Effects of slag and fly ash on reinforcement corrosion in concrete in chloride environment - Research from the Netherlands

Rob B. Polder

TNO Technical Sciences, Structural Reliability, Delft, the Netherlands
Delft University of Technology, Civil Engineering and Geosciences, Delft, the Netherlands

A review is given of research on the durability performance of concrete made with blast furnace slag and fly ash related to chloride induced reinforcement corrosion, carried out in The Netherlands, where slag has been used in cement for almost a century. Results are presented from field studies on concrete in marine environment and laboratory studies involving chloride exposure. Chloride surface content, diffusion coefficient, electrical resistivity, critical chloride content and corrosion rate are discussed. Both slag and fly ash concrete show improved behaviour compared to Ordinary Portland cement in aggressive environments, in particular where penetration of chloride presents the risk of reinforcement corrosion.

Keywords: Durability, concrete, chloride, corrosion, diffusion, resistivity, blast furnace slag

1 Introduction

1.1 General
Presently various reasons exist for an increasing interest in “blended cements” that incorporate supplementary cementing materials other than Portland clinker: usage of industrial by-products and waste materials, thus saving precious raw materials; reduction of Portland clinker usage in order to reduce CO$_2$ emission; and increased durability, in particular in chloride contaminated environment, thus increasing the service life of structures. Using ground granulated blast furnace slag (GGBS or BFS, for simplicity further called slag) as a cement component in The Netherlands dates back to the 1920’s
Later, pulverised fuel ash or fly ash from powder coal fired power stations has become increasingly used in cement. Both slag and fly ash concrete showed improved durability behaviour compared to ordinary Portland cement in aggressive environments, in particular where penetration of chloride presents the risk of reinforcement corrosion. After briefly relating the history of slag use in The Netherlands, this paper focuses on research carried out in the Netherlands on slag and fly ash with regard to chloride transport and reinforcement corrosion, both in the field and in the laboratory.

1.2 History of slag and fly ash use in concrete in the Netherlands
This brief historical overview is based on [Bijen 1996, Gaal 2004, Heinemann & Nijland 2009]. Slag cement production started in Germany in 1888, from which slag cement was imported. Between 1919 and 1930 slag cement was used for building the North Sea canal locks at IJmuiden; testing showed the good resistance to sea water. In 1931 a slag cement plant was established at IJmuiden in collaboration between steel and cement producers. The regulations issued between 1912 and 1962 reflect the changing attitude towards slag use in concrete. In the regulations for reinforced concrete of 1912 [GBV 1912], slag was prohibited in concrete; in GBV 1918 high slag percentages (70 - 85%) were prohibited in reinforced concrete, but cement with a maximum of 30% slag (Iron Portland cement) was not mentioned, but it was not prohibited. Since 1930 using slag cement was only allowed if client and contractor agreed so in advance; this remained the position in the 1930, 1940 and 1952 regulations. In the 1962 code the choice of cement type was free; it was stated that slag cement has better characteristics in aggressive environment than Portland cement. In 1984, slag cement was recommended and Portland was discouraged for use in aggressive environments [VB 1974/1984]. The 1986 concrete technology standard [VBT 1986], in which environmental (exposure) classes were introduced, recommended using slag cement with high sulfate resistance, i.e. with at least 65% slag, for marine environment. What is now called CEM III/B 42.5 LH HS (or most recently: SR), in the Netherlands with about 70% slag, became the dominant cement type in the 1970s. In The Netherlands, about 10 million cubic metres of slag cement concrete are produced annually, in particular for concrete cast in situ. The low heat of hydration is seen as a major advantage with regard to early age cracking. Fly ash has been used since the 1980s, either as factory produced CEM II/B-V or as mixtures of CEM I with fly ash, both typically with about 27% of clinker replacement.
Traditionally slag and fly ash were intermixed (and in case of slag also interground) with clinker in the cement plant and sold as “cements”, with dedicated amounts of calcium sulfate. The manufacturer would carefully compose these products to have similar 28 day strength as Portland cement, typically with 32.5 or 42.5 MPa of (mortar) compressive strength. In the 1990s CEM III/A 52.5 N was introduced, with 52 - 57% slag, aimed at the precast industry, with increased early strength. Slag cements contain typically 0.6% of Na₂Oeq. Recently, separate slag for addition to Portland cement in the concrete mixing plant has become available (regulated by a certification scheme [BRL 9340 2003].

Since the 1990s, The Ministry of Infrastructure regulations require concrete based on cements with at least 50% slag or 25% fly ash (for precast concrete only), among others for preventing deleterious ASR [ROK 1.0 2011]. Concerns arose from finding damage due to ASR [Heijnen & Larbi 1999, Nijland & Siemes 2002], upon which a Recommendation for prevention was issued, that was later updated [CUR38 1994, CUR89 2002]. All these studies and regulations recommend use of slag cement to prevent ASR. For reference to practice in other countries, traditional concrete compositions for aggressive environments (XD, XS) typically involve about 340 kg cement per cubic meter, a target w/b of 0.43 and rounded siliceous aggregate of 32 mm maximum size.

