Chloride diffusion tests as experimental basis for full probabilistic service life prediction and life-cycle assessment of concrete with fly ash in a submerged marine environment

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ABSTRACT: Today, a correct quantification of the reduced greenhouse gas emissions associated with partial replacement of cement by fly ash (FA), is still lacking. Too often, this environmental benefit is simply equaled with the FA percentage in concrete, an estimation in violation with two basic rules in life cycle assessment: (i) Environmental impacts should be calculated for durability and strength related functional units (FU), (ii) justified impacts of coal fired electricity production should be allocated to its industrial by-product FA. Therefore, a centrically loaded column with a 100 years service life in a submerged marine environment, was adopted as FU with economic allocation of the FA impact. The number of column replacements within 100 years due to corrosion was estimated from probabilistic service life prediction based on chloride diffusion tests. Global warming potentials for concrete with 15-50 % FA were at least 45-48 % less than for traditional concrete.

1 INTRODUCTION

Nowadays, policymakers stimulate architects, engineers and contractors to use more and more environmentally friendly materials when designing and constructing buildings, bridges, etc. Since a lot of the currently available building materials are claimed to be ‘green’, this seems fairly easy. Often though, little quantitative proof of this actual environmental benefit is being provided by the manufacturers.

For instance, partial replacement of ordinary Portland cement (OPC) in concrete with fly ash (FA), an industrial by-product, is considered as a more than valid strategy to reduce cement related greenhouse gas emissions. As the amount of CO$_2$ emitted per ton cement produced – around 800 kg (Josa et al., 2004) – is well-known today, a precise environmental impact calculation of concrete with a given (reduced) cement content seems perfectly possible. However, this simple estimation method, misses two key ingredients of the life cycle assessment (LCA) methodology: (i) an adequate functional unit (FU) choice and (ii) a justified allocation method for the by-product impact.

(i) The FU should include all relevant concrete aspects, being its strength, its durability and to some extent its workability. To take into account both strength and durability, it should comprise the concrete amount needed to manufacture a structural element with a given mechanical load and a predefined service life. The concrete’s life span should be evaluated in relation to the latter, using probabilistic service life prediction models based on experimental durability tests representative for the application field (Van den Heede & De Belie, 2012a).

(ii) Since the publication of European Directive 2008/98/EC (2008), an industrial by-product, such as FA, is no longer considered as a mere waste product. As a result, a certain impact of its main product, i.e. electricity produced by a coal fired power plant, needs to be allocated to FA. This effect cannot simply be neglected in the environmental evaluation of this by-product since the amount of CO$_2$ emitted per kWh of electricity is around 1.022 kg (Spath, 1999) and 1 kg FA corresponds with about 19.2 kWh of electricity (Van den Heede & De Belie, 2012a). An allocation coefficient based on the economic (instead of the mass) value ratio between FA and electricity is preferred in order to guarantee the enduring use of FA as cement replacing material (Chen et al., 2010).

Both aspects (i) en (ii) were taken into account in this paper. It presents the results of a full probabilistic service life prediction of concrete with various amounts of fly ash (0 %, 15 % and 50 %) assumed to be located in a permanently submerged marine environment. The limit state function used was similar to the one proposed by the Fib Bulletin 34 (2006) which has already been applied in Van den Heede et al. (2011). Only now the experimental input to the model was provided by diffusion coefficients from accelerated chloride diffusion tests (cf. NT Build 443, 1995), instead of chloride migration coefficients obtained after forcing chlorides into concrete under the application of an electrical field (NT Build
492, 1995). The obtained service life estimates together with the strength classes of the studied concrete mixes were used as LCA input to quantify the global warming potential (GWP) of the concrete amount needed to construct and maintain a centrically loaded column in a submerged marine environment for 100 years with an appropriate impact assigned to the FA by means of economic allocation.

2 MATERIALS AND METHODS

2.1 Concrete mixtures

In total, three concrete mixtures were manufactured (Table 1). Mix T(0.45) has a cement content and water-to-cement (W/C) ratio of 340 kg/m³ and 0.45, respectively. It is seen as the appropriate OPC reference concrete for exposure class XS2 conforming to NBN B15-001 (2004). This exposure class corresponds with an environment where steel reinforced concrete is permanently submerged in sea water. As a consequence, the concrete is considered to be susceptible to corrosion induced by chlorides.

