one with the shorter τ will be selected. Based on the estimated data, the τ for this investment is calculated and presented in Table 5.7.

c. Evaluation of investment

From the above results the following conclusions are observed:
- The rate of return on investment is much higher than the current bank interest, fact which ensures that the investment is viable and it is suggested to be undertaken (if a sensitivity analysis is also positive).
- The payout period is considered as satisfactory, given that the main part of the equipment is new, and for its estimation depreciation has not been included in profit.

5.6.3 Sensitivity and risk analyses

Having a first positive result suggesting to undertake the investment, the positive limits should be identified and evaluated, as well as the influence of operational or market parameters on the investment outcome.

a. Effect of capacity

The effect of capacity (production rate, t/y) is the first analysis that should be performed as it gives essential information and estimation of break-even point, height of the potential losses, height of the maximum profits and efficiencies, and the targeted point of operation.

In Table 5.8 the investment characteristics are presented as a function of capacity. For a capacity of 500 t/y no profit – but losses are estimated. For 2000 t/y a return on investment of 36% is estimated, whereas for 4000 t/y (maximum total production in both Greek rice industry's factories) a very high return on investment 57% is estimated offering profits of 470,000 € with a payout period of less than two years.

In Fig. 5.5 the rate of return on investment is given as a function of capacity, showing the specific curve type. One significant outcome from this figure is the estimation of the **break-even point, as Q=532 t/y**, that capacity where zero profits are estimated (i.e., revenues=expenses). **However, no operation is recommended for a capacity less than 700 t/y** as it gives return on investment lower or equal to a bank interest.

Table 5.8 Dependence on capacity of the investment characteristics for the pozzolanic material production (product price 420 €/t).

| *Economical parameter*	*Q= 500 t/y*	*Q= 1000 t/y*	*Q= 2000 t/y*	*Q= 4000 t/y*
Total fixed cost, C (€)	213,130	308,550	460,370	707,920
Initial working capital, IC (€)	38,364	55,540	82,870	126,350
Operational cost (no tax), OC´(€/y)	215,810	333,340	562,722	1,012,460
Revenues, R (€/y)	210,000	420,000	840,000	1,680,000
Taxes, [T = 0.3(R – OC´)] (€/y)	0	26,000	83,180	200,260
Net profit, (K = R-OC'-T) (€/y)	-5,810	60,660	194,090	467,280
Return on investment, i_r (%)	**-**	**16.7**	**35.7**	**56.5**
Payout period, τ (years)	**-**	**6.0**	**2.8**	**1.8**
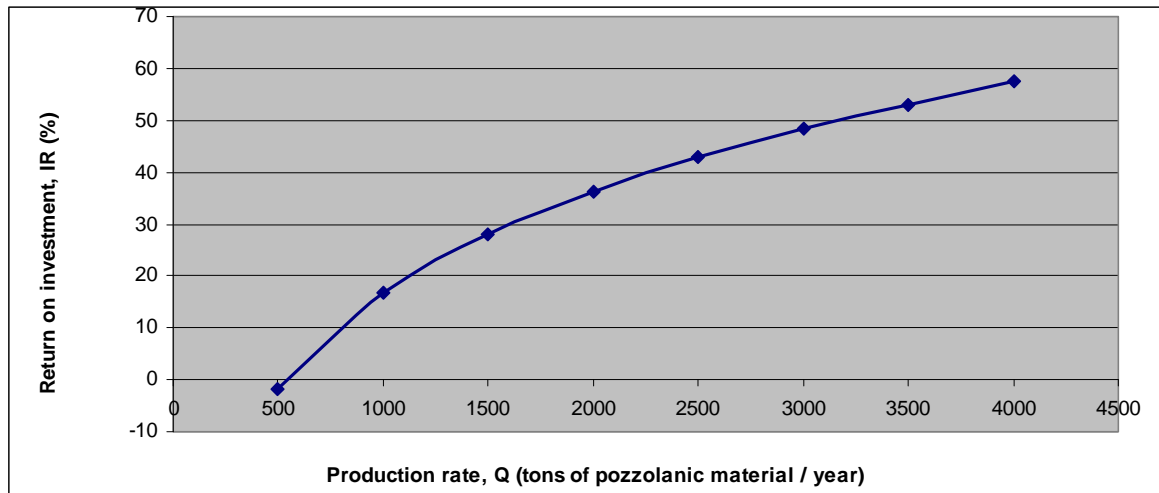
Figure 5.5 Return on investment vs. production rate for pozzolanic material production from RHA.

b. Effect of product price

In Table 5.9 the investment characteristics are presented as a function of product price (for a stable production of 1000 t/y). The **break-even point** for this case is for **P=330 €/t**, a product price where zero profits are estimated (i.e., revenues=expenses). However, **no operation is recommended for a product price less than 360 €/t** as it gives return on investment lower or equal to a bank interest.

For a product price of **500 €/t** (maximum price equal to silica fume value) a high return on investment 32% is estimated giving a payout period of about three years.

c. Effect of operational parameters

At this point the comparative contribution of each operational component to total operational cost is illustrated. In Fig. 5.6, such a diagram is given. It is observed a rather rational and no-risk hiding disribution. Among the four more importants parameters *administrative expenses, workpower, raw materials, and energy* can be distinguised. None of these could cause a potential risk to the investment, as raw material is a property of the Greek rice industry and all others cannot threat this specific investement.

Table 5.9   Dependence on product price of the investment characteristics for the pozzolanic material production (Q= 1000 t/y).

| Economical parameter	P=330 €/t	P=360 €/t	P=420 €/t	P=500 €/t
Total fixed cost, C (€)	308,550	308,550	308,550	308,550
Initial working capital, IC (€)	55,540	55,540	55,540	55,540
Operational cost (no tax), OC′(€/y)	330,640	331,540	333,340	335,740
Revenues, R (€/y)	330,000	360,000	420,000	500,000
Taxes, [T = 0.3(R – OC′)] (€/y)	0	8,540	26,000	49,280
Net profit, (K = R-OC′-T) (€/y)	0	19,920	60,660	114,980
Return on investment, i_r (%)	**0**	**5.5**	**16.7**	**31.6**
Payout period, τ (years)	**-**	**18.3**	**6.0**	**3.2**
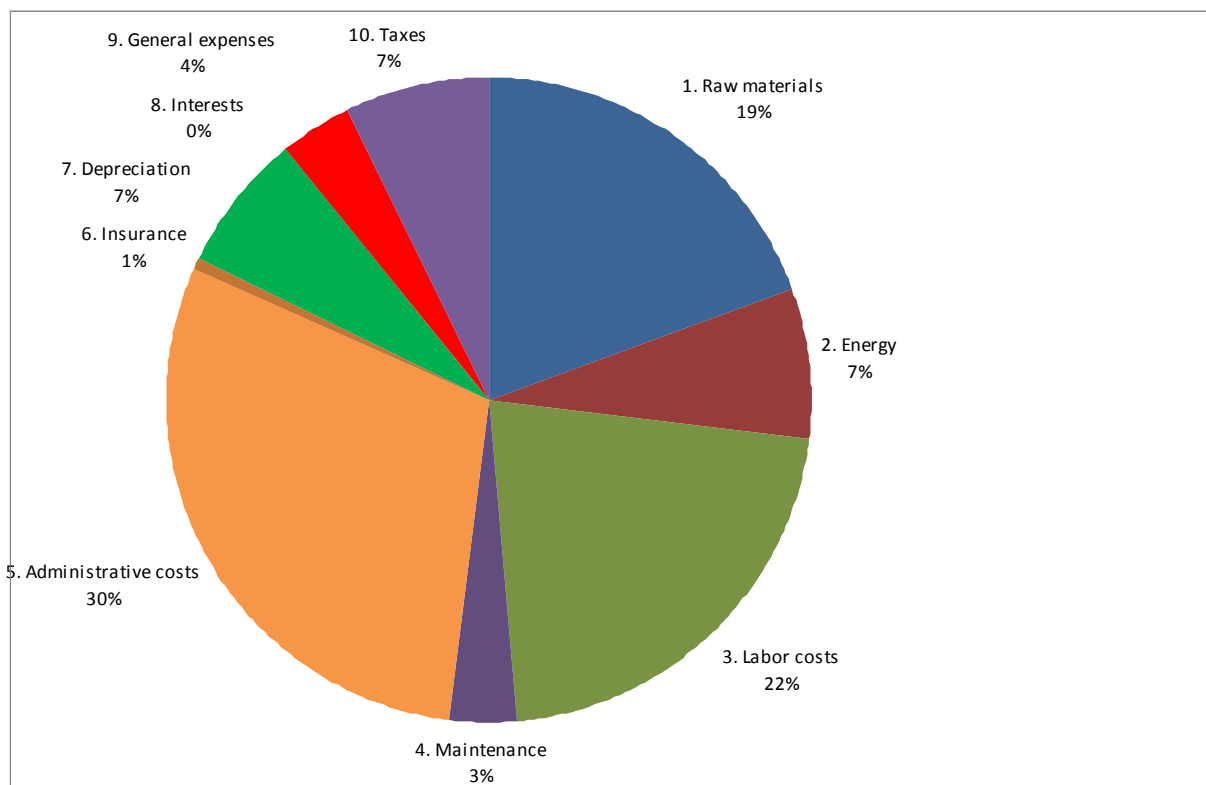
Figure 5.6 Comparative distribution of various operational components for pozzolanic material production from RHA (Q=1000 t/y, P=420 €/t).

5.6.4   Cost-benefit analysis for RHA valorisation as insulation material

Depending on the combustion method chosen, RHA can vary from having a negative value, where costs have to be incurred to dispose of it, to having various positive values depending on its quality and the market for its beneficial use.

The main characteristics that determine the potential value of RHA as an insulation material are:

- residual carbon content,
- significant quantity of crystalline phases of silica dioxide present
- mainly amorphous silica with little or no crystalline phases

Given the premise that a viable rice husk fuelled power plant is to be built (or to be re-arranged in order to meet the above requirements), the cost-benefit resulting from increased expenditure to produce an RHA with higher value than would otherwise result is assessed in this section.

In order to examine the cost benefit analysis for RHA, we have chosen a generic rice husk fuelled power plant sized to produce 3MWe (net) has been chosen. Unless stated otherwise, the analyses use the following assumptions:

- ash content of fuel is 18%
- annual operating time of plant 7,500 hours
- all prices are in €

In order to put into perspective the additional revenues attributable to RHA use, it is useful to keep in mind that, if electricity has a value of 0.05 €/kWh and all the plant output is sold at this price, the annual revenue from electrical sales is 1,125,000 €.

a. *RHA disposal – Negative benefit*

The predominant reason why RHA would only be suitable for disposal is when its residual carbon content exceeds 7%. Based on the power generation technologies examined within the scope of this work, those that seem to result most often in a higher residual carbon content are gasifiers.