2 Slag cement research related to chloride penetration and corrosion

A lot of independent research has been devoted to slag cement in concrete and its durability over the last 40 years, both in the field and in the laboratory. Here the focus is on chloride and corrosion related research carried out in The Netherlands. This is not intended to play down the importance of pioneering work elsewhere in the laboratory [Page et al. 1991] and studies based on field exposure [Bamforth & Chapman-Andrews 1994, Bamforth 1994, Bamforth 1997]. In the 1970s durability was investigated of structures in marine environment [Wiebenga 1980]. Slag cement concrete appeared to perform very well, with hardly any visible corrosion in about 50 structures up to 63 years of age. Carbonation was found to be 5 mm or less in the large majority. Five structures were cored and chloride profiles determined. Chloride diffusion coefficients were found to be lower for slag cement than for Portland cement, by a factor of 10 to 16 [Bijen 1996]. Exposure for 16 years of concrete prisms submerged in the North Sea showed that slag cement had much lower chloride penetration than Portland cement concrete [Polder & Larbi 1995]. Results from chloride profile analysis and electrical resistivities are reported in Table 1. An
overview was published including examples of slag in structures in the Middle East, underpinning its durability [Bijen 1996]. In depth investigation in the early 2000s of six marine structures of up to 40 years of age showed that chloride penetration was consistently slow in slag structures [Polder & Rooij 2005]. An overview of results from chloride penetration profile fitting the error function solution of Fick’s second law of diffusion is given in Table 2.

*Table 1: Chloride diffusion coefficients and surface contents from profile fitting to prisms submerged for 16 years in the North Sea [Polder & Larbi 1995]*

<table>
<thead>
<tr>
<th></th>
<th>CEM I</th>
<th>CEM III/B</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCl (*10¹² m²/s)</td>
<td>1 - 3</td>
<td>0.3</td>
<td>CEM I: depending on w/c, curing and age at start of exposure</td>
</tr>
<tr>
<td>Cs (% by mass of cement)</td>
<td>3.5 - 5</td>
<td>2.5 - 5</td>
<td>depending on curing and age at start of exposure</td>
</tr>
<tr>
<td>Resistivity (Ωm)</td>
<td>120 - 155</td>
<td>400 - 1000</td>
<td>depending on curing and age at start of exposure; CEM I depending on w/c</td>
</tr>
</tbody>
</table>

*Table 2: Overview of chloride penetration results from six marine structures [Polder & Rooij 2005]*

<table>
<thead>
<tr>
<th>Structure, age (year)</th>
<th>DCl (10¹² m²/s)</th>
<th>Cs (% by mass of cement)</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pier, 40</td>
<td>0.14 - 0.28</td>
<td>3</td>
<td>CEM I, low w/c; higher splash zone, sheltered from rain</td>
</tr>
<tr>
<td>Pier, 40</td>
<td>0.33</td>
<td>3</td>
<td>CEM III/B, higher splash zone, sheltered from rain</td>
</tr>
<tr>
<td>Barrier, 40</td>
<td>0.12</td>
<td>2.8</td>
<td>CEM III/B; lower splash zone</td>
</tr>
<tr>
<td>Barrier, 20</td>
<td>0.24</td>
<td>2.2 - 5</td>
<td>CEM III/B; Cs depends on height above sea level</td>
</tr>
<tr>
<td>3 harbour quays, 20 - 33</td>
<td>0.12 - 0.19</td>
<td>3 - 4</td>
<td>-</td>
</tr>
</tbody>
</table>
In the laboratory, various durability and corrosion related properties of slag cement concrete have been investigated since the 1980s, including electrical resistivity [Polder & Ketelaars 1991, Osterminksi et al. 2012] and its relationship to chloride transport [Polder 1997], corrosion rates with mixed in chloride [Fiore et al. 1996] or penetrated chloride [Polder & Peelen 2002], see also [Bertolini & Polder 1997, Bertolini et al. 2004]. Cubes with embedded electrodes were cast in 1989 and resistivity was measured over the years. Slag cement consistently showed a higher resistivity than Portland cement, and slag resistivity appears to continue increasing for over more than a decade. For more details see [Osterminksi et al. 2012]. Prisms with embedded steel electrodes were cast in 1998 with four binder types (Portland, Portland fly ash, slag and composite cement, with slag and fly ash) and three w/c’s (0.40 – 0.55). They were subjected to half a year of cyclic wetting with salt solution and drying, simulating de-icing salt exposure. Subsequently, they were stored in wet and semi-dry environment and outdoors for two more years. Steel potential, corrosion rate (by linear polarisation resistance) and resistivity were monitored. Chloride profiles were determined after half a year and after 2.5 years and fitted. Chloride surface contents and diffusion coefficients are shown in Figure 1 [Polder & Peelen 2002, Polder 2000]. Exposure was continued since 2004 on an open roof and resistivity was again measured in 2010 [Pacheco et al. 2012]. Development of resistivity over 11 years is shown in Figure 2. Summarising this laboratory research, slag cement concrete was shown to have higher electrical resistivity and lower corrosion rates than Portland cement concrete under comparable conditions of chloride and moisture. The higher electrical resistivity of slag cement concrete correlated with lower chloride diffusion coefficients.

