EFFECT OF CARBONATION ON THE CHLORIDE DIFFUSION OF MORTAR SPECIMENS EXPOSED TO CYCLIC WETTING AND DRYING

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Abstract

Carbonation and chloride ingress are the two main causes of corrosion in reinforced concrete structures. Despite the combined action of these mechanisms being a reality, there is little research on the effect of carbonation on the chloride diffusion in concrete. This work intends to study the influence of carbonation on chloride diffusion of mortar specimens. Cubic mortar specimens were cast with 0.55 of water-cement ratio. After curing, the specimens were subjected to 56 days of wetting and drying cycles. Half the samples were immersed for a day in a 3.5% NaCl solution and then placed for 6 days in a carbonation chamber (4%CO_2); the other half were also kept a day in 3.5% NaCl, but after were kept during 6 days in laboratory environment. Afterwards, the depth of chlorides and CO_2 penetration was evaluated. Complementary tests were also carried out, such as rapid chloride migration coefficient and water capillary absorption. The results show that carbonation has a direct influence on chloride penetration, decreasing it. The noncarbonated samples showed a profile with higher amount of chloride than carbonated ones. This fact can be related to the refinement of the mortar pores caused by carbonation and observed in water absorption tests.

Key words: chloride, carbonation, mortar, deterioration, combined degradation, accelerated testing

1 INTRODUCTION

A significant number of concrete structures around the world have been damaged by steel reinforcement corrosion. Among the factors that contribute to this kind of damage is the aggressiveness of chloride ions, one of the main reasons for damage to ordinary concrete structures due to reinforcement corrosion [1].

According to Tilly and Jacobs [2] simultaneous chloride ingress and carbonation account for over 50% percent of the deterioration of concrete structures . It is well known that the corrosive effect of chlorides is based on their ability to destroy the electrochemical condition of the passive state of reinforcement even under the existing alkalinity in the concrete. Regarding carbonation, the corrosive effect is based on the decreasing trend of alkalinity of pore liquid in concrete and the resulting depassivation of steel, enabling the conditions for corrosion to occur.

The service life of concrete structures is directly affected by its durability. Thus, several authors have been studying the action of chloride ions and carbonation [3,4]. However, previous studies were confined mostly to the deterioration of concrete structures under a single deteriorating factor, although the real environment is actually a combination of factors [5].

Recently research has begun to look into the effect of combined degradation mechanisms. Chloride ingress and carbonation are among the most studied, however, there is no consensus on the effect of the combined action of chlorides and carbonation on the durability of concrete. In their experimental research, Chengfang *et al.* [6], for example, conclude that after carbonation, chloride diffusivity coefficient increases and it will increase with the increasing of carbonation time. On the other hand, Backus *et al.* [7], for example, say that the combination of carbonation with the entrance of chloride can act reducing the penetration of chlorides in concrete. However, the lack of standardization about the various parameters involved in the tests such as type of test, temperature, humidity and concentration of NaCl and CO_2 makes it difficult to compare results.

This experimental work studies the influence of carbonation on chloride transport into mortar specimens using accelerated tests.

2 EXPERIMENTAL WORK

Cubic mortar specimens with 50x50x50mm^3 were cast with ordinary Portland cement (CEM I 42.5) based mortar manufactured with 0.55 of water-cement ratio and a common river sand. Chemical composition of cement is presented in Table 1. Mortar mixture and its main characteristics in fresh (flow table test) and hardened state (compressive strength at 28 and 90 days, open porosity and permeability to oxygen and water) are presented in Table 2.

Table 1: Chemical composition of cement

Composition	Portland cement
SiO_2	19.65
Al_2O_3	4.28
FeO_3	3.35
CaO	61.35
MgO	1.7
SO_3	3.36
K_2O	0.89
Na_2O	0.19
Insoluble residue – IR	1.7
Loss on ignition – Li	2.82

Table 2: Mixture and properties of mortar

Material and Properties	Mortar
Cement: sand (kg)	1:3
Flow value (mm)	190
Compressive strength (MPa) – 28/ 90 days	37.6/ 39.1
Open porosity (%)	21.4
Oxygen permeability (K) - 10^{-16} m^2	0.797
Water permeability (K_W) - m^2	11.16

After casted, these specimens were covered with a plastic sheet and they were stored, for one day, in a controller chamber (21ºC and 98%RH). After, they were removed from the moulds and they were cured for 28 days in wet a chamber (21ºC and 100%RH). Completed curing the specimens one had painted five of their six faces with an epoxy resin (3 days). Finished painting the specimens were drying more 4 days in laboratory environment (20ºC and 60%RH).