A plant producing 3MWe using gasifier technology will have multiple units because the application of gasification to rice husks has not been proven in units larger than about 750kWe. The rice husk consumption will be approximately 3.75 tonne/hr and the RHA leaving the gasifiers will be 0.675 tonne/hr. Over the course of a year of operation, the total RHA produced will be 5063 tonnes.

Typical disposal cost for RHA for transport and disposal at disposal site range from approximately 4€/tonne for local disposal in developing countries where land costs are low, to 40€/tonne and higher for disposal to engineered landfills in developed countries. When disposal costs are as low as 4€/tonne, the negative cost of producing RHA which has no beneficial use would be 20,000 €/year or less than 2% of the revenue from electricity. However, when they are 40€/tonne, the negative cost attributable to disposal could be 200,000€/year, almost 20% of the revenue from electricity.

One solution that has been considered for removing carbon from RHA is to use a fluidized bubbling bed incinerator that would burn off the residual carbon in the RHA. A bubbling bed incinerator is estimated to have a capital cost of 250,000€. Assuming that operating costs are no more than the costs to operate the basic power plant and allowing for maintenance costs of about 4% of capital cost, the annual maintenance cost would be 10,000€.

The application of this type of unit could reduce the RHA carbon content to below 7%. This would eliminate a disposal cost 20,000 € (developing country) to 200,000 € (developed country). Allowing for the maintenance costs, the potential benefit from installing the fluidized bed boiler could be 10,000€/year (developing country) to 290,000€/year (developed country). Based on the additional capital cost of 250,000€, the number of years to recover this amount could be 25 years (developing country) to one year (developed country).

The above suggests that in developing countries, where sites for RHA disposal are low cost, treating RHA from gasifiers to reduce residual carbon content is unlikely to be attractive. In developed countries, where disposal costs are high, such treatment of ash could be attractive provided there is a beneficial use for RHA with below 7% residual carbon exists.

b. *RHA with significant quantity of crystalline silica*

Combustion of rice husks, typically in stoker fired boilers, where the ash experiences sustained temperature above 750°C leads to a significant quantity of crystalline silica in the resultant ash. The steel market is preferred for this type of ash.

A stoker boiler power plant designed to produce 3MWe (net) will typically consume 4.11tonne/hr rice husk. This will result in 0.74 tonne/hr RHA. Over a full year of operation, 5550 tonnes of RHA will be available.

The net value to the producer for RHA sold to the steel industry has been reported to fall in the range 100€ to 150€/tonne. Based on the **mid-range value of 125€/tonne**, the potential revenue from producing RHA acceptable to the steel industry is 694,000€/year. This could be more then 60% of the revenue stream from sales of electricity and is, therefore, an important commercial objective.

There are no significant additional costs needed to achieve RHA with qualities suitable for acceptance by the steel industry. On the contrary, stoker boiler technology with over grate feeders for the fuel, and no need to pre-grind the husks, is at the low cost end of the range of equipment choices.

It is wise to choose boiler suppliers who can demonstrate their track record in producing consistent quality RHA for the steel industry. This could tend to limit competition and hence introduce a hidden cost in the final price. With a typical boiler cost of about 900,000€, it is clear that a premium of 10% to ensure RHA quality would be recovered in a few months of sales of RHA.

The only other additional costs for rice husk power plant generation will be related to tests on ash samples, a higher level of quality control and probably additional employees to handle the RHA side of the business. Clearly, with revenue from sales of potentially 694,000€/year, these costs will often be no more than 20% of the revenue.

c. RHA with high amorphous ash content

The only technology to have achieved a good long term record in producing a high amorphous RHA uses suspension firing of pre-ground rice husk ash. Although the ground husk material can be expected to experience temperatures above 750°C, the time at temperature seems to be insufficient to change the amorphous ash to crystalline form.

The cost of the boiler will be similar to a stoker fired unit of the same size. The main difference will be that there is no need for a moving grate, but the fuel will be fed pneumatically using burners suited to fine particulate material. The extra cost for this approach is mainly associated with husk preparation which will require rice husk grinders.

Based on a 4.11 tonne/hr husk feed, as required for the generic 3MWe (net) plant, installed cost of hammer mill grinders is estimated to be 186,000€. In addition to the capital cost, the grinders require considerable maintenance, including replacement screens, hammers and refurbishment of cutting plates. Based on an annual throughput of 32,500 tonne/year, the maintenance is estimated at 35,000€/year. In addition, the hammer mills will consume electricity at an annual rate of 772,000kWh. Based on a value of electricity of 0.08 €/kWh, the value of the electricity for grinding the husk is 60,000€/year.

The RHA from a plant producing predominantly amorphous ash has a net value of approximately 90€/tonne (allowing 30€/tonne for freight to market). On this basis the total yearly revenue from sale of the RHA from the generic plant would be 505,000€. After deducting the annual cost for maintaining the hammermills and the value of electricity to run them, the remaining revenue is 300,000€. Even allowing for additional work related to managing the sale of the RHA, the payback time for the additional equipment needed to produce amorphous RHA will be less than six months.

Based on the above, the best choice would seem to be to produce RHA for the steel industry as this has the best returns. However, growth in the market for RHA to the steel market is limited. Growth in the market for RHA in the cement industry is potentially very large. For this reason, a new entrant to the marketplace may prefer to target the somewhat less high returns but better longer term prospects of the cement market.

d. Potential to earn carbon credits

The Kyoto Protocol is part of the UN's Framework Convention on Climate Change and has set an agenda for reducing global greenhouse gas emissions. If CO_2 emissions can be shown and verified to be reduced due to different practices, then Certified Emission Reductions (CERs) can be generated.

If RHA is used in concrete manufacture as a cement substitute then there is the potential to earn CERs. Cement manufacturing is a major source of greenhouse gas emissions, accounting for approximately 7% to 8% of CO_2 globally.

There is an emerging market globally for CER's, with current prices around US$5/tonne of CO_2. It is hard to predict the size and future prices within the market, but using RHA as a cement substitute can generate CERs, and one company (Alchemix) has already investigated selling these on the international market.

The cement industry is reducing its CO_2 emissions by improving manufacturing processes, concentrating more production in the most efficient plants and using wastes productively as alternative fuels in the cement kiln. Despite this, for every tonne of cement produced, roughly 0.75 tonnes of CO_2 (greenhouse gas) is released by the burning fuel, and an additional 0.5 tonnes of CO_2 is released in the chemical reaction that changes raw material to clinker (calcination).

The potential to earn CERs comes primarily from substituting Portland cement with RHA. There are other environmental benefits of substituting Portland cement with RHA. The need for quarrying of primary raw materials is reduced, and overall reductions in emissions of dust, CO_2 and acid gases are attained.

The World Bank Prototype Carbon Fund provides examples of acceptable CERs from substituting Portland Cement. Their guidelines have been adapted to show the potential income from CERs for the generic 3MW rice husk to energy power plant used for the Cost Benefit Analysis.

A 3MW suspension fired boiler plant would typically produce 5550 tonnes annually of RHA. Assuming 50% of RHA produced is sold for cement substitution:

$$\text{Rice Husk Ash produced (5555 tonne/yr)} \quad \times \quad 50\% \quad = \quad \text{RHA sold for cement substitution (2775 tonne/yr)}$$

Emission reductions from substitution of Portland cement are calculated as totalling 1.25 tonnes of CO_2 per tonne of cement substituted, derived as follows:

0.75 tonnes of CO_2 per tonne of cement from energy use
0.50 tonnes of CO_2 per tonne of cement from calcinating limestone

Thus the total annual emission reduction for cement with RHA substitution in cement is:

RHA sold for cement substitution (2775 tonne/yr)	x	1.25 tonnes of CO_2 per tonne cement	=	Annual Emissions (3469 tonnes CO_2/yr)

Using estimates of approximately US$5/tonne of CO_2, this could provide an additional annual income stream of US$17,345. This is not significant compared to the potential income from sales to the steel market and to the cement market, but could make a difference in a marginal project.

5.7   Optimization and testing runs

5.7.1   Introduction

Generally, reactivity of a pozzolanic material can be favoured by increasing fineness (Mehta 1994, Saraswathy 2007). When burning temperature exceeds 600ºC partially changing silica to cristobalite, quartz and trydimite (a crystalline material), grinding is especially important. The burning of rice husk generates a significant volume of RHA that commonly ends up being dumped, blemishing the environmental footprint of the rice industry. Given that rice husk comprises approximately 20% of the unrefined rice and that RHA is 18% of rice husk, it is estimated that the total quantity of RHA generated globally is close to 21 million tons per year. It has been demonstrated that RHA exhibits significant pozzolanic potential; however the way in which the material develops its potential is largely influenced by inherent factors, principally fineness and reactive silica (Mehta 1978, Mehta 1992, Malhotra and Mehta 1996, Agarwal 2006).

The study presented herein, examines the potential of a Greek rice industry's treated RHA where two types were considered differing in reactive silica content and then fineness, in order to better understand the nature of this stream. Fineness levels were kept, for one RHA type, first at a regular level and then at a significantly lower level than those reported in the literature, in an effort to assess the reactivity of the material as a function of grinding. RHA was added in mortar systems and then in concrete and factors like strength and durability characteristics were determined to conclude on the potential of the local by-product.

5.7.2 Testing program

In a first study, the cement replacement considered was 10% and 15% with two different types of RHA obtained from a Greek rice industry, named A (Agrinio) and Θ (Thessaloniki). Mortars with 10% and 15% cement (CEM I) replacement with each RHA were produced, as well as a silica fume mortar with 10% cement replacement by commercial silica fume. All mortars with the same water/binder ratio were dosed with superplasticizer in order to present equivalent workability. Specimens were tested for strength, absorption by capillarity, chloride ion penetration, accelerated carbonation and resistivity. In the first study, the fineness of RHA presented a mean particle diameter much greater than cement (65-70 μm for RHA in comparison to cement of 20 μm). In a second study, RHA (type A) was ground very finely (with mean particle size of 6μm) and the cement replacement was 10 and 20%.

a. Materials

Materials used to produce mortar were tap water, CEM I 42,5 R type of cement, commercially available silica fume and the two experimental types of rice husk ash A and Θ, superplasticizer and standard CEN sand. Particle size distribution curves of RHA and cement and SEM photos of RHA are shown in Fig 5.7 Chemical analyses are shown in Table 5.10 and compared to results by other authors.