In the 1990s, a practical accelerated test method for chloride penetration was developed in Scandinavia, NTBuild 492 or Rapid Chloride Migration test, RCM [NTBuild 492 1999, Tang & Nilsson 1992, Tang 1996, Tang & Sørensen 2001]. This method was adopted as an important element of service life evaluation and a method for quality control based on resistivity was proposed [DuraCrete 2000]. Parallel development of probabilistic service life modelling will not be addressed here [DuraCrete 2000, Gehlen 2000]. However, the combination of rapid chloride migration testing and quantitative service life design requirements stimulated testing of large numbers of concrete compositions. Concrete with various binders was tested for RCM at ages up to 3 years [Visser & Polder 2006]. Dutch regulations committee CUR VC81 collected about 500 test results obtained from a wide range of concrete compositions used in the field, a.o. in the Green Heart tunnel [Rooij et al. 2007]. They were among others analysed for the influence of w/b, see Figure 3. In the typical range of w/b’s from 0.40 to 0.55, slag cement concrete has a considerably lower
Figure 1: Chloride surface contents (top) and diffusion coefficients (bottom) after 26 weeks salt solution/drying cycles in concrete prisms [Polder & Peelen 2002, Polder 2000]
Note: CEM I 0.55 $D_{\text{eff}}$ is out of scale; value approx. $140 \cdot 10^{-12}$ m$^2$/s

Figure 2: Electrical resistivity of concrete with four binders and w/c 0.45 during outdoor exposure from 1 week until 11 years of age, after [Polder & Peelen 2002, Polder 2000 Pacheco et al. 2012]
Note: Y-axis log scale
chloride migration coefficient than Portland cement concrete. Further analysis showed that there is a linear relationship between w/b and chloride migration coefficient, with a slope and intercept that strongly depend on binder type. The dependency of the migration coefficient on w/b is much smaller for slag cement concrete than for Portland cement [Polder et al. 2010, Polder et al. 2011, Wegen et al. XX]. Similar dependencies on w/b were found in Scandinavia [Frederiksen et al. 1997] and Germany [Gehlen 2000]. This implies that small deviations from the target w/b have a small effect on the migration coefficient for slag cement concrete, making it more tolerable for production related fluctuations. The results were used to underpin a Guideline for simplified (semi-probabilistic) service life design in XS/XD environment [Polder et al. 2010, Polder et al. 2011, Wegen et al. 2012].

From further analysis of the database, the time dependency of migration coefficients was shown to depend on the binder type. For ages between 28 days and three years, migration coefficients showed exponential decrease with a high exponent for fly ash binder; an intermediate value for slag binder and a relatively low exponent for Portland cement. Similar results were found by [Bamforth 1994, Gehlen 2000].

A concern with regard to slag cement may be its relatively slow early hydration, as a more porous microstructure at early age may be a disadvantage when the concrete is exposed to chloride at earlier ages than 28 days, as is usually assumed. Recent work has clarified this
issue: it appears that up to seven days the diffusion coefficient for chloride in slag cement mortar is higher than for Portland cement mortar, but from then on progressively becomes much lower as shown in Figure 4. Modelling has shown that the effect of exposure to chloride at one day age compared to 28 days for a total exposure period of 50 years is very small [Caballero et al. 2010, Caballero et al. 2012]. Over 50 years, chloride penetration is much lower for slag cement than for Portland cement in a comparable situation.