Apart from the OPC mix, a FA containing concrete composition (F15) conforming to the k-value concept of NBN B15-001 (2004) was made. By using the k-value concept, the maximum fly ash-to-binder (F/B) ratio for a minimum total binder content equals only 15 %.

With 50% of the binder consisting of FA, mix F50 is obviously a high-volume fly ash (HVFA) concrete composition cf. Malhotra & Mehta (2005). Note that the HVFA mix design is characterized by a rather high total binder content (450 kg/m³) and low water-to-binder (W/B) ratio (0.35). The authors made this particular choice to ensure a strength class rather high total binder content (450 kg/m³) and low water-to-binder (W/B) ratio of 0.35. The obtained solutions were stirred carefully and then heated onto a hot plate until they just started to boil. After cooling them down, they were filtered.

Table 1. Mix proportions and properties of the tested concrete mixtures.

<table>
<thead>
<tr>
<th></th>
<th>T(0.45)</th>
<th>F15</th>
<th>F50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand 0/4 (kg/m³)</td>
<td>715</td>
<td>696</td>
<td>645</td>
</tr>
<tr>
<td>Aggregates 2/8 (kg/m³)</td>
<td>515</td>
<td>502</td>
<td>465</td>
</tr>
<tr>
<td>Aggregates 8/16 (kg/m³)</td>
<td>671</td>
<td>654</td>
<td>606</td>
</tr>
<tr>
<td>CEM I 52.5 N (kg/m³)</td>
<td>340</td>
<td>317.6</td>
<td>225</td>
</tr>
<tr>
<td>Fly ash (kg/m³)</td>
<td>-</td>
<td>56</td>
<td>225</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>153</td>
<td>153</td>
<td>158</td>
</tr>
<tr>
<td>SP (ml/kg B)</td>
<td>3.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>W/B (%)</td>
<td>0.45</td>
<td>0.41</td>
<td>0.35</td>
</tr>
<tr>
<td>F/B (%)</td>
<td>0</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>Slump</td>
<td>S4</td>
<td>S4</td>
<td>S4</td>
</tr>
<tr>
<td>Strength class</td>
<td>C45/55</td>
<td>C40/50</td>
<td>C35/45</td>
</tr>
</tbody>
</table>

2.2 Curing and immersion in NaCl solution

Nine cubes with a 150 mm side were cast per concrete mix. After casting, the cubes were kept at a constant temperature and relative humidity (RH) of 20 °C and 95 %, respectively. Demoulding took place the next day whereupon the specimens were stored again under the same conditions until the age of 21, 84 or 357 days. At that time, a core with a diameter of 100 mm was drilled out of each cube. Three of them were used for accelerated and more realistic chloride diffusion tests at the age of 28 days, another three were subjected to the same tests after 91 days, while the last three provided the specimens for only the accelerated diffusion tests at the age of 1 year. The outermost 10 mm, containing the cast surface, was cut from the two ends of each core in correspondence with NT Build 443 (1995). Starting from these saw cuts, two cylindrical specimens with a thickness of 50 mm were taken from each core. Per testing age, three of the eventually obtained cylinders (n = 3), were preconditioned as prescribed in NT Build 443 (1995). Firstly, they were immersed in a saturated Ca(OH)₂ solution until constant mass, thereafter they were treated with an epoxy coating on all sides except the surface to be exposed. After the epoxy layer had hardened, the samples were stored again in this Ca(OH)₂ solution until constant mass. Then, these cylinders were immersed in a aqueous NaCl solution with a concentration of 165 g/l for 9 weeks (accelerated diffusion test). The other three cylinders were not preconditioned with Ca(OH)₂. After applying the epoxy coating, they were stored in an aqueous 33 g/l NaCl solution for 18 weeks (realistic diffusion test). The latter concentration corresponds with the normal Cl− concentration in sea water according to CUR report 100 (1981). During exposure, the temperature of the NaCl solutions was kept constant at around 20 °C.