Table 5.10 Chemical analysis for cement and RHA A and RHA Θ and results for RHA by other authors (Umamaheswaran and Batra 2008, Mehta 1994).

	cement	RHA A	RHA A	RHA Θ	RHA Θ	RHA	RHA
		IETCC	supplier	IETCC	supplier	Umamaheswaran and Batra 2008	Mehta 1994
LOI [%]	2,85	6,34	-	6,30		0,80	3-18
total SiO₂ [%]	20,41	89,05	88 - 98	86,50	88 - 98	93,52	80-95
reactive SiO₂ [%]	-	81,43	-	78,64	-	-	-
Al₂O₃ [%]	4,74	1,73	< 1	2,70	< 1	0,01	-
Fe₂O₃ [%]	3,08	1,31	-	0,00	-	0,51	-
CaO [%]	62,28	3,05	< 1	4,40	< 1	0,68	-
MgO [%]	1,90	2,15	-	1,97	-	-	-
free CaO [%]	1,01	0,46	-	0,0	-	-	-
K₂O [%]	-	-	< 1	-	< 1	-	1-2

Reactive SiO₂ determined by EN -197-1

RHA A

RHA A ×2000

RHA Θ

RHA Θ ×2000

Cement CEMI 42,5R

	A	Θ	CEM
		μm	
d(0,1)	15,63	17,29	2,43
d(0,5)	65,93	70,46	19,91
d(0,9)	206,56	19,91	55,76
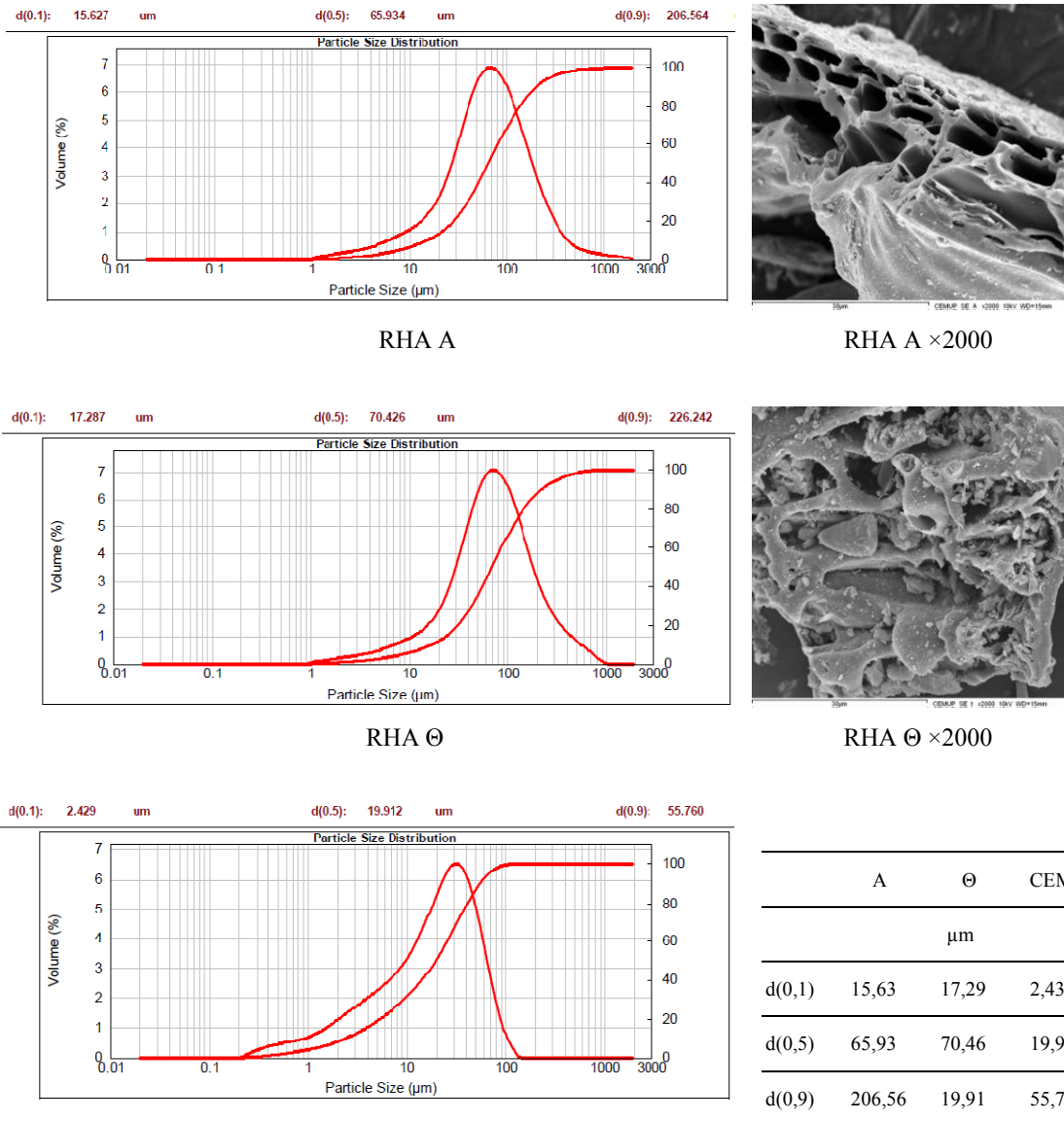
Figure 5.7   Particle size distribution curves of RHA (non-ground) and cement and SEM photos of RHA

b. *Mixture proportions and workability*

Mortar specimens according to mixture proportions shown in Table 5.11 were produced according to NP EN 196-1 (1996) after assessing workability. Workability was measured following the procedure described in ASTM C230 (2003) and ASTM 1437 (2001). Control mortar (CTL) workability was set as target workability and superplasticizer added so as to obtain equivalent workability (±10mm) for all types of mortar.

Table 5.11   Mixture proportions and workability.

	CTL	$SF_{10\%}$	$A_{10\%}$	$A_{15\%}$	$\Theta_{10\%}$	$\Theta_{15\%}$
sand (g)	1350	1350	1350	1350	1350	1350
Cement (g)	450	405	405	382,5	405	382,5
ash (g)	0	45	45	67,5	45	67,5
water (g)	225	225	225	225	225	225
Superplasticizer (g)	0	3.4	1.2	2.2	1.2	2.2
workability	210.2	210.1	204.4	209.6	203.3	206.1

c. Strength

Mortar strength was determined at 7, 28 and 90 days, following the standard procedure described in NP EN 196-1 (1996).

d. Absorption by capillarity

Transport properties of the concrete surface, which play a major role in durability of reinforced concrete, are controlled by three mechanisms; namely, capillary absorption, permeability, and diffusion (Neville 1998). Usually, concrete that is more resistant to the ingress of aggressive agents (water or carried ions, oxygen, and carbon dioxide) will be more durable. In the present study water absorption by capillarity, chloride ion migration, resistivity, and accelerated carbonation tests were carried out to assess durability. To consider the ability of the concrete surface to absorb water by capillary suction, the RILEM TC116-PCD (1999) recommendation was adopted as a basis. The moulded side faces of 100 mm diameter and 50 mm height cylindrical specimens were tested, instead of the moulded bottom face of 150 mm cube specimens used in the RILEM recommendation. The 56 (instead of 28) days old standard-cured (water at 20ºC) specimens were allowed to dry in a ventilated heater at 40ºC until constant mass was achieved. After cooling to 20ºC, the specimens were put on rods in a shallow bath of water at 20ºC, approximately 3 mm deep. The uptake of water by capillary absorption was measured through the weight gain of each specimen at time intervals until 4-1/2 h of contact with water. The absorption of water into concrete under capillary action is dependent on the square-root of time and may be modeled as (Hall 1989):

$$A = a_0 + St^{0.5} \tag{5.7}$$

where, A (mg/mm^2) is the water absorption by unit area since the time the specimen was dipped in the shallow bath; S (mg/(mm^2×min.$^{0.5}$)) is the "sorptivity" of the material; t is the elapsed time in minutes, and a_0 (mg/mm^2) is the water initially absorbed by pores in contact with water. Testing each specimen led to average (of 3) sorptivity results with correlation coefficients (R) over 0.978.

e. *Chloride ion penetration*

Chloride ion penetration was assessed by the Luping method, which is a non-steady state migration method based on a theoretical relation between diffusion and migration. The method enables the calculation of the apparent chloride diffusion coefficient (Dns) from an accelerated test (NT BUILD 492 1999). It is based on measuring the depth of colour change of a silver nitrate solution sprayed on the specimens previously submitted to a migration test. Specimens (100 mm diameter by 50 mm height) were submitted to an electrical current corresponding to a potential difference, in this case, of 30 V, during 24 h. Chloride ions are forced to migrate out of a NaCl solution subjected to a negative charge at the surface of the specimen, through the concrete into a NaOH solution maintained at a positive potential at the opposite surface of the specimen. The specimens are then split open, sprayed with nitrate solution and the chloride penetration depth (x_d) is measured in order to enable calculation of the apparent diffusion coefficient (D_{ns}) (Eq. 5.9).

$$D_{ns} = \frac{0.0239(273 + \mathrm{T})\,\mathrm{L}}{(\mathrm{U} - 2)\,\mathrm{t}}\left(x_d - 0.0238\sqrt{\frac{(273 + T)Lx_d}{U - 2}} \right) \tag{5.9}$$

where D_{ns} is the non-steady-state migration coefficient (×10^{-12} m^2/s), U is the absolute value of the applied voltage (V), T is the average value of the initial and final temperatures in the anodic solution (ºC), L is the thickness of the specimen, usually 50 mm, x_d is the average value of measured chloride penetration depth (mm), and t is the testing period (h).

f. **Resistivity**

Concrete resistivity is another parameter that contributes to durability assessment. When pores are saturated, electric current flows more easily, depending on the pore structure. Prior to the chloride

migration test described above, specimens are pre-saturated. Therefore, when current is imposed during the test it is possible to evaluate resistivity, Eq. (5.10), in saturated conditions to compare different types of concrete, in this case, mortar.

$$\rho \equiv R \cdot \frac{A}{L} \equiv \frac{V \cdot A}{L \cdot I} \qquad (5.10)$$

where R is the electric resistance, (Ω - Ohm), I, current (A), V, voltage (V), ρ, electric resistivity (Ω.m), L, length (m), and A (m^2), the area of the test specimen across which current passes.

g. Carbonation

Accelerated carbonation tests were carried out following the procedure described in LNEC E391 [1993], using a chamber with 5% carbon dioxide and relative humidity (RH) of approximately 65%. 40×40×160 mm test specimens of each mortar type were kept in the chamber for two months, after 28 day curing in water at 20ºC. A slice from each test specimen was sawed off and sprayed with phenolphthalein solution, enabling the measurement of the carbonation depths.

5.7.3   Test results & discussion

Strength results at 7, 28 and 90 days, sorptivity results, resistance to chloride penetration, resistivity results at 56 days and carbonation results of each mortar type, are shown in Table 5.12. All these results refer to the regular ground form of RHA. Both types of RHA mortar with 10% and 15% cement replacement performed worse than the control mortar regarding strength, resistance to chloride penetration and carbonation resistance. Although a similar reduction, on average, in compressive strength was noticed at 28 and 90 days (10 % and 9% respectively) for all the RHA mortar samples, samples incorporating 15% RHA produced much higher carbonation depths (89% increase) than those incorporating 10% (17 % to 33 % increase).

