

Discussion on paper published in
Magazine of Concrete Research
1993, 45, No. 162, Mar., 63–69

Theoretical description of impact of blastfurnace slag (BFS) on steel passivation in concrete

D. E. Macphee and H. T. Cao

Contribution by R. B. Polder* and R. F. M. Bakker†

* TNO Building and Construction Research, Building Technology Department, PO Box 49, 2600 AA Delft, The Netherlands

† CEMIJ, IJmuiden, The Netherlands

The word 'theoretical' in the title of this Paper suggests a certain limitation of the significance of the findings for concrete practice, yet both the abstract and the concluding remarks suggest that there are indeed practical implications of these findings, which may be summarized as follows: the formation of the passive layer on steel in blastfurnace slag (BFS) pastes is impeded at an early stage or the layer may be degraded at a later stage; consequently steel in BFS pastes is not as well protected as in OPC pastes. Both the technical contents of the Paper and the implications for practice may be commented on, starting with the latter.

It is surprising that the practical experience with BFS concrete, which spans several decades, is not mentioned. In the Netherlands, concrete with a high percentage of BFS has been used for about 60 years in most civil structures. The corrosion protection of the embedded steel in BFS concrete is adequate, as has been shown by several investigations of existing structures.¹ Information from more fundamental research on steel in BFS concrete is also available.

The high early corrosion rates mentioned (within 24 h) are irrelevant to any practical behaviour. There is ample

evidence that corrosion rates decrease quickly on the time-scale of weeks after casting in all cases, with or without BFS.²

On the time-scale of the reported investigation, one day to four weeks, a lower oxygen activity at the steel is inferred in the case of BFS pastes as compared with OPC pastes. It is important that the experiments concern submerged specimens. Oxygen transport through water-saturated paste is severely limited; as a result of the usually finer pore structure of BFS paste, it is probable that less oxygen is available for passive film formation than in OPC pastes. In atmospheric conditions, oxygen availability is always sufficient to allow more positive steel potentials to develop, suggesting passivation in both BFS and OPC concrete.^{3,4}

The more porous structure of the oxide film in BFS paste is inferred from the micrographs shown after 11 months' exposure to expressed pore solution. Unfortunately, no information is given on the composition of this solution or on the level of aeration. If the liquid is not well aerated, quite different reactions are possible to months' exposure to expressed pore solution. Unfortunately, no information is given on the composition of

those that happen in aerated conditions, which prevail in real (atmospheric) structures.⁵ This may explain the different behaviour shown in the polarization curves as well. The meaning of the results can be questioned: it seems there is no proof of the formation of Fe(II) rather than Fe(III) oxide layers in the case of BFS paste.

Recent investigation of concrete specimens submerged in the North Sea shows the absence of corrosion of embedded bars, both in OPC and BFS concrete, despite significant chloride levels at the steel. This shows that even in less aerated conditions, no deleterious processes take place at steel in BFS concrete.⁶

The unit of the current in Table 2 is probably a misprint: a passivation current of 1 mA/cm^2 , as reported, is equivalent to 10 A/m^2 , which would be considered high even for electrochemical chloride removal treatment! Probably the correct unit is $\mu\text{A/cm}^2$. Even then, a level of $1 \mu\text{A/cm}^2$ is high for a passivation current, which is considered to be below 0.1 and normally even below $0.01 \mu\text{A/cm}^2$.^{7,8}

Table 2 suggests that 40% BFS behaves as pure OPC, while 20% slag does not (higher currents). A similar 'reversed order' of effects is seen with 60% and 80% slag. This suggests considerable scatter in the data, which raises the question of the reliability of the results as a function of the replacement level.

The values of the maximum currents I_{max} are extremely high in case of BFS pastes; $200 \mu\text{A/cm}^2$ (2 A/m^2 steel) would be equivalent to 2 mm of steel loss per year, which is unrealistic unless large amounts of chloride and a low local pH are present. It is more probable that the high currents in the tests carried out are caused by the oxidation of reduced species present in the slag paste. If this is true, the conclusion concerning poor oxide layer formation is no longer valid.