![Figure 4: Chloride migration coefficient for Portland and slag cement mortar between one and 28 days age; Note: Y-axis log scale [29]](image)

With service life modelling as the objective, questions regarding the critical chloride content arose. The case for slag concrete has not been clarified completely, but present limited information suggests that critical chloride levels in slag cement concrete are similar to those in Portland cement concrete [Breit 1998, Polder 2009]. In the experiments with salt/drying exposure described above [Polder & Peelen 2002], steel potentials were used to determine initiation of corrosion. As multiple steel bars were subjected to the same chloride content, the probability of corrosion initiation could be determined [Polder 2009]. Subsequent evaluation of the relationship between the probability of corrosion and the chloride content at the depth of the steel bars showed that the critical chloride content depended most strongly on w/b. It did not significantly depend on binder type. It was also observed that the corrosion rate of steel bars, after corrosion had initiated and with similar chloride contents, was lower in slag cement concrete than in Portland cement concrete.
3 Fly ash research related to chloride penetration and corrosion

Research on fly ash parallel to that mentioned for slag has been conducted in The Netherlands since the 1990s. In the study mentioned above high resistivities and low corrosion rates were found for CEM II/B-V concrete with 27% fly ash, see Figure 2 [Polder & Peelen 2002]. This is the typical fly ash replacement level applied, both intermixed in the cement plant in CEM II/B-V as in mixes with fly ash addition to CEM I in the concrete plant. Chloride diffusion may be relatively high at 28 days, but progressively becomes much lower over say up to one year, approaching that of slag cement. Fly ash hydration is slower than slag hydration, requiring up to several months to fully develop its beneficial effects, including high resistivity [Polder & Peelen 2002, Pacheco et al. 2012]. Fly ash diffusion coefficient dependency on w/b (note: counting all fly ash as binder) is intermediate between slag and Portland cement [Polder et al. 2010, Polder et al. 2011, Wegen et al 2012] as shown in Figure 3. A recent study exploring extremely low clinker contents showed that with 250 kg “binder” per cubic meter with 30 to 70% fly ash of total binder, relatively low diffusion coefficients could be obtained at one year age [Valcke et al. 2010, Valcke et al. 2012]. Such concretes, however, are very sensitive to poor curing, as they carbonate rather quickly and show increased freeze-thaw damage if not hydrated properly, that is, by long wet curing.

Although studied much less, Dutch work on “ternary” blends of slag and fly ash and of fly ash and silica fume may provide additional data. Concretes made with so-called composite cements, CEM V/A (S-V), containing c. 25% slag and c. 25% fly ash, were found to produce low chloride migration coefficients and high resistivity, see Figures 1 and 2 [Polder & Peelen 2002, Pacheco et al. 2012]. In the 1990s a mix with 10% fly ash and 5% silica fume was studied for chloride diffusion (by immersion) and resistivity: it produced low diffusion and high resistivity values [Polder 1996, Polder 1997]. It approached the behaviour of classic slag cement concrete. In these respects, it performed particularly better than a mix with 5% silica fume (to Portland cement) only.
4 Summary and conclusions

Studies of concrete in the field in marine environment on structures up to 60 years of age and several decades of laboratory work have shown that concrete made with cement that contains about 70% of blast furnace slag (nowadays termed CEM III/B LH SR) shows excellent behaviour with respect to chloride penetration and reinforcement corrosion. In comparative studies it was observed that chloride penetration in Portland cement concrete was deeper and faster. Chloride profile analysis revealed that chloride surface contents were similar, but diffusion coefficients were consistently lower for slag cement than for Portland cement. The decrease over time of apparent diffusion coefficients in slag cement is stronger than in Portland cement concrete. Slag cement concrete has a higher electrical resistivity and lower corrosion rate after depassivation. Slag cement hydration is slower than Portland cement hydration, but from about seven days age on chloride migration is slower in the former than in the latter. Similarly, cement with moderate fly ash replacement of Portland clinker shows lower diffusion coefficients and higher resistivities than Portland cement, in particular after a few months of hydration. Composite cements with slag and fly ash at about 25% clinker replacement each behave similarly. Critical (corrosion initiating) chloride contents appear comparable for all cement types mentioned. Summarising, replacement of clinker by slag at high levels (50 – 70%) and fly ash at intermediate levels (20 – 30%) produces high chloride penetration resistance and high electrical resistivity, overall decreasing the risk of corrosion in chloride contaminated environments.

References


BRL 9340. “Combinatie van gemalen gegraneulde hoogovenslak en portlandcement voor toepassing als bindmiddel in beton.” BMC, Gouda, 2003. (Combination of ground granulated blast furnace slag and Portland cement for binders in concrete), in Dutch


CUR38, “Measures to prevent damage of concrete by alkali-silica reaction (ASR)”, CUR Recommendation 38, CUR, Gouda, 1994, 8 pp.

CUR89, “Measures to prevent damage of concrete by alkali-silica reaction (ASR)”, CUR Recommendation 89, CUR, Gouda, 2002, pp. in Dutch


Nijland, T.G. & Heinemann, H.A., “Beton, een materiaalgeschiedenis vanuit de componenten”. Praktijkspeeks Cultureel Erfgoed 4(12), 2008, 28 pp. (Concrete, a material history from the components) in Dutch

NTBuild 492, “Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments”, NORDTEST, Espoo, 1999


Polder, R.B., “Chloride diffusion and resistivity testing of five concrete mixes for marine environment”, Proceedings, RILEM. International Workshop on Chloride Penetration