In terms of resistivity, samples incorporating 15% RHA produced an increase compared to control (9% and 15% for RHA type A and Θ respectively), while on samples with 10% RHA the resistivity was decreased (16% maximum decrease for RHA type Θ). In terms of sorptivity, performance increased with replacement percentage (a 65% increase was noticed on samples incorporating 15% RHA type Θ).

Table 5.12 Mechanical and durability test results and enhancement by the use of RHA (regular ground).

Results and Enhancement		*CTL*	$A_{10\%}$	$A_{15\%}$	$\Theta_{10\%}$	$\Theta_{15\%}$	$SF_{10\%}$
$\sigma_{\,7\,days}$ [Mpa]	*Rslt.*	38,7	37,1	37,5	38,6	37,1	48,7
	Enh.		-4%	-3%	0%	-4%	26%
$\sigma_{\,28\,days}$ [Mpa]	*Rslt.*	48,0	42,5	42,9	44,6	42,6	58,8
	Enh.		-11%	-11%	-7%	-11%	22%
$\sigma_{\,90\,days}$ [Mpa]	*Rslt.*	53,3	48,4	49,0	49,1	47,7	58,0
	Enh.		-9%	-8%	-8%	-11%	9%
S [mg/(mm^2.min$^{1/2}$)]	*Rslt.*	0,1510	0,1233	0,0653	0,1023	0,0533	0,0883
	Enh.		18%	57%	32%	65%	42%
D_{ns} [×10^{-12} m^2/s]	*Rslt.*	15,31	16,32	17,62	17,24	16,59	2,44
	Enh.		-7%	-15%	-13%	-8%	84%
Carbonation [mm]	*Rslt.*	3,0	3,5	5,7	4,0	5,7	4,8
	Enh.		-17%	-89%	-33%	-89%	-61%
Resistivity [Ω.m]	*Rslt.*	53,7	48,6	58,4	44,9	61,8	279,5
	Enh.		-9%	9%	-16%	15%	420%

Enhancement (Enh.)=(Rslt.$_{RHA}$-Rslt.$_{CTL}$)/Rslt.$_{CTL}$

In Table 5.13, strength and accelerated chloride test results on concrete are given for the second study, where RHA (type A) was ground very finely to obtain SRHA (Fig. 5.8) and used as 10 and 20% cement replacement in concrete.
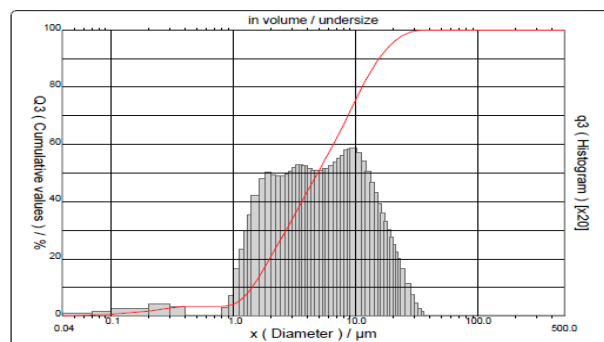
d(0,1): 1,41μm
d(0,5): 4,85μm
d(0,9): 15,43μm

Figure 5.8 Particle size distribution curve of SRHA

Table 5.13 Mechanical test results, left and electric charge, right, in concrete with superfine RHA.

	Control	10% SRHA	20% SRHA		Charge passed [Coulombs]	Permeability Class [ASTM]
7 d	38.7	39.2	38.9	Control	2719	Moderate
28 d	48.0	51.2	50.2	10% SRHA	2569	Moderate
				20% SRHA	864	Very Low

At 7 days the compressive strength proved to be similar to control samples (1% increase for both 10% and 20% levels of RHA), while at 28 days strength was slightly increased up to 7% for samples incorporating 10% RHA. Superfine RHA performs better than cement, even for 20% replacement. In this second study the chloride resistance of mortar incorporating SRHA was also evaluated, using the ASTM accelerated penetration test method. The samples before testing, were immersed for a period of 55 days in saturated Ca(OH)$_2$ solution. This period of time is more than adequate for a sufficient level of cement hydration and pozzolanic reactions of the ash used, as previously shown. The overall excellent behavior of the samples tested (in comparison to control) is given in Table 5.13, right, where the electric charge passed through the samples is given for both levels of SRHA used.

It is obvious that the mechanical grinding led to the development of smaller grain sizes than those of cement. It is generally acceptable that, at concrete level, the small grain sizes of ash strengthen (through the filler effect) packing among aggregates (especially in the case of fine aggregates) and cement grains. This is further enhanced with pozzolanic ash, reducing in this way the overall porosity (hence the permeability) of the final product. This is confirmed by results obtained according to the official classification by ASTM C1202 (see Table 5.13, right), where mortar incorporating SRHA exhibits low permeability to chloride ingress, in contrast to conventional mortar where permeability observed is of medium level.

5.7.4 Discussion and further suggestions

The work presented in this study, examines the potential use of a Greek rice indusrty's upgraded RHA where two types were considered differing in reactive silica and then fineness so as to better understand the nature of this waste stream. Fineness levels were kept, for one RHA type, first at a regular level and then at a significantly lower level than those reported in literature, in an effort to assess the reactivity of

the material as a function of grinding. RHA was added in mortar systems and factors like strength and durability characteristics were determined to conclude on the potential of the local by-product.

● In the first study, cement replacement considered was 10 and 15% with the two different types of RHA, with regular grinding. Both types of RHA mortar with 10 and 15% cement replacement performed worse than control mortar in regard to strength, resistance to chloride penetration and carbonation resistance. Performance in terms of resistivity was similar to control and in terms of sorptivity, performance increased with replacement percentage. Unsatisfactory results were explained by insufficient fineness evaluated by laser particle distribution on the RHA samples.

● A second study involving cement replacement with 10 and 20% of RHA ground very finely, led to equivalent or better results compared to control concrete in terms of strength but, principally, chloride resistance was dramatically increased thus leading to the conclusion that fineness is a key issue in terms of RHA use as a cement replacement material.

As cement industry contributes significantly to global CO_2 emissions, making cement production greener is currently a very urgent challenge. Reducing the rate of clinker production by using mineral replacements, i.e., additions or supplementary cementing materials such as RHA with enhanced reactivity, contributes to greener concrete and thus sustainable construction.

Although the above recent results showed that RHA is a good pozzolanic material – i.e. hydraulic character may result when moisture is present - and also building materials acquire a number of desirable properties because of it (water demand reduction in comparison to silica fume, increased resistance to alkali, reduced erosion due to improved packing, etc.), this Greek product still faces two challenges in order to increase its exploitation in the building sector:

• its limited availability
• its reduced activity - in relation to silica fume

Because of the above, there is limited interest of the domestic cement industry for the Greek RHA (as this industry is now into additives with substantial and continuous supply, and moreover due to current economical crisis). The apparent abandoning of RHA use in composite cements leads to the implementation of "special" applications or products, e.g. RHA use in special mortars (e.g. repair), or to concrete with specific requirements (e.g. "gunite") at rates that are allowed by the Greek concrete norms.

For the above solutions to be realistic and given that the activity of the Greek RHA is not proportional to the activity of additives such as silica fume (k = 3) or metakaolin (k = 2.5), the k of the Greek RHA needs to be increased. Thus, ways for its activation should be further sought. This combined with the inherent property of RHA to "demand" less water for the same workable and the proved durability in time, can lead to an end product of high value that will be used almost exclusively in the dry construction.

The two features of RHA that need to be affected in order to activate it are: (a) its rich siliceous structure and (b) its fineness. If any of these (or both) are affected significant changes in the activity of RHA may be caused. Previous experience with less active materials (eg fly ash, slag, etc.) has shown that such changes can be catalytic and financially advantageous.

The following activation methods are proposed to be studied:

Ultra-fine jet milling: the mechanical activation is tested by grinding to a special air jet mill. This does not work like the conventional sphere mill, but works with collision with air flow that ensure collisions of RHA and lead (using embedded splitter) in very fine particles. Given the extreme sensitivity of RHA to fineness change, it is estimated that ultra-fine jet milling will activate RHA more than it was achieved with the sphere or vibrated mill.

Selective fractionation: refers to the processing of the coarse fraction (e.g. 45 mm) of RHA. We take advantage of the expected enrichment in active SiO_2 to a higher quality pozzolan than the original. Sieving and grinding is required (in order not to lose the filler effect of RHA) while attention is given to factors such as unburned carbon (LOI), which also is expected in coarse fractions. Similar experiments in the Greek fly ashes gave impressive results by demonstrating higher strength (mostly final)> 10-15%.

Grinding in the presence of grinding aid/strength enhancer: The separate grinding of pozzolans is a trend in many European countries. Usually grinding improvers are used when grinding pozzolans and clinker together. However, research has progressed a lot and now there are additives that can help the grinding and also **unleash the potential of pozzolans (strength enhancers).** Similar experiments with slag have shown that the individual components of these enhancers (usually a mixture of organic compounds) intervene in the ingredients of pozzolana and activate them. In the case of the RHA this is a new field, but given the mineralogy of the material a number of additional auxiliaries can be studied. It is also a fact that the separate grinding of RHA and its subsequent integration into cement is expected to give better results than grinding it together with clinker.

Cooling rate: a key factor for the percentage of amorphism (and thus activity) of RHA. Generally, the more rapid cooling takes place the higher level of amorphism of the material is expected. Along with the investigation at laboratory scale (simulation of production conditions and application of different cooling rates from the slowest to very sudden water extinction - and 1-2 intermediate), the extension to an industrial level plant is proposed as long as there is such a possibility for the Greek rice industry.

5.8   Environmental benefits

Under the scope of the present study, an evaluation of RHA, alone or as mixes with other ashes, as Type II additives on CEM I type of cement, and their effects in terms of their performance in carbonation and chloride exposure, for a service life of 50 years, in addition to their environmental output is carried out. The overall aim is to portray the basis for the previously mentioned balanced approach between sustainability and durability of reinforced concrete structures (optimum solution, Chapter 3).

5.8.1   Estimation of concrete service life

The effect of cement type on the overall durability design of concrete exposed to corrosive environments, due to carbonation and chloride diffusion, is briefly presented in this section for reasons of integrity (despite it has been presented in Chapter 2). As durability indicators, calculation of the carbon dioxide penetration front, for a period of 50 years, was used for carbonation exposure, while under chloride ingress, the estimation of the adequate concrete cover needed to sustain a service life of 50 years was calculated.

The service-life, and compressive strength, evaluation were made using a software tool (EUCON), based on proven predictive models (according to performance-related methods for assessing durability) developed and validated elsewhere (Papadakis 1999, Papadakis and Efstathiou 2005), for the estimation of concrete service life when designing for durability under harsh environments. Concrete service life is reliably predicted using fundamental mathematical models that simulate the basic deterioration mechanisms of reinforced concrete (carbonation, chloride penetration). Principles of chemical and material engineering have been applied to model the physicochemical processes leading to concrete carbonation, as well as the processes of chloride diffusion in the aqueous phase of pores, their absorption and binding in the solid phase of concrete and their desorption.