After this, in order to simulate the combined action of chloride ions and carbonation, the specimens were subjected to wetting and drying cycles during 56 days. Half of the specimens were immersed for a day in 3.5% NaCl solution and then placed for 6 days in a carbonation chamber (20ºC, 55%RH and 4%CO_2); the other half specimens was used as reference specimens and were also kept a day in 3.5% NaCl solution, but after were stored 6 days in laboratory environment, Figure 1.

Figure 1: (A) Immersion in NaCl (B) Drying in carbonation chamber (C) Drying in laboratory environment

After the exposure period, the depth of penetration of chlorides and CO_2 was determined. To evaluate the chloride penetration, a chloride profile was determined with 5mm interval until 30mm depth. Total chloride content was measured using the Volhard´s method [8]. To evaluate the carbonation depth, the specimens were splitted along the direction of penetration of CO_2. Afterward, the fractured surfaces were sprayed with phenolphthalein and then the carbonation depth was measured [9]. Complementary tests were also carried out such as rapid chloride migration coefficient [10] and water capillary absorption [11].

3 RESULTS

3.1 Wetting and drying cycles

Figure 2 shows chloride profiles obtained after wetting and drying cycles. Each point depicted represents the average value determined from three samples for each depth.

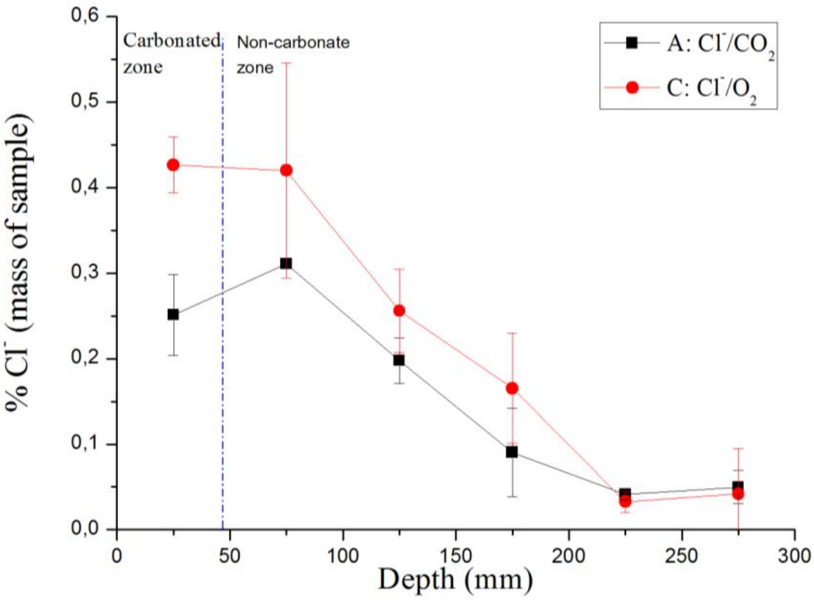

Figure 2: Chloride profiles

The chloride penetration achieved for specimens under combined cycles (A) was lesser than the one achieved for specimens under chloride cycles (C). This condition is more pronounced on the surface but it is maintained along almost entire profile.

The carbonation average depth obtained to specimens under combined cycles was 4.9 ± 0.04 mm .

3.2 Complementary tests

The rapid chloride migration coefficient was evaluated for two types of specimens: specimens that were kept 56 days in a carbonation chamber only and specimens that were stored 56 days in a laboratory environment. The rapid chloride migration coefficient obtained for carbonated specimens was $8.35x10^{-12}m^2/s$, while the reference specimens showed higher results, $15.15\ x10^{-12}m^2/s$.

Figure 3 shows capillary absorption results obtained after the wetting and drying cycles. Each point depicted represents the average value from three specimens. The capillary absorption obtained for specimens under combined cycles (A) is bigger than results obtained for specimens under chloride cycles (C).