2.3 Chloride diffusion tests

Immediately after removal from the aqueous NaCl solutions, 10 concrete powders were collected per cylinder by grinding off material in 2 mm layers parallel to the exposed surface. By doing so, the average chloride content could be determined at a depth of 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 mm. This was done by means of an acid soluble extraction in a nitric acid solution followed by a potentiometric titration against silver nitrate (cf. Qian, 2009). First, the powders (passing through a 160 μm sieve) were dried at 80 °C until constant mass. After cooling down to room temperature, 2 g of each powder was weighed in a 150 ml glass beaker. 5 ml of nitric acid (concentration: 0.3 mol/l) and 35 ml de-ionized water were added. The obtained solutions were stirred carefully and then heated onto a hot plate until they just started to boil. After cooling them down, they were fil-
terminated and diluted with water in a 100 ml pycnometer. From these 100 ml solutions, 10 ml was pipetted for determination of the chloride concentration per powder using a Metrohm MET 702 automatic titration apparatus with 0.01 mol/l silver nitrate as titration solution. From the resulting chloride profiles, the surface concentration \( C_s \) (wt-%) and the effective chloride transport coefficient \( D_e \) (m\(^2\)/s) were estimated by fitting equation (1) to the measured chloride contents using non-linear regression analysis with omission of the first point of the profile (0-2 mm).

\[
C(x,t) = C_s - (C_s - C_0) \cdot \text{erf} \left( \frac{x}{2 \cdot \sqrt{D_e \cdot t}} \right) \tag{1}
\]

Where \( C(x,t) \) is the chloride concentration at depth \( x \) and time \( t \), \( C_0 \) is the initial chloride concentration (assumed to be 0 wt-%) and \( \text{erf}(.) \) is the error function.

### 2.4 Evaluation of equivalent performance

A concrete mix with 50 % of the cement replaced by fly ash is not in correspondence with the k-value concept (NBN B15-001, 2004). As a consequence, these concrete mixes can normally not be used in any of the more severe exposure classes. Therefore, the Belgian standard NBN B15-100 (2008) has been developed. It provides a methodology for the assessment and the validation of the fitness for use of cements or additions of type II (e.g. FA) for concrete. According to this standard, HVFA concretes can be applied in more severe environments when proof of an equivalent performance compared to the proper reference concrete exists. Regarding the resistance to chloride penetration, this proof can result from a diffusion test. The applicable evaluation criterion for equivalent performance states that the \( D_e \) values for the tested concretes should not exceed 1.4 times the value obtained for the reference concrete (NBN B15-100, 2008).

### 2.5 Service life prediction

The Fib Bulletin 34 (2006) is a design code providing the necessary models for a full probabilistic prediction of the concrete’s service life. In general, this design approach consists of defining a suitable limit state equation (2) containing the necessary load and resistance variables for the deterioration mechanism under investigation, in this case chloride initiated steel corrosion:

\[
C_{cr} = C_o + (C_{s,crit} - C_o) \cdot \left[ 1 - \text{erf} \left( \frac{d - Ax}{2 \cdot \sqrt{D_{app,c} \cdot t}} \right) \right] \tag{2}
\]

with \( C_{cr} \): critical chloride content (wt-%/binder), \( C_o \): initial chloride content (wt-%/binder), \( C_{s,crit} \) chloride content at depth \( Ax \) (wt-%/binder), \( d \): concrete cover, \( Ax \): depth of the convection zone (mm), \( t \): time (years), \( \text{erf}(.) \): error function and \( D_{app,c} \): apparent coefficient of chloride diffusion through concrete (mm\(^2\)/years). According to the Fib Bulletin 34 (2006), a value for the latter parameter is normally obtained from chloride profiles determined on either specimens taken from existing structures or laboratory test samples stored under the conditions that are expected in practice. However, since it takes quite some time before an adequate natural in situ chloride profile can be measured, the model code provides an equation (3) to estimate \( D_{app,c} \) from a non-steady state migration coefficient cf. NT Build 492 (1999):

\[
D_{app,c} = \exp \left[ b_\alpha \left( \frac{1}{T_{ref} - 1} - \frac{1}{T_{real}} \right) \right] \cdot D_{RCM,0} \cdot k_t \left( \frac{t_0}{t} \right) \tag{3}
\]

with \( b_\alpha \): regression parameter (K), \( T_{ref} \): standard test temperature (K), \( T_{real} \): temperature of the structural element or the ambient air (K), \( D_{RCM,0} \): non-steady state chloride migration coefficient (mm\(^2\)/years), \( k_t \): transfer parameter (-), \( t_0 \): reference point of time (years), \( t \): time (years) and \( \alpha \): ageing exponent (-).