A constant volume unit (1 m^3) of concrete was chosen as a common basis. When an SCM (or a mixture of SCM) was added to this unit, then an equal volume of another component, either cement or aggregate, was removed in order to keep the same total volume and the common comparison basis. A typical CEM I mix, water cured for 28 days (as it is assumed by the proven predictive model used) was selected as the reference type of cement (w/c: 0.5, cement content 300 kg/m^3, 31.5 mm crushed aggregates, no additives, no admixtures). Several mix design configurations were considered, where each time addition of *FA, RHA* and a mixture of 50 % *FA* and 50 % *RHA*, (as Type II additives) took place, as cement and as aggregate replacement. 10, 20 and 30 % replacement levels of the control cement mass were chosen, with the water content (kg/m^3) kept constant for all specimens. The mix design configuration and the results observed are given in Table 5.14.

Table 5.14 Mix design and durability indicators.*

SCM type	SCM (%)	C	W	w/c	A	FA	RHA	f_{cu}	Δf_{cu}	r_{FA}	r_{RHA}	X_c	Δx_c	C_{50}	ΔC_{50}
	0	300	150	0.5	1925	-	-	44.6	-	-	-	19.6	-	29	-
FA	*As aggregate replacement*														
	10	300	150	0.50	1896	30	-	51.4	15.3	1	-	15.9	-19	19	-34.5
	20	300	150	0.50	1866	60	-	58.0	30.0	1	-	12.4	-37	11	-62.1
	30	300	150	0.50	1837	90	-	64.4	44.4	1	-	9.8	-50	5	-82.8
	As cement replacement														
	-10	270	150	0.56	1920	30	-	45.8	2.69	1	-	21.3	8.7	25	-13.8
	-20	240	150	0.63	1916	60	-	46.9	5.16	1	-	23.3	18.9	21	-27.6
	-30	210	150	0.71	1911	90	-	48.0	7.62	1	-	25.5	30	17	-41.1
RHA	*As aggregate replacement*														
	10	300	150	0.5	1890	-	30	51.4	15.3	-	1	17.7	-9.7	11	-62.1
	20	300	150	0.5	1856	-	60	56.3	26.2	-	0.87	16.1	-18	3	-89.7
	30	300	150	0.5	1821	-	90	56.3	26.2	-	0.58	15	-23	3	-89.7
	As cement replacement														
	-10	270	150	0.556	1915	-	30	45.8	2.69	-	1	23.4	19.4	17	-41.4
	-20	240	150	0.625	1905	-	60	42.8	-4.04	-	0.7	28.2	43.8	13	-55.2
	-30	210	150	0.714	1895	-	90	35.9	-19.5	-	0.41	34.4	75.5	23	-20.7
	As aggregate replacement														
	10	300	150	0.5	1893	15	15	51.4	15.3	1	1	16.6	-15	15	-48.3
	20	300	150	0.5	1861	30	30	58	30.0	1	1	14.4	-26	5	-82.8
	30	300	150	0.5	1829	45	45	59.1	32.5	0,45	1	14.1	-28	3	-89.7
FA+RHA	*As cement replacement*														
	-10	270	150	0.556	1918	15	15	45.8	2.69	1	1	22.1	12.8	21	-27.6
	-20	240	150	0.625	1910	30	30	46.9	5.16	1	1	25.4	29.6	13	-55.2
	-30	210	150	0.714	1903	45	45	35.9	-19.5	0	0.82	35.1	79,1	23	-20.7

* C, cement content (kg/m^3), W, water content (kg/m^3), W/C water/cement ratio, FA fly ash content (kg/m^3) RHA rice husk ash content (kg/m^3), f_c concrete compressive strength (MPa), x_c carbonation depth (mm), C_{50} adequate concrete cover needed to sustain chloride exposure for 50 years (mm).

Overall it was seen that when SCM were used for aggregate replacement, the carbonation depth was decreased compared to the control mix. Incorporation of *FA* in CEM I type of cement, produced a better performance under carbonation exposure than the other SCM types and mixtures used. Addition of 30% of *FA* reduced the carbonation depth by 50%, compared to 23.5% and 28.1% reductions, when *RHA* and their mixture (50% *RHA* and 50% *FA*) were used respectively. In the case where SCM were used as cement replacement materials, the carbonation depth was increased, with the increasing content of every type of SCM used.

As far as chloride exposure is concerned, specimens incorporating SCM whether aggregate or cement was substituted, produced smaller concrete cover values needed to sustain chloride exposure for a service life of 50 years, compared to control. *RHA* proved to inhibit chloride diffusion more efficiently than *FA*. A 89.7% reduction of the previously mentioned adequate concrete cover was noticed, compared to 82.8% reduction when *FA* was used, for a 30% content of SCM.

Overall utilisation of SCM in concrete mix design produced considerable gains in the 28 days concrete compressive strength. Incorporation of FA produced an increase of 44.4% (from 44.6 MPa to 64.4 MPa) compared to the 26.2% and 32.5% increases when RHA and the RHA-FA mixture were used, respectively.

5.8.2   Environmental impact of concrete

It was previously mentioned that in producing concrete the main emissions to air are associated with cement manufacturing. However, other concrete constituents also contribute in that sense. In general, it can be said that the CO_2 emissions from concrete production are the summation of the emissions from, the chemical conversion process in clinker production (during cement manufacturing), from the energy consumption due to fossil fuel combustion (also during cement manufacturing), from the electrical energy required for the grinding of any additive materials and from the energy required (in terms of fuel consumption) for the transportation of the raw materials and of the final product. A more precise estimation of the environmental footprint (environmental factors) of each individual concrete component, based on the literature and on data derived from a Greek cement manufacturing company, is presented in this section. The overall environmental footprint of concrete (E_{conc}) can be calculated as:

$$E_{conc} = C \cdot E_c + R \cdot E_R + F \cdot E_F + A \cdot E_A + W \cdot E_W + D \cdot E_D \qquad (5.11)$$

C, R, F, A, W, D: are the contents (in kg / m^3 of concrete) of cement, rice husk ash, fly ash, aggregate, water and admixtures, respectively, and

E_C, E_R, E_F, E_A, E_W, E_D: the environmental cost (in kg of CO_2 / kg of cement) of cement, rice husk ash, fly ash, aggregates, water, admixtures, respectively.

For the calculation of the environmental cost of the individual concrete components the following were taken under consideration.

In terms of cement, according to the literature, the CO_2 emissions associated with cement production vary from 700 to 1000 kg CO_2/kg cement (Flower *et al.* 2007). According to Hoeing *et al.* (2010) 0.65-0.92 kg of CO_2 is produced for per kg cement produced based on a cement plant with a modern technology and equipment. The CO_2 emission for cement Type I is approximately 800 g/kg cement, less for the other cement types with lower clinker contents (Josaa *et al.* 2004).

In this study a more precise estimation was made using operational and production data from the Greek cement-manufacturing company. By taking under consideration the chemical equation of incomplete combustion of coal (Eq. 2), where 94 kcal/mol of energy is produced (Q), since it is an exothermic reaction, the amount of CO_2 produced from energy consumption of 1KWh is calculated as 0.404 kg (1 cal is equal to $1.162 \cdot 10^{-6}$ kWh, hence 94 kcal equal to 0.109 KWh producing 44 g of CO_2).

$$C + O_2 \rightarrow CO_2 + Q \qquad\qquad (5.12)$$

By taking into account data as, the amount of cement produced (1,700,000 tn/year), the electrical energy required (500,000 kWh/day) the level of CO_2 emissions measured (3,801,000 kg/day) and the total days of operation per year (335) the total CO_2 emissions were calculated to be in the range of 1,341,005 t/year. Hence in order to produce 1 t of cement 0.79 tn of CO_2 are emitted into the atmosphere. In addition to the later, the derived CO_2 emissions from transportation should be added. Considering that on average 2.74 kg of CO_2 is emitted per litre of fuel, using vehicle transport, and that fuel consumption is estimated to be 1 lt / 3 km for 5 tn of raw materials, the overall emissions arise from transportation are estimated to be 0.183 kg / km / t of raw material (GHG Protocol 2001).

In order to extract, process and grind aggregates the overall CO_2 emissions are estimated to be 5.96 kg / t of aggregates (considering that 2.53 kWh are required for the production of 1 tone of aggregates and that 9

lt of fuel are required for the transportation of a 5 tones shipment, resulting in 4.94 kg of CO_2 / t of aggregates).

When fly ash is used as a secondary cementing material, since it is a by-product of coal burning in electrical power stations, the emissions associated with power generation are not considered of being part of the environmental burden of fly ash. A small amount of energy required for the grinding of the raw material into very fine powder and for its transportation, are the only sources of greenhouse gasses. According to the literature (Integrated Pollution Prevention and Control (IPPC) 2010, U.S. Environmental Protection Agency 2008) the previously mentioned energy requirement is estimated to be in the order of 20 kWh per tone of fly ash produced, hence 8.06 kg of CO_2 per tone of fly ash (emissions from transportation, similar to cement transportation, should also be added).

Table 5.15   Mix design and environmental indicators.

SCM type	SCM (%)	C	W	w/c	A	FA	RHA	X_c	C_{50}	E_C	ΔE_C (%)	P_C
	0	300	150	0.5	1925	-	-	19.6	29	311.47	-	44.76
FA	*As aggregate replacement*											
	10	300	150	0.50	1896	30	-	15.9	19	311.56	-	45.07
	20	300	150	0.50	1866	60	-	12.4	11	311.64	-	45.38
	30	300	150	0.50	1837	90	-	9.8	5	311.72	-	45.70
	As cement replacement											
	-10	270	150	0.56	1920	30	-	21.3	25	281.70	-9.6	42.66
	-20	240	150	0.63	1916	60	-	23.3	21	251.94	-19.1	40.56
	-30	210	150	0.71	1911	90	-	25.5	17	222.16	-28.7	38.47
RHA	*As aggregate replacement*											
	10	300	150	0.5	1890	-	30	17.7	11	311,30	-	46.96
	20	300	150	0.5	1856	-	60	16.1	3	311.13	-	49.17
	30	300	150	0.5	1821	-	90	15	3	310.95	-	51.37
	As cement replacement											
	-10	270	150	0.556	1915	-	30	23.4	17	281.45	-9.7	44.55
	-20	240	150	0.625	1905	-	60	28.2	13	251.42	-19.3	44.34
	-30	210	150	0.714	1895	-	90	34.4	23	221.39	-28.9	44.14
FA + RHA	*As aggregate replacement*											
	10	300	150	0.5	1893	15	15	16.6	15	311.43	-	46.02
	20	300	150	0.5	1861	30	30	14.4	5	311.38	-	47.28
	30	300	150	0.5	1829	45	45	14.1	3	311.34	-	48.54
	As cement replacement											
	-10	270	150	0.556	1918	15	15	22.1	21	281.58	-9.6	43.61
	-20	240	150	0.625	1910	30	30	25.4	13	251.67	-19.2	42.45
	-30	210	150	0.714	1903	45	45	35.1	23	221.78	-28.8	41.30

In the case of rice husk ash, since it is available from limited regions on European level, the related emissions arise from the amounts of energy required for the controlled burning of rice husk, for the grinding of the raw material into very fine powder and for its transportation. They can be safely assumed to be twice of those of fly ash.