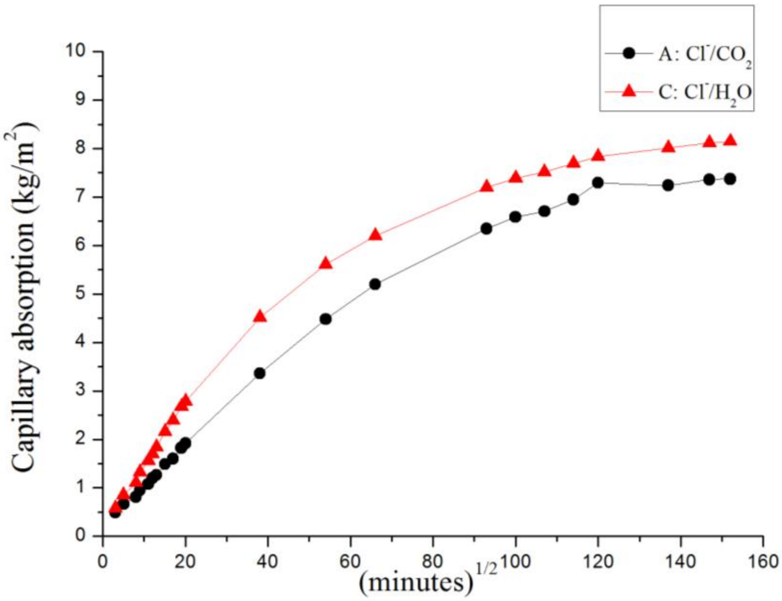

Figure 3: Water capillarity absorption to the situations studied

4 DISUSSION

4.1 Influence of carbonation on chloride penetration

The carbonation can reduce the capacity of chloride binding [12] and, consequently, lead to an increase in the rate of chloride ion ingress. On the other hand, carbonation can reduce the porosity and, consequently, lead to a decrease in the rate of chloride ion ingress. The chloride profiles presented in Figure 2 clearly show the influence of carbonation on chloride penetration for the studied mixtures. In this case, the carbonation acts by reducing the amount of total chlorides present throughout the depth of the specimens. This fact can be related to the refinement of the pores of the mortar caused by carbonation.

There is a consensus that carbonation promotes microstructural changes that culminate in the densification of pores. The carbonation reaction gives rise to calcium carbonate ($CaCO_3$) which solubility is limited and, therefore, tends to precipitate during the carbonation process [13]. This precipitation, at an initial phase, results in the aforementioned pore densification and consequent reduction of permeability.

The reduction in the permeability of the carbonated mortar can be confirmed by the water capillarity absorption results showed in Figure 3. It is possible to observe that the situation where the specimens were subjected to carbonation are those with a smaller water capillary absorption.

It is important to note that capillary absorption plays a key role in the wetting and drying cycles. In these tests, the chloride profile is generally different from those in which the relative humidity is approximately constant, Figure 4. For wetting and drying cycles there is a tendency to the formation of chloride´s peaks in the region close to the surface. These peaks are typical formations of the cycles of gain and loss of moisture in the material surface [14].

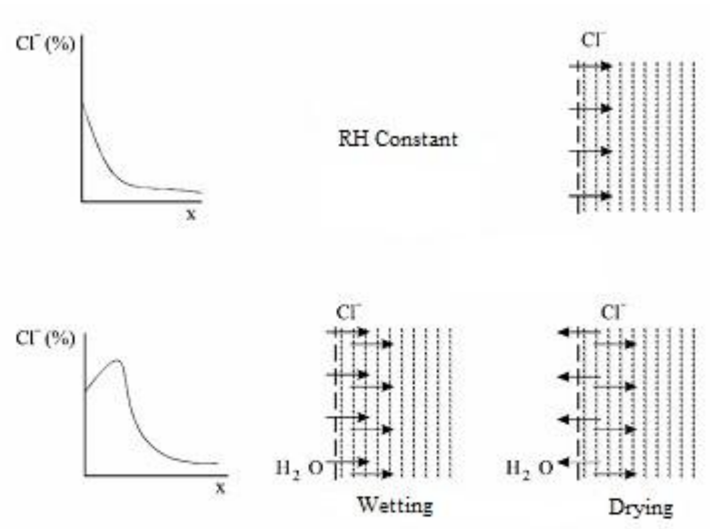

Figure 4: Simulation of chloride penetration in an environment with constant relative humidity (RH) and environment subjected to wetting and drying [13]

The chloride profiles presented in Figure 2 show the expected configuration for this type of test. However, the difference between the porosity of carbonated and non-carbonated zones may have increased the chloride peak observed in the combined cycle profile (A). The formation of a peak of chlorides after the carbonation front had already been verified by Lee and Yon [4] in a study on the deterioration of concrete, taking into account the combined action of carbonation and chloride ions. The skin effect cited by Andrade *et al.* [15] may explain this behaviour.