Since the exposure temperature for both diffusion tests – one with samples immersed in a 165 g/l aqueous NaCl solution and another with samples immersed in a 33 g/l aqueous NaCl solution – was identical (20 °C), it is for the moment not yet possible to estimate parameter \( b_\alpha \) for linking the test temperature with the exposure temperature in practice, the transfer parameter \( k_t \) for linking the accelerated with the more realistic diffusion test and the ageing exponent \( \alpha \). However, the aim of this research was an estimation of \( D_{app,c} \) based on the \( D_e \) value obtained from chloride profiles of specimens exposed to a 165 g/l aqueous NaCl solution for 9 weeks. Evidently, \( D_e \) cannot simply replace \( D_{RCM,0} \) in equation (3). According to DARTS (2004) rapid test methods should always be calibrated against the chloride profiling method under natural conditions. This will normally result in other values for the regression variable \( b_\alpha \) for linking the test temperature with the exposure temperature in practice, the transfer parameter \( k_t \) for linking the accelerated with the more realistic diffusion test and the ageing exponent \( \alpha \).
studied concrete mixes and testing ages, $D_{\text{acc}}$ needed to be multiplied with 0.9 ± 0.1 to obtain $D_{\text{real}}$.

The outcome of the accelerated diffusion tests were used to estimate the ageing exponent $\alpha$ for each concrete mix. Therefore, equation (4) was first filled in three times with the data obtained at each testing age (28 days, 91 days and 1 year):

$$D_{\text{acc},t}=D_{\text{acc},0}\left(\frac{t_0}{t}\right)^{\alpha}$$ (4)

where $D_{\text{acc},t}$ is the diffusion coefficient at time $t$ and $D_{\text{acc},0}$ is the diffusion coefficient at a reference point of time $t_0$ (in this case 28 days). Then, an ageing exponent $\alpha$ for every concrete mix was determined by means of non-linear regression analysis in accordance with the method of the least squares fit.

This calculation resulted in ageing exponents of 0.1, 0.4 and 0.4 for mixes T(0.45), F15 and F50. It is known that concrete with FA is characterized by a higher ageing exponent. However, in comparison with the ageing exponents reported in Fib Bulletin 34 (2006) for OPC ($\alpha = 0.3$) and FA concrete ($\alpha = 0.6$), the values are considerably lower. Since the values of Fib Bulletin 34 (2006) ought to be only valid when $D_{\text{acc},0}$ is estimated from a non-steady state migration coefficient, this difference is not considered to be a problem.

The characteristics of all variables in limit state function (2) (without the factor covering the temperature effect) are shown in Table 2. The applied distribution functions, standard deviations (stdv) and lower and upper boundary values (where necessary) are also given in this table.

### Table 2. Quantification of the input parameters for the limit state function defined by (2) and (3) with omission of the temperature effect.

<table>
<thead>
<tr>
<th>Distribution</th>
<th>Mean</th>
<th>Stdv</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{cr}}$</td>
<td>Beta</td>
<td>1.9</td>
<td>0.15</td>
<td>0.2</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Constant</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$C_{\text{acc}}$</td>
<td>Normal</td>
<td>3.0</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>$d$ (mm)</td>
<td>Lognormal</td>
<td>40</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta x$ (mm)</td>
<td>Constant</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$D_{\text{acc}}$ (mm²/yr)</td>
<td>Normal</td>
<td>0.9</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>$t_0$ (yr)</td>
<td>Constant</td>
<td>0.0767 (28d)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\sigma$ (-)</td>
<td>Beta</td>
<td>0.1 (T(0.45))</td>
<td>0.03</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Note that the assumed critical chloride content $C_{\text{cr}}$ significantly differs from the value 0.6 wt-%/binder, mentioned in the Fib Bulletin 34 (2006). It is known that critical chloride contents found in literature can vary considerably (Song et al., 2009). For example, Duracrete (2000) gives much higher values for permanently submerged OPC concrete structures. For W/C ratios between 0.5 and 0.4, $C_{\text{cr}}$ values should range between 1.6 and 2.1 wt-%/cement. This means that a value of about 1.9 wt-%/cement can be assumed for reference T(0.45) with a W/C ratio of 0.45. Van den Heede et al. (2011) found that only under the assumption of this higher $C_{\text{cr}}$ value, a service life of around 50 years – the minimum service life of this composition for common buildings and other structures (NBN B15-001, 2004, NBN EN 206-1, 2000) – could be obtained. Even then, the steel reinforcements needed more concrete cover (60 mm) than the 40 mm minimum for a XS2 environment according to NBN EN 1992 (2005). Since it is still uncertain whether the critical chloride content increases or decreases in the presence of FA (Angst et al., 2009, Thomas, 1996, Oh et al., 2003, Alonso et al., 2002), the same $C_{\text{cr}}$ value (1.9 wt-%/binder) was adopted for F15 and F50.