As far as water is concerned, the only source of emissions arises from the electrical energy required to pump the water, which in this study is considered to be negligible. The total volume of admixtures added in a concrete mix is usually less than two litres per cubic metre of concrete. In addition, the CO_2 emissions generated from admixtures are very small ($2.2 - 53$ x 10^{-3} kg CO_2-e/l admixtures). Therefore, the environmental footprint of admixtures can be ignored. Since no admixtures were used on the mix design of the different concrete configurations used in this study, the environmental impact of admixtures is ignored. In this way, based on the proportions of the concrete constituent materials used (Table 5.14) and on the environmental factors, as derived above, the overall environmental cost of concrete was calculated (Table 5.15). For reasons of comparison, the durability indicators (carbonation depth "x_c" and adequate concrete cover to sustain chloride exposure for 50 years "c_{50}") as well as, an estimation of the economical cost of each mix design used, based on the individual prices of the raw materials are also given in Table 5.15.

A first observation is that utilization of SCM as aggregate replacements did not change significantly the environmental output of concrete, however, when SCM were used as cement replacements, considerable reductions of up to 28.9 % of the environmental footprint were noticed. A comparative assessment of every **durability, environmental and economical cost indicators**, calculated in this study, for every type of SCM used is given in Figure 5.9. In this way, the reduction of environmental cost observed can be weighted against the durability and service life indicators (especially for chloride exposure) calculated. Overall, the mixture of FA with RHA produced the best balanced behavior, followed by the case when only FA was incorporated in the concrete mix.

A 20 % addition of RHA and FA increased the concrete compressive strength by 5.2 % (same increase as in the case of FA) and produced a 55.2 % reduction of the adequate concrete cover needed to sustain a chloride free structure for 50 years (compared to a 27.6 % when FA was used) resulting also in a 19.2 % reduction of the overall associated CO_2 emissions. However, at higher rates of cement replacement (30 %) FA proved to be more effective resulting in 7.6 % increase of concrete compressive strength and to 20.7 % and 28.7 % reductions of the concrete cover in terms of chloride attack and of the associated

environmental cost. At this rate of cement replacement RHA and RHA/FA mixture gave a lesser performance than FA. The reasons for such a behavior are analyzed in the following section.

5.8.3   Discussion and conclusions

A thorough design of reinforced concrete structures must be the combination of an integrated study and a techno-economic optimization. Economical, environmental and technical parameters must be taken into account for the definition of the best solution. On this note, the aim of this study is to evaluate in terms of service life and environmental cost indicators, the effect of different supplementary cementing by-products. A software package based on proven, verified predictive models was used for the evaluation. As far as carbonation exposure is concerned, carbonation depth was estimated for a period of 50 years. In terms of chloride ingress, the adequate concrete cover needed to sustain that ingress for a period of also 50 years was estimated. The environmental footprint of concrete was calculated, based on the estimation of the range of CO_2 emissions of each individual concrete component, using data from the literature and from a cement production company.

The results of this study, as far as the service life estimation is concerned, showed that FA, RHA and its combination reduced considerably the carbonation depth values, compared to the control mix when used as aggregate replacements, an observation also reached by other researchers (Khunthingkeaw *et al.* 2006, Valcuende and Parra 2010). However, when the above mentioned materials were used as cement replacements, larger carbonation depths were produced, compared to control. The explanation for such a behaviour lays in the way these materials were incorporated into the mix. In the first case, the total amount of carbonatable constituents remains almost the same, resulting in decreased porosity and lower carbonation rates (Papadakis 2000). While in the second case, by reducing the cement and clinker content, the amount of carbonatable materials is also reduced (due to the decrease in total CaO), resulting in higher carbonation rates (Valcuende and Parra 2010). In general SCM materials (as cement replacements) proved to be less resistant to carbonation, mainly due to their low binding capacity of CO_2, caused by their smaller concentrations of $Ca(OH)_2$, compared to control (due to the consumption by pozzolanic reaction, and lower cement content).

Under chloride exposure they all behaved much better than control. It has been noticed that specimens incorporating an SCM, whether it substitutes aggregate or cement, exhibit significantly lower total chloride content for all depths from the surface (Hosam *et al.* 2010). RHA, when used as additive, proved to be most efficient in inhibiting chloride ingress (up to 20 % replacement). RHA, composed by very

small spherical particles, due to its ultra fineness and activity led to the formation of intense pozzolanic reaction products (with increased chloride ion binding capacity than fly ash) within the capillary pore spaces and as a consequence, a finer and more segmented pore system is produced (Antiohos *et al.* 2014, Papadakis and Tsimas 2002). The reactivity of RHA can be attributed to its high content of non-crystalline silica, and to its very large surface area governed by the cellular structure of the particles (Mehta 1994, Zhang and Mlhotra 1996, Chandra 1997). When pozzolanic materials with high active silica content are added to cement, the silica (SiO_2) present in these materials reacts with free lime released during the hydration of cement and forms additional calcium silicate hydrate (CSH) as new hydration products which improve the mechanical properties of concrete formulation (Ganesan and Thangavel 2007). However when all the available free lime is depleted, the pozzolanic reactions stops and the remaining levels of silica remain inactive. Such an observation is further reinforced by the rate of the pozzolanic reaction of RHA, which at high replacement levels drops bellow 0.8 (even bellow 0.5 when RHA is solely used).

On the contrary, when FA is used, a full pozzolanic reaction level is observed (rate of pozzolanic reaction equal to 1) resulting in higher reductions of concrete cover able to resist a chloride attack and also in further increases of concrete compressive strength, for higher replacement levels than when RHA is used (30%). FA, due to its high calcium oxide content, apart of being pozzolonic active, reacts faster than the siliceous cement replacement materials, since it contains higher amounts of aluminate-cementing compounds (C_3A, C_4AF), leading to a more increased chloride ion binding capacity (Antiohos *et al.* 2007).

Overall, by taking under consideration the environmental and economical cost, as estimated in this study (Table 5.15), a more complete portrait of the properties and effects of every particular mix design used was created (Fig. 5.9). In this way and for any type of SCM used, the designer can balance its mix design based on the properties of durability and environmental (or economical) cost (Fig. 5.10) to achieve the best possible (optimum) solution, according to the requirements of his particular study.

The concrete industry is facing the challenge of providing and safeguarding a sustainable design of buildings and structures. To achieve that, relevant environmental, financial and service life factors should be taken under consideration.

On this note, an assessment of durability and environmental cost indicators of a concrete mix utilising supplementary cementing by-products took place, aiming to achieve a balanced level of sustainable and durable design (green durability). The most important finding of this study can by summarised as follows:
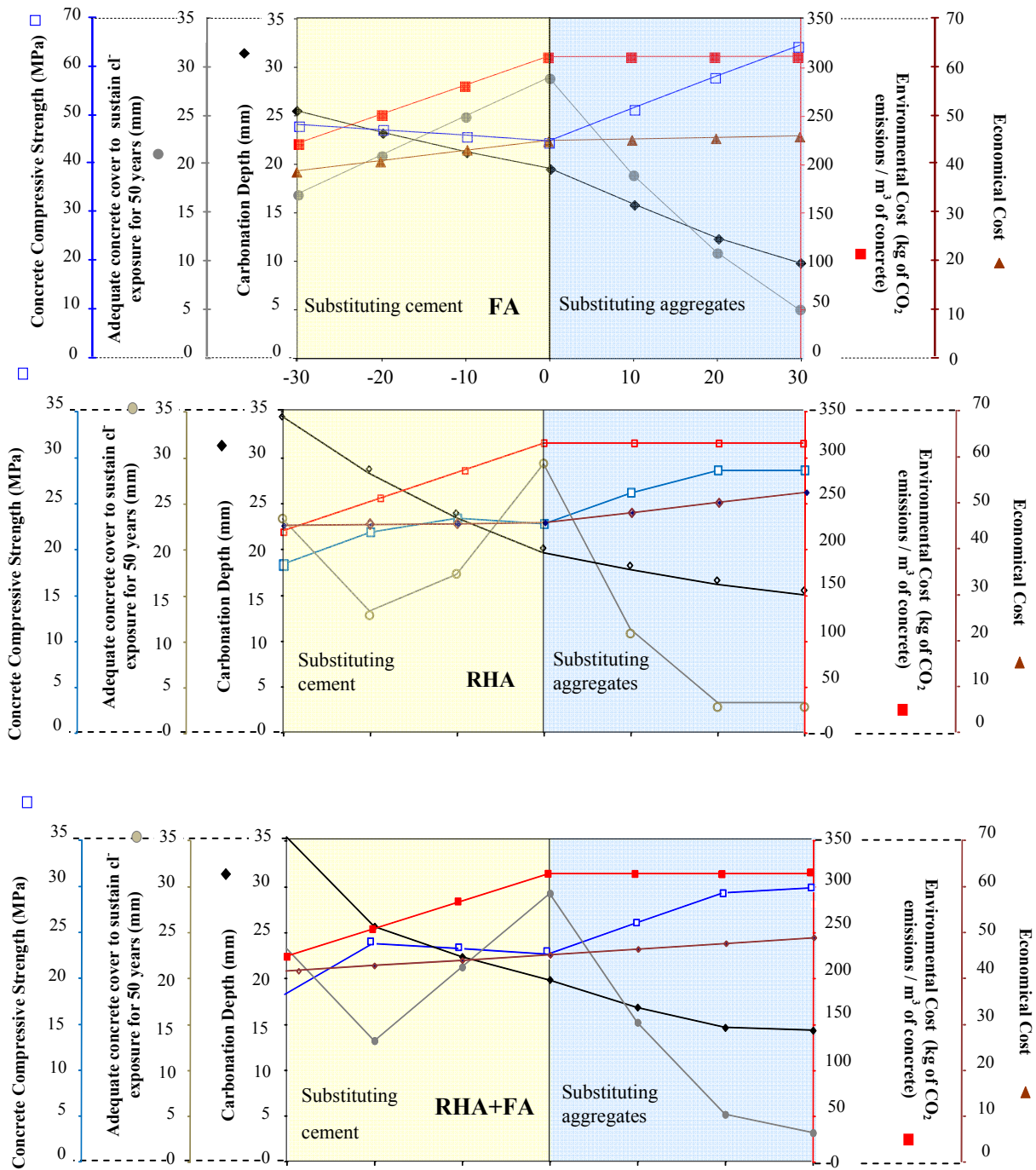
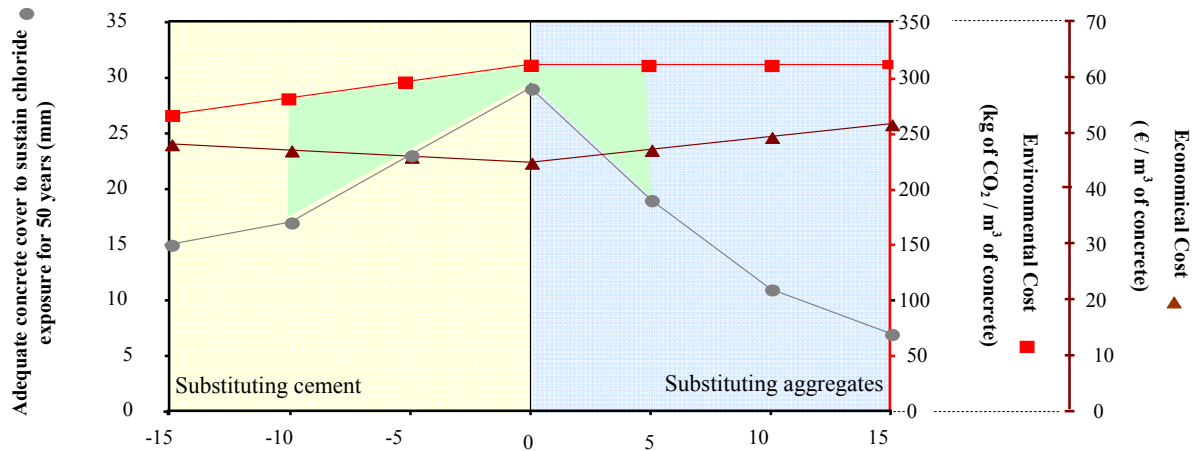*Figure 5.9   Durability and cost indicators for SCM mixes.*