Concrete skin is considered the closest zone to the surface of concrete cover of reinforcements. It usually has a different composition than the internal concrete due to wall-effect phenomena or segregation of aggregates. In addition, environmental actions induce a gradient of moisture along the cover depth. These circumstances sometimes produce an irregular chloride profile in the cover, which either exhibits a maximum of chloride content some millimetres inside the outer surface or sometimes shows an anomalously high chloride concentration right at the concrete surface [15].

The extension of the test period and thus the carbonation depth may help to indicate the actual cause of the formation of the chloride peak observed in the combined cycle profile (A).

Concerning migration test, the results obtained emphasize the idea that the carbonation acts reducing the penetration of chlorides in mortars subjected to the combined action of the carbonation and chloride.

4.2 Test time and humidity control

Based on the obtained depth of carbonation, the carbonation front needs a longer test time to accentuate its depth and to clearly interact with the mechanism of chloride penetration. The time influence on the wetting and drying cycles was also observed by Lee *et al.* [5] for specimens subjected to the combination of carbonation and chlorides. Furthermore, the prolongation of the test time can cause leaching of precipitated calcium carbonate which may lead to open pores and cause an opposite effect.

Another important factor for the development of the carbonation front is moisture control. The drying time used (6 days) may have not been sufficient to provide a moisture content that could allow a maximum advance of the carbonation front inside the specimens. The presence of epoxy resin on five of the six faces of the specimens may have contributed to this behaviour.

5 CONCLUSION

Based on the obtained results one may conclude that the chloride profiles presented clearly show the influence of carbonation on chloride penetration for the studied mixtures. In this case, carbonation reduces the amount of total chlorides present throughout the depth of the specimens. The diffusion coefficients of chloride obtained by the migration test corroborate this idea as they present lower values for carbonated samples than for those non-carbonated.

These statements, together, suggest that the passage of chloride ions through the carbonated zone of studied mortars becomes more difficult. Once the carbonated zone is on the surface of the specimen, it seems that this difficulty leads to a decrease of the initial amount of chlorides which can penetrate the sample and consequently reach its interior. However, more prolonged exposures can cause leaching of precipitated calcium carbonate which may lead to an increase in open pores and can cause an opposite effect.

ACKNOWLEDGMENTS

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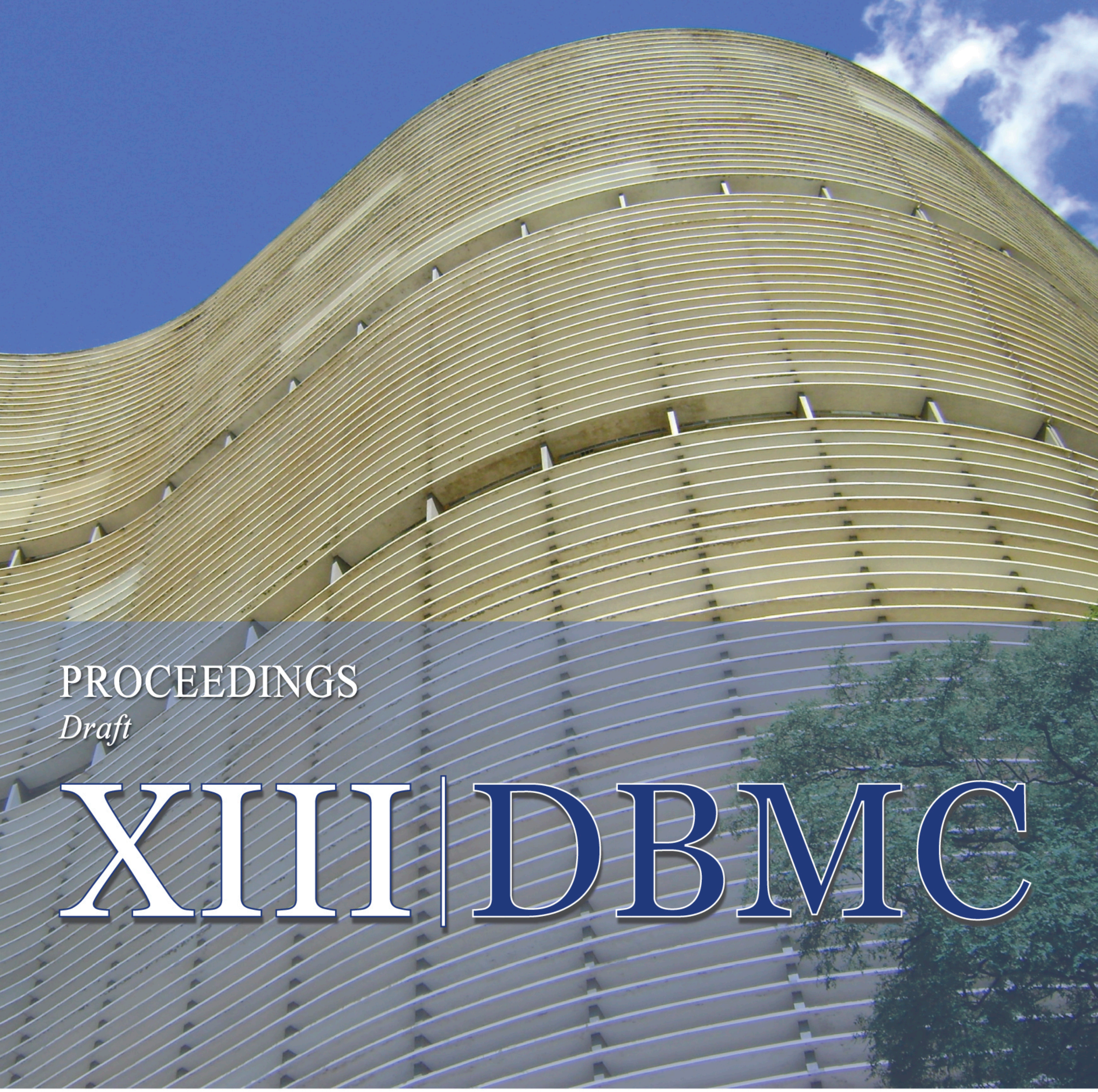