Per concrete mix, three different concrete covers (40, 60 and 80 mm) and three different testing ages (28 days, 91 days and 1 year) were considered in the service life prediction. The reliability indices ($\beta$) and probabilities of failure ($P_f$) associated with limit state function (2) were calculated using the First Order Reliability Method (FORM) available in the COMREL software. In compliance with the Fib Bulletin 34 (2006), these parameters need to meet the requirements for the depassivation limit state ($\beta \geq 1.3$ and $P_f \leq 0.10$) to qualify for use in a XS2 environment.

### 2.6 Life cycle assessment

In correspondence with ISO 14040 (2006), the LCA consisted of four major steps: the definition of goal and scope, the inventory analysis, the impact analysis and the interpretation.

#### 2.6.1 Definition of goal and scope

This LCA was conducted to quantify the environmental benefits of partially replacing OPC with FA. Special attention was paid to its influence on the reduction of GHG emissions, since this is the reason why concrete mixes with considerable amounts of FA were developed in the first place.

Since both the strength and durability aspect were included in this LCA study, an axially loaded column carrying a design load of 1500 kN for 100 years was chosen as the functional unit (Fig. 1). The experimental strength classes given in Table 1 were used for the column design. All calculations regarding concrete and steel reinforcement dimensioning were done in accordance with NBN EN 1992 (2005). Logically, a higher concrete strength class reduces the column dimensions. As a result, the concrete...
volume $V$ required to construct a column with composition $T(0.45)$ (C45/55, $V$: 0.15 m$^3$), is less than the amount needed when using mix F15 (C40/50, $V$: 0.17 m$^3$) or F50 (C35/45, $V$: 0.19 m$^3$).

$$N_d = 1500 \text{kN}$$

Figure 1. Column dimensions based on their experimental strength classes.

2.6.2 Inventory analysis
Per concrete constituent, the necessary inventory data were collected from the Ecoinvent database (Frischknecht & Jungbluth, 2007). Their proper short descriptions as mentioned in the database together with the amounts used to manufacture 1 m$^3$ of each concrete mix, are shown in Table 3.

Table 3. Overview of the life cycle inventory data used per m$^3$ of each concrete mix.

<table>
<thead>
<tr>
<th>Material data (kg)</th>
<th>T(0.45)</th>
<th>F15</th>
<th>F50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand, at mine/CEI U</td>
<td>766 ± 44</td>
<td>746 ± 44</td>
<td>691 ± 41</td>
</tr>
<tr>
<td>Gravel, round, at mine/CEI U</td>
<td>1135 ± 109</td>
<td>1106 ± 107</td>
<td>1025 ± 99</td>
</tr>
<tr>
<td>Portland cement, strength class 340</td>
<td>317.6</td>
<td>225</td>
<td></td>
</tr>
<tr>
<td>Z 52.5, at plant/CEI U</td>
<td>-</td>
<td>56</td>
<td>225</td>
</tr>
<tr>
<td>Fly ash*</td>
<td>-</td>
<td>56</td>
<td>225</td>
</tr>
<tr>
<td>Tap water, at user/CEI U</td>
<td>153</td>
<td>153</td>
<td>158</td>
</tr>
<tr>
<td>Superplasticizer (EFCA 2006)</td>
<td>1.1</td>
<td>0.8</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Processing data (kWh)

| Electricity, low voltage, production BE, at grid/BE U | 3.83 | 3.83 | 3.83 |

* partially contains following Ecoinvent data: ‘Electricity, hard coal, at power plant/BE U’, through economic allocation

The mean values and standard deviations for the sand and aggregates, were calculated from Fuller’s optimal particle size distribution curve for three deliveries of sand and aggregates to our laboratory. The probabilistic distribution of these amounts is assumed to be normal.

The amounts of cement, FA, water and superplasticizer (SP) were assumed to be accurately weighed and therefore considered as constants. For the allocation of impacts attributed to FA, the economic allocation coefficient ($= 1.0$ % of the impact of coal fired electricity production associated with 1 kg FA) as proposed by Chen et al. (2010) was applied.

Inventory data regarding SPs were obtained from an environmental declaration published by the European Federation of Concrete Admixture Associations (EFCA, 2006).