Figure 5.10   Area of balanced (optimum) sustainable and durable design incorporating SCM.

- The effects of the SCM materials on the behaviour of the concrete mix differ when used as aggregate or cement replacements.

- The use of SCM as an addition to a concrete mix, replacing either aggregates or cement, significantly decreases the adequate concrete cover needed to sustain chloride exposure for a service life of 50 years.

- The environmental footprint of each individual concrete component can be quickly estimated, based on data from the literature or from production and operational data from cement-manufacturing companies.

- Utilisation of SCM as cement replacement reduces considerably the total concrete CO_2 emissions.

- By taking under consideration the environmental and economical cost a complete portrait of the properties and effects of every particular mix design used, was created

- RHA and FA mixture proved to be the most promising SCM material, for a replacement level up to 20%, in providing a balanced environmentally friendly durable solution (under chloride exposure).

- While FA gave the most coherent overall behavior at larger replacement levels (30%).

Bearing all of the above in mind, it was shown that it is possible to achieve an adequate level of "green" durability (under chloride exposure) in concrete design, in other words a balance between sustainability and durability, by utilising SCM by-products (and mixtures) in the concrete mix. It is hoped that the results of this study will pave the way for a more rigorous approach to be adopted by the research community on the level of sustainability afforded by using such types of materials.

Chapter 6. Conclusions

In the Introduction (**Chapter 1**), a brief description of the building sector is presented in terms of basic characteristics, production rates, and relevance with the economy growth. The various environmental impacts of the building sector are analyzed and grouped, whereas the potential measures, products and techniques for reducing the environmental cost of the constructions are outlined. The interest is focuses on concrete as the main building material. The environmental cost of each individual concrete constituent can be estimated, based on data from the literature or from production and operational data from building materials' manufacturing companies. Therefore, it is possible to estimate the environmental footprint of concrete and achieve an adequate level of sustainability and durability in the design of reinforced concrete buildings and structures.

Main objective of the present Thesis is to introduce **a new indicator: the environmental cost**, which, in addition to the existing characteristics or indicators connected with mechanical, durability and economical performance, to offer a complete view able to perform an overall design optimization for concrete structures. Moreover, as new supplementary cementing materials have been appeared, such as **biomass ashes**, very efficient on concrete properties' improvement, a special attention is given as materials for reducing the environmental cost. Among them, **rice husk ash** is the most promising biomass ash, deserving thus an in depth techno-economic analysis.

Service life and durability of concrete are strongly related with the environmental footprint of constructions. It is obvious that a structure with a longer service life is less harmful to the environment during the phase of operation. In **Chapter 2**, therefore the concrete durability according to the European Standard EN 206 is first presented, then, the development of a concrete mix design is given including the concrete constituents and, finally, the concrete service life estimation tool (EUCON) is presented **with the improvements made in the present Thesis on environmental cost assessment**. More specifically, the concept and the main principles of this software tool (EUCON, based on

deterministic proven predictive models) for the estimation of concrete service life were presented. Its structure is in full compliance with the European Standards for cement (EN-197) and concrete (EN-206). Emphasis was given on the mathematical modelling of the physicochemical processes leading to concrete deterioration (due to carbonation and chloride ingress) and their outputs. In addition the results of a wide validation scheme implemented were presented, to further reinforce the effectiveness of the mathematical models used.

The tool presented offers a comprehensive approach on concrete service life estimation, in terms of:

- Defining the concrete mix design and the main chemical/volumetric characteristics of concrete.
- Estimating the compressive strength class.
- Accurately predicting the concrete service life, for carbonation and chloride exposure, by taking under consideration the relative exposure classes and by utilising proven predictive mathematical models of the physicochemical processes leading to such deterioration.

It should also be noted that even though service life predictions are usually made in a probabilistic framework (to account for the many uncertainties associated with the composition, processing, construction, curing/maintenance of reinforced concrete, etc.), based on the validity of the results presented in this study, this particular deterministic model can serve as a basis for modeling within such probabilistic frameworks. Supplementary cementing materials (SCM) can replace either cement or aggregates in the concrete mix. In this way and for any type of SCM used, **the designer can balance its mix design based on the properties of durability and environmental (or economical) cost to achieve the best possible (optimum) solution, according to the requirements of the particular study.**

In **Chapter 3**, trying to investigate the relationship of sustainable and durable design, a (4-step) structured methodology was presented aiming to provide a concrete mix design with accepted strength and service life properties, but **with the minimum environmental cost**. First, the concept of the environmental cost is analysed and then it is estimated for the concrete production according to literature and industry data. A structured methodology for concrete mix design optimization (*Integrated Design Process*) is then presented in details and utilized for typical applications offering a significant tool towards sustainable concrete constructions. Considering the increased demand for cement and concrete, in addition to the considerable levels of CO_2 emissions associated with the cement manufacturing process, a more sustainable design of concrete mixes should be enforced. Under this scope, utilization of industrial by-products as cement (clinker) replacement materials is a promising solution. The main findings, as discussed in this study can be summarized as:

- The effects of the SCM materials on the behaviour of the concrete mix differ when used as aggregate or cement replacements (in terms of service life to carbonation).

- Calcareous fly ash proved to be the most promising SCM material (for up to 30%), in providing a balanced environmentally friendly and durable solution. A further decrease in the environmental burden (up to 45 %) was achieved, when the rate of the pozzolanic reaction dropped below 1.

- By taking under consideration the calculated environmental cost of a concrete mix and the derived strength and service life values, an area of accepted performance upon initially selected target values (40 MPa, 50 years) was created.

In this way, a mix design incorporating a particular type of SCM can be further adjusted in achieving an optimum sustainable and durable performance, according to the principles set in the newly imposed relevant EN 15643 Standards. It is hoped that the results of this study will pave the way for a more rigorous approach to be adopted by the research community on the level of sustainability afforded by using such types of materials.

The main aim of **<u>Chapter 4</u>** was to shed light on the specific influence of the main characteristics of biomass ashes (new SCM) on concrete strength development and performance in chloride exposure, exploring in this way their future utilization in cement and concrete manufacturing. Types and evaluation methodology for biomass ashes are presented together with results and discussion on their evaluation as concrete constituents. By investigating the efficiency of a range of biomass ashes, identified in the literature, as cementitious materials, in terms of efficiency factors for concrete strength and chloride penetration, it can be concluded that:

- Variations in the operating conditions (temperature of combustion, technology used) and source of the biomass can influence to a great extend the chemical characteristics of the biomass ashes, even of the same group.

- High SiO_2 content in the biomass ash, does not automatically implies an effective pozzolanic material with a high efficiency factor.

- It appears that after certain percentages in the concentration of the ash in Al_2O_3, Fe_2O_3 and CaO, even for high SiO_2 content, high level of fineness, and low values of LOI, the derived efficiency factors drop below 1.0.

- Biomass ashes (except wood related aches) from a variety of agro-industrial by products can be used as cement replacement materials with beneficial results in strength development and performance in chloride penetration.

- Concrete impermeability properties are considerably improved due to pore refinement in biomass ash blended concretes compared to control concrete.

- Utilization of RHA drastically reduced the Coulomb values and subsequently the corresponding chloride penetration.
- Overall, utilization of agro-industrial by-products for biomass ash production can be a valid source of a future pozzolanic material in concrete production.

It is hoped that the results of this study can be used for in depth evaluation of a wider range of biomass ashes on cement and concrete production towards a sustainable construction.

Focusing on rice husk ash (RHA) - a main biomass ash and efficient pozzolanic material, provided its amorphous and fine state – techno-economical aspects are analyzed in detail in **Chapter 5**. A technical and financial study and a preliminary design for the industrial production of the RHA-derivatives for building applications, including an environmental analysis, are performed. The limitations that may arise are examined, such as the registration of these new materials according to EU and national regulations. Knowing the above components, the rate of return on investment is estimated and the first conclusions for the undertaking of this investment are drawn, offering as well high environmental benefits to the construction industry. From market analyses performed, it was suggested that the target products (i.e., the RHA-derivatives) at an order of *increasing price* have as follows:

1. Production of tundish powder / insulator for steel industry (70-140 €/t)
2. Production of pozzolanic material for construction industry (300-420 €/t)

RHA costs already about -40 €/t for handling and safe disposal, thus the finding of a valorisation solution, viable, and possibly profitable is obligatory. In a Greek rice industry's premises, already there are some husk burners for steam production. A certain upgrade and re-arrangement is required for RHA enhancement in order to meet the technical requirements for insulator and pozzolan production. The idea is to use these units both for insulation materials production as well as for the production of pozzolanic materials; it is thus an advanced unit that involves a milling line.