PROCEEDINGS

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XIII | DBMC

XIII International Conference on Durability of Building Materials and Components

02-05 September 2014 São Paulo - Brazil

Preface

The ability to predict the service life—the durability—of a new building material is being ardently sought after in many parts of the world. Widespread efforts are correspondingly being made to increase the durability of materials already in wide use. Any estimate of the economic losses resulting from failures in durability lead inevitably to dollar figures so astronomically large that they are usually regarded with incredulity.

R. F. Legget
Proc. of the 1st DBMC
Ottawa, 21-23 Aug. 1978.

Some 35 years after the 1st DBMC (Ottawa, 1978), sponsored by ASTM, NIST and NRC, durability is an even more important subject. At that time, an accurate service life estimate was considered a condition to life cycle cost (LCC) analysis. Nowadays, service life is also crucial information for the environmental life cycle analysis (LCA). The relevance of durability became widely recognized among scientists: in 1992 the World Business Council for Sustainable Development coined the term “eco-efficiency”, referring to a higher production with fewer environmental and economic resources and less environmental impact. The increase of durability (or service life) of products is one of the critical tools to improve eco-efficiency.

In that period the research community, which was organized into CIB and RILEM working groups, developed a methodology to plan and predict the service life of buildings and constructed assets at the design stage, which was consolidated in the ISO 15686-x standards. As a result of these scientific advances, the degradation factors and mechanisms of most materials and their assemblies are now much better comprehended. Information Technology advances facilitate to mapping the relevant environmental variables by using GIS platforms. Dose-response functions are available, making possible the estimation of degradation rates by combining environmental variables with material characteristics. Even effects of climate change on service life have been a matter of discussion. Altogether, it is an impressive achievement, recorded in the previous 12 DBMC conference. However, despite this scientific progress, the use of these tools in day-to-day production processes, including materials and components R&D, architecture and civil engineering design, and environmental and economic life cycle analysis is still very limited in most countries. Today’s research challenge is not only to increase the knowledge in the field, but also to make this knowledge readily available to the society, by developing more user friendly tools and better educate engineers and architects on the use of these tools.

The 13th edition of the DBMC conference was sponsored by ASTM, NIST, Rilem, CIB and University of Porto. It was joint organized by Polytechnic School of University of São Paulo and Secovi-SP, the most important Brazilian real estate industry’s association, an union that simbolizes our commitment to transfer the knowledge to the society. The support of Saint Gobain Group, Grace Construction Products, Votorantim Cimentos, Gerdau, Fapesp, CNPq and Capes made the conference possible.

We expect that these proceedings will help professionals and academy to incorporate service life planning concepts in their day-to-day decision-making processes.

São Paulo, 25-Aug-2014
Marco Quattrone
Vanderley M. John
Editors

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