The transport of each constituent to the concrete mixing plant was not incorporated in the LCA study since its environmental impact is always very case specific. In Van den Heede & De Belie (2012b), it was found that around 40 % of the GWP value for a concrete composition is attributable to the transport of its constituents. Preferably, an optimal location for the mixing plant is sought to establish minimal transport distances between the plant and its suppliers of raw materials. However, this was not a goal in the current LCA study.

For all Ecoinvent data, unit processes (U) were used in the modelling of each concrete mix. This was done to enable a full probabilistic uncertainty analysis of the calculated environmental scores using Monte Carlo simulations (number of runs: 500).

2.6.3 Impact analysis and interpretation
The IPCC 2007 GWP 100a impact method was adopted to calculate the concrete’s Global Warming Potential (GWP) expressed in CO$_2$ equivalents for a timeframe of 100 years. All calculations were done in the LCA software SimaPro 7.3.2.

3 RESULTS AND DISCUSSION
3.1 Diffusion coefficients & surface concentrations
Figure 1 shows the accelerated ($D_{acc}$) and the more realistic ($D_{real}$) coefficients for the two fly ash containing concrete mixes (F15 and F50) in comparison with OPC reference $T(0.45)$. Analysis of its upper and lower graphs, seems to indicate that the diffusion coefficients obtained after 9 weeks immersion in a 165 g/l aqueous NaCl solution ($D_{acc}$) and 18 weeks immersion in a 33 g/l aqueous NaCl solution ($D_{real}$) are more or less similar. As already mentioned in Section 2.5, $D_{real}$ is on average about 0.9 ($= k$, Table 2) times $D_{acc}$. Thus, $D_{acc}$ actually gives a fairly realistic value already.

When comparing the results of all three concrete compositions, it can be seen that both fly ash containing concrete mixes have significantly lower diffusion coefficients than reference $T(0.45)$. Hence, the criterion for equivalent performance of mix F50 has been met: $D_v$ values are at all time lower than 1.4 times the diffusion coefficients of the OPC reference (cf. NBN B15-100, 2008). Therefore, this mix seems as applicable in practice as the $k$-value approved composition with only 15% FA. Nevertheless, the measured decrease in diffusion coefficient of mix F50 between 28 and 91 days of curing seems to be somewhat smaller. Yet, similar low $D_{acc}$ values ($= k$, Table 2) times $D_{acc}$.
1.5 \times 10^{-12} \, \text{m}^2/\text{s}) for both F15 and F50 were finally obtained after 1 year.

Surface chloride concentrations $C_s$ are another output of the diffusion tests. The $C_s$ values obtained for two curing ages (28 and 91 days) and the two types of diffusion experiments – accelerated and realistic – are presented in Figure 3.

As expected, the chloride surface concentrations after immersion in 165 g/l aqueous NaCl solution (accelerated diffusion test; ± 5.0 wt.-% binder) are much higher than after immersion in 33 g/l aqueous NaCl solution (realistic diffusion test; ± 3.0 wt.-% binder). With respect to the $C_{s,acc}$ values obtained from the accelerated test, only slight differences seem to exist between the two curing ages per concrete mix. These differences are more pronounced in the case of the realistic test. However, the $C_{s,real}$ values remain within the range (3.0 ± 0.8 wt.-% binder) proposed by CUR (2007) for service life prediction (see Table 2).

3.2 Service life prediction

By means of example, the reliability indices $\beta$ and corresponding probabilities of failure $P_f$ with respect to limit state function (2) for OPC reference T(0.45) with 40, 60 and 80 mm concrete cover, are shown in Figure 4. From a comparison between these calculated values and the prescribed criteria for the depassivation limit state ($\beta \geq 1.3$ and $P_f \leq 0.10$), it is clear that the 100 years life span is not met for any of the assumed concrete covers (40 mm: 10 years, 60 mm: 28 years, 80 mm: 56 years).

![Figure 2. Influence of the concrete type (OPC versus FA concrete) on the measured diffusion coefficients $D_{acc}$ and $D_{real}$.](image-url)

![Figure 3. Influence of the type of diffusion test (accelerated versus realistic) on the measured chloride surface concentration $C_s$ (wt.-% binder).](image-url)

![Figure 4. Example: reliability indices $\beta$ and probabilities of failure $P_f$ as a function of time for OPC reference T(0.45) with 40, 60 and 80 mm concrete cover d after 28 days of curing.](image-url)
The concrete amount needed for these replacements needs to be included in the LCA study in order to have a correct, durability related environmental impact calculation. Since a 100 years service life seems achievable for compositions F15 and F50, only the concrete volume for the initial manufacture of the column needs to be considered in the LCA.