For the case of insulation materials production the development of upgraded and standardized RHA as insulator /tundish powder for steel industries, insulation panel constructors, etc., ensures viability and remarkable profits. The best choice seems to be to produce RHA for the steel industry as this requires no significant boiler modifications and attracts a high price. However growth in the market for RHA to the steel market is limited. Growth in the market for RHA in the cement industry appears to be growing and is potentially very large. A new entrant to the market place may prefer to target the somewhat less high returns but better longer term prospects of the cement market.

In the case of RHA conversion to pozzolanic material for building applications, the revenues of this enterprise are higher than the operational costs *leaving a net profit of 60,000 euro/y for a pozzolanic material production of 1000 t/y and a positive return on investment of 17%.* The break-even point for this production is about 530 t/y (but production rate greater than 700 t/y is recommended), whereas when the production approaches 4000 t/y a much higher return on investment of 57% is estimated (net profits of 470,000 euros).

In addition, experimental verification of the derived RHA as pozzolanic materials was performed. Contrary to most studies available, RHAs – not prior treated, with a mean particle diameter of 70 microns– were used as cement replacements. The aim was to assess their influence on mechanical and durability properties of cement-based mortars. Even though their mechanical pre-treatment has been shown to upgrade basic properties of the final product, it remains of interest to determine the respective RHA contribution in the absence of a preparation that is energy demanding (i.e. grinding or classifying). Major conclusions are as follows:

- Untreated RHAs exhibit pozzolanicity due to their siliceous character which is almost entirely (90%) amorphous. It is low, compared to commonly used treated-SCMs. Despite its porous nature, untreated RHA does not increase appreciably the water requirement of cement for the same consistency. This is important for concrete applications since it won't compromise strength development.

- Untreated RHA exhibits a late-strength gain that reaches approximately 4 MPa. This is acceptable considering that the respective gain for a very reactive, extremely fine SCM (silica fume) is 10 MPa. Its efficiency was measured in the area of 0.5-0.6; that practically means that if added to concrete without prior grinding it could not replace more than half of the selected dosages (approx. 5%) for sustaining the non-RHA performance. A previously reported theoretical expression linking k-value with active silica ratio was not validated for untreated RHA. Modifications are required for untreated SCMs.

- Despite the high chemical reactivity of untreated RHA (about 90%), the lack of adequate specific surface slows down their engagement in hydration reactions. Both non –evaporable water content and strength results indicate an advantage of higher quality RHA (A) at later ages.

- Untreated RHA significantly aids sorptivity of mortar. Increases of up to 50% were achieved for 15% RHA incorporation. Performance increases with higher RHA inclusion exceeding even the water resistance of SF-based system. Given the coarse nature of the RHAs, the improved water resistance cannot be attributed to the pore filling effect but rather on the inherent water repellency of the RHA. It is not clear whether this is due to the hydrophobic nature of carbonaceous residues that are present in the ash. Resistivity was also found to be similar to the control specimen.

- On the contrary, the coarse nature of untreated RHA affects resistance against chloride penetration and - mainly - carbonation. When 15% of untreated RHA was used, carbonation depth was almost doubled. Being pozzolanic, RHAs consume $Ca(OH)_2$ which reduces alkalinity and increases the rate of carbonation. This is the case for SF as well. In addition, slow pozzolanic evolution of coarse RHA does not allow a quick and substantial formation of secondary hydration products that could assist pores closing, thus enhanced carbonation resistance.

By performing an overall assessment of the use of RHA in concrete, it was found that the RHA (alone or as a mixture with calcareous fly ash) can improve significantly mechanical and durability characteristics, decreasing as well the environmental cost of concrete production.

In general, the present Thesis contributes to the evaluation of the environmental cost of each component of concrete and provides the best possible mix design configuration (by means of a holistic analytical software tool) in terms of low environmental cost and fulfilling strength and durability requirements. However, further research is required in these topics and some main **suggestions for future work include**:

- Estimation of the environmental cost of other construction materials except concrete components (steel, ceramics, various mortars, aluminium, wood, plastic, glass, etc.) that are used in the construction and structures: In this way, *the total fixed environmental cost* could be assessed.

- Estimation of the environmental cost during the use of the building or the structure (CO_2, emission, "grey" energy consumption, etc.): In this way, *the total operational environmental cost* could be assessed.

- By having both, total fixed environmental cost & total operational environmental cost, *the total capitalized environmental cost* could be assessed, permitting a more global optimization.

- In addition, the study of other new SCMs (new biomass ashes & new industrial by-products) or the upgrading of existing SCMs, and their extended use in construction could further enhance the environmental profile of structures in practice.

From the above conclusions from all Chapters of the present thesis, a more general conclusion can be derived. Governments should give financial and legislative incentives to manufactures and industries and urge them to apply new methods and a more sustainable technology. There are many different ways for the reduction of CO_2 emissions due to building industry. The methodology presented in this study can forward the development of new policies in the construction industry and the adoption by engineers and technicians of a sustainable perception for designing reinforced concrete structures. A characteristic phrase of Henri David Thoreau summarizes all mentioned above: *"What's the use of a fine house if you haven't got a tolerable planet to put it on?"*

Chapter 7. **References**

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Dates	2008 -2009
Title of qualification awarded	Master Degree in "Design, Organization and Management of Transport Systems"
Principal subjects / occupational skills covered	• Transportation Planning, Logistics, Freight Forwarding • During my Master's program I have elaborated my diploma thesis with my supervisor Prof. Evangelos Sambrakos, Professor of Economics at the University of Piraeus, entitled: "FUNDING FOR GREEK AND GREEK – OWNED SHIPPING COMPANIES"
Name and type of organisation providing education and training	Aristotle University of Thessaloniki
Level in national or international classification	Higher education / University
Dates	2000 - 2007
Title of qualification awarded	Civil Engineer
Principal subjects / occupational skills covered	• Reinforced concrete and steel constructions, Geotechnical Works, Plumbing Projects • During my graduate studies I have elaborated my diploma thesis under the supervision of Mrs Glykeria Kalfakakou, Professor at Aristotle University of Thessaloniki, entitled "PUBLIC-PRIVATE PARTNERSHIPS (PPP's) - PRESENTATION OF CASE 'ZEP' AT KOZANI".
Name and type of organisation providing education and training	Aristotle University of Thessaloniki
Level in national or international classification	Higher education / University

Personal skills and competences

Mother tongue(s)	**Greek**
Other language(s)	

Self-assessment

European level (*)

	Understanding				Speaking				Writing	
	Listening		Reading		Spoken interaction		Spoken production			
English	C2	Proficient user	C2	Proficient user	C2	Proficient user	C2	Proficient user	C2	Proficient user
French	A1	Basic User	A1	Basic User	A1	Basic User	A1	Basic User	A1	Basic User

Computer skills and competences	I hold a certificate of computer skills. I work every day using a computer and I have also experience of web (internet) and programs such as:

- Text editor - spreadsheets (Microsoft Office: Word, Excel)

- Software for transportation planning, traffic simulation and GIS (SATURN, ArcGIS)

- Software application for Design (AutoCAD)

- Static Programs (SAP, INSTANT)

- Program of statistical analysis (SPSS)

Artistic skills and competences	I enjoy drawing and reading history of art.
Driving licence(s)	B

Additional Information

SEMINARS – WORKSHOPS

- Conference: "Renewal and expansion of the rail network".

- Seminar in FREIGHT AND LOGISTICS: "Organization and Design of Freight Centres".

- Seminar: "Organization and Management of Air Transport and Airports".

- 5th International Congress on Transportation Research (September 2010, Volos, Greece).

- EVIPAR: 3rd National Conference on the use of industrial by-products in construction (24-25 September 2012, Thessaloniki, Greece).

- EUROCOALASH Conference (25-27 September 2012, Thessaloniki, Greece).

RESEARCH PUBLICATIONS AND PRESENTATIONS FROM THE PRESENT THESIS

A. Publications in International Journals

1. Antiohos, S.K., J.G. Tapali, M. Zervaki, J. Sousa-Coutinho, S. Tsimas, and V.G. Papadakis, "Low-embodied energy cement containing untreated RHA: A strength development and durability study", *Construction and Building Materials,* **49**, 455-463 (2013).

2. Tapali, J.G., S. Demis, and V.G. Papadakis, "Sustainable concrete mix design for a target strength and service life", *Computers & Concrete,* **12**(6), 377-392 (2013).

3. Demis, S., J.G. Tapali, and V.G. Papadakis, "An Investigation of the Effectiveness of the Utilization of Biomass Ashes as Pozzolanic Materials", *Construction and Building Materials,* **68**, 291-300 (2014).

4. Tapali, J.G., S. Demis, and V.G. Papadakis, "Plant design & economics of rice husk ash exploitation as pozzolanic material", *Waste & Biomass Valorization,* accepted (2014).

B. Presentations in International Conferences with Reviewers

1. Tapali, J.G., S. Demis and V.G. Papadakis, "Use of new industrial by-products and mixtures for reducing the environmental cost of constructions", *EUROCOALASH 2012 Conference*, Thessaloniki, Greece, September 25-27, *2012*.

2. Tapali, J. and V.G. Papadakis, "An optimum design of reinforced concrete structures for prolongation of service life time at the lowest environmental cost", *3rd International Symposium on Life-Cycle Civil Engineering (IALCCE 2012)*, Vienna, Austria, 3-6 October, 2012.

3. Tapali, J. and V.G. Papadakis, "Plant design & economics for rice husk ash exploitation as pozzolanic material", SYMBIOSIS Conference, Athens, Greece, 19-21 June, 2014.

4. Tapali, J. and V.G. Papadakis, "Exlpoitation of rice husk ash as a pozzolanic material for the construction industry", *4th International Conference on Industrial and Hazardous Waste Management (Crete 2014)*, Chania, Greece, 2-5 September 2014.

C. Presentations in Greek Conferences with Reviewers

1. Λίτος, Λ., Α. Πιστιόλας, Κ. Πιστιόλας, J. Sousa-Coutinho, Τ.Γ. Τάπαλη, Ε.Γ. Παπαδάκης, «Αξιοποίηση τέφρας φλοιών ρυζιού στη παραγωγή κονιαμάτων & σκυροδέματος υψηλής ανθεκτικότητας και χαμηλού περιβαλλοντικού κόστους», 3º Πανελλήνιο Συνέδριο για την Αξιοποίηση Βιομηχανικών Παραπροϊόντων στη Δόμηση, ΕΒΙΠΑΡ, Θεσσαλονίκη, 24-25/9/2012.

2. Τάπαλη, Τ.Γ., Σ. Δέμης, Ε.Γ. Παπαδάκης, «Τεχνική, οικονομική & περιβαλλοντική αριστοποίηση περιεκτικότητας σκυροδέματος σε ιπτάμενη τέφρα με στόχο τη βιώσιμη κατασκευή», 9º Πανελλήνιο Συνέδριο Χημικής Μηχανικής, Αθήνα, 23-25/5/2013.