The pH-reducing effect of the oxidation of sulphur species is mentioned (reactions (2) and (3)); the question is whether there is evidence for the occurrence of this under natural circumstances. The pH of BFS concrete (13.0–13.5) may be lower than that of OPC concrete (usually in excess of 13.5), which is usually explained from the lower (available, i.e. not bound in the glass) alkali content of the former.^{9,10} Significant oxidation of the sulphide (here 1% by mass as SO_3) would produce a much stronger pH decrease, which has never been reported. The attack associated with such acid production would be visible by simple microscopic techniques, but has not been seen.¹¹ Moreover, the (lower) pH of BFS concrete is stable in time, which would not be the case if it were caused by the oxidation of sulphide.

In the Paper it is considered important for the long-term behaviour of slag-containing systems that all reduced species may eventually be oxidized. The question is on which time-scale this may happen. In our experience, well-made BFS concrete retains its characteristic dark-blue colour, associated with reduced manganese and sulphur species, for decades. At the same time, steel embedded in this concrete behaves as in well-aerated

conditions. Apparently, the oxidation rate of these substances is low; the kinetics of the oxidation reactions impede the thermodynamical equilibrium.

The corrosion localized on the gas–liquid interface level of steel bars (described under the heading 'Implications of the model') is normal for any such system of cementitious liquid and air containing CO_2 , and is not caused by specific slag properties. It is caused by the coincidence of the depassivated (by lack of alkalinity) atmospheric steel and the close distance to the (submerged) cathodical steel surface, with ions conducting the cathodic current to the liquid–air interface.

Practical experience of BFS concrete shows overwhelming evidence of 'perfect' passivity of steel embedded in it. The same factors as in OPC concrete may cause corrosion: carbonation and chloride (provided water and oxygen are available). There is evidence that corrosion rates are lower for steel in BFS concrete than in OPC concrete.² Corrosion macrocell experiments have shown that the critical chloride threshold for corrosion initiation in BFS is higher than in OPC concrete; the passivity seems even 'better' in slag cement.¹²

Finally, the main advantage of BFS concrete (provided it is well graded, mixed, cast and cured) is its much higher resistance than OPC concrete to chloride penetration. That, however, is not the subject of the Paper.

Reply by the authors

The Authors thank Dr Polder and Dr Bakker for their comments on this Paper. We are aware of the extensive use of BFS in construction and of the excellent performance of BFS-containing concretes in aggressive exposure environments, so that in general we accept the comments relating to the longevity of existing, well-made and suitably cured concrete structures containing BFS. It is well known, for example, that cured pastes containing BFS have reduced interconnected porosity compared with those of neat OPC. This factor alone is likely to limit migration of moisture and aggressive species and thus has undoubtedly played an important part in providing the protection in the concretes cited above and the persistence of the characteristic dark-blue coloration in the interior of BFS-containing concretes. It might be argued, therefore, that the electrochemical effects at the steel–concrete interface are unimportant but corrosion initiation and propagation will be sensitive to the chemical and electrochemical environment in the region of the interface. Thus, the fundamental mechanisms of corrosion should not be ignored even though the physical characteristics (permeability) of the cover concrete give the impression of 'perfect' passivity.

In a study of iron in alkaline systems containing sulphides, Salvarezza *et al.*¹³ reported a reduction in iron passivity due to the formation of mackinawite (FeS) and/or $\text{Fe}(\text{OH})_2$, depending on the HS^-/OH^- ratio. We know that pore solutions from BFS–OPC pastes are alkaline and can have significant concentrations (up to around

1000 ppm expressed as S^{2-}) of reduced sulphur species,¹⁴ and although bulk HS^-/OH^- ratios may be lower in BFS cements than in the solutions studied by Salvarezza *et al.*,¹³ our original study seems appropriate as an assessment of the relative performances of steel in a series of BFS-blended pastes and in OPC pastes. Even the short-term data reported in the Paper have some relevance, therefore, in highlighting the differences in the electrochemical environments existing in the respective systems, particularly where early conditioning of the electrode surface may have longer term implications for performance.

Although the scatter in our data has attracted criticism, the measured passivation current densities clearly indicate a reduced passivation when high-BFS-loaded pastes are compared with OPC pastes. This is consistent with the observations of Preece *et al.*,¹⁵ who refer to thicker but less protective films and considerable increases in passive current densities for steel in BFS cements as compared with OPC and SRPC specimens. Their reference to layer thickness and reduced protection is consistent with the interpretation offered in the Paper based on the SEM and polarization data. More recent results¹⁶ confirm our earlier data, which are also supported by more practical related studies.^{17,18} Torii *et al.*¹⁷ report that the protective ability of their BFS-containing concrete (50% cement replacement) was lower than that of concretes containing fly ash (30% cement replacement) and silica fume (10% replacement) over a five-year period, and Parrott¹⁸ reports broadly greater weight losses from pre-cleaned

bars embedded in the uncarbonated portion of concretes based on a binder containing 50% BFS than were found for concretes based on OPC and a PFA (30%) blend at ages of up to four years after casting.

We are therefore confident in the observations that were made, although we do not know what the long-term nature of the effect will be. Our ongoing studies using a.c. impedance spectroscopy¹⁹ have confirmed the short-term observations, i.e. a gradual decrease in the charge transfer resistance R_{CT} (diameter of the semicircle in Fig. 1) within the first few days. The development of an interfacial layer, as observed from the response at high frequencies (Fig. 2), becomes apparent after only two days, but the R_{CT} data indicate that it is poorly insulating and not an effective passivation. This supports the high I_{max} data that are criticized by Dr Polder and Dr Bakker.

This criticism raises two points. First, potentiodynamic polarization, the technique used in the original study, does not provide an equilibrium measurement so the translation of measured currents to an annual weight loss has little meaning,²⁰ and second, the high measured currents, regardless of their origin, necessarily flow across the paste-electrode interface, reflecting the poor insulating properties of the interfacial layer(s). In any case, further ageing causes R_{CT} to increase again (Fig. 1), suggesting only transient depassivation during the short time-scales of the study. But BFS hydration is known to proceed in stages with a well-defined dormant period after an initial burst of activity.^{21,22} If the corrosion process is influenced by the release of reduced species from the

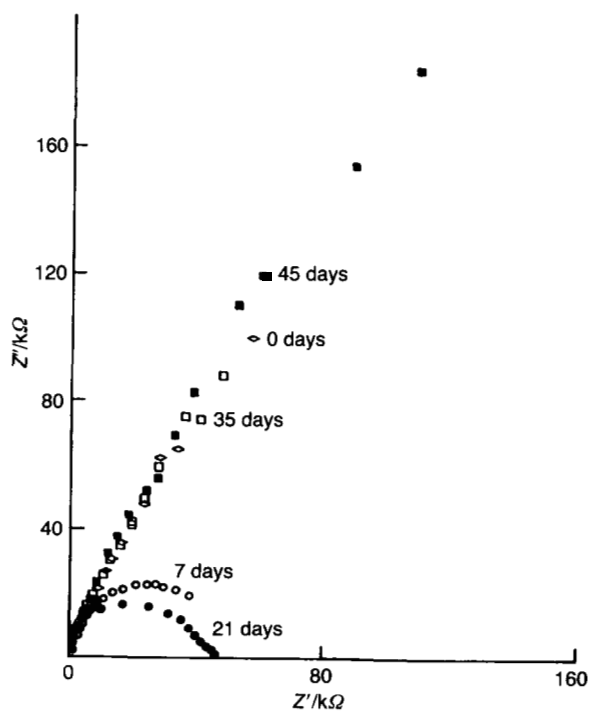


Fig. 1. Nyquist plot for iron in the pore solution of an 85% BFS-15% OPC paste: charge transfer resistance R_{CT} is given by the intersection of the semicircular elements of the response with the real (Z') axis