Table 4. Influence of the applied concrete cover on the estimated service life $t_{est}$ of concrete mixes T(0.45), F15 and F50.

<table>
<thead>
<tr>
<th>$d$ (mm)</th>
<th>$t_{est}$ 40 days (years)</th>
<th>$t_{est}$ 91 days (years)</th>
<th>$t_{est}$ 1 year (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>10</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>60</td>
<td>28</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>80</td>
<td>56</td>
<td>64</td>
<td>54</td>
</tr>
</tbody>
</table>

F15

<table>
<thead>
<tr>
<th>$d$ (mm)</th>
<th>$t_{est}$ 40 days (years)</th>
<th>$t_{est}$ 91 days (years)</th>
<th>$t_{est}$ 1 year (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>60</td>
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F50

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<th>$d$ (mm)</th>
<th>$t_{est}$ 40 days (years)</th>
<th>$t_{est}$ 91 days (years)</th>
<th>$t_{est}$ 1 year (years)</th>
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3.3 Life cycle assessment

Figure 5 presents the global warming potentials (GWP expressed in kg CO$_2$ eq) for the amounts of each concrete mix needed to manufacture and maintain an axially loaded column (design load: 1500 kN, design service life: 100 years).

Due to the extra amount of concrete needed for the T(0.45) column replacements over time, the environmental impact of the OPC reference column with 40 mm concrete cover is about 9 times higher than the impacts of the columns made with mixes F15 and F50. The GWPs of F15 and F50 are 27-26 % and 55-52 % of the OPC reference value, and this for concrete covers of 60 and 80 mm, respectively. Despite the lower strength values of the latter concrete mixes with FA (Table 1), the negative effect of their higher column dimensions (Fig. 1) is completely compensated because of their better chloride penetration resistance, even with an economically allocated impact (1.0% of the impact of coal fired electricity production according to Chen et al., 2010) attributed to the FA. In case FA would be wrongfully seen as waste with no impact allocated to it, the GWP values would seem another 2.2 and 8.6 kg CO$_2$ eq lower. Logically, the allocation related difference increases with an increasing FA content of the concrete. For a 50% FA content, this difference is significant.

4 CONCLUSIONS

In conclusion, this paper shows the importance of choosing a strength and durability related functional unit for LCA when quantifying the reduced greenhouse gas emissions of concrete with FA intended to be used in a submerged marine environment.

An adequate assessment of durability and service life, requires the execution of chloride diffusion tests after immersion in high concentration and realistic (cf. seawater) aqueous NaCl solutions at different curing ages (28 days, 91 days and 1 year). This approach enables the determination of an ageing exponent (0.1 for OPC reference concrete, 0.4 for FA concrete) per concrete type and the calculation of a factor (0.9) to convert an accelerated diffusion coefficient into a more realistic one.

The diffusion coefficients of concrete with 15 % and 50 % FA were significantly lower than the values for the OPC reference, and this after already 28 days. After 1 year, their values amounted to only 1.5 x 10$^{-12}$ m$^2$/s while the OPC reference still gave a value of around 6.0 x 10$^{-12}$ m$^2$/s.

With the current assumption of an equivalent critical chloride threshold value for each concrete type and omission of the temperature effect in the limit state function of Fib Bulletin 34 (2006), the estimated service lives of the concrete mixes with 15 and 50 % FA exceed 100 years. A concrete cover of no less than a practically not feasible 80 mm would be needed to obtain about half of this service life with a traditional concrete. As a result, additional concrete manufacturing for column replacement is necessary to realize a service life of 100 years when using the latter concrete type in a submerged marine environment with exposure to chloride induced corrosion.

Comparative life cycle assessment of centrically loaded concrete columns made with a predefined service life of 100 years and inclusion of the required column replacements, gives much lower (at least – 45-48 %) global warming potentials for concrete with 15 and 50% FA than for OPC concrete. Economic allocation of the FA impact adds another
REFERENCES


Oh, B. H., Jang S.Y., Shin, Y. S. 2003. Experimental investigation of the threshold chloride concentration for corrosion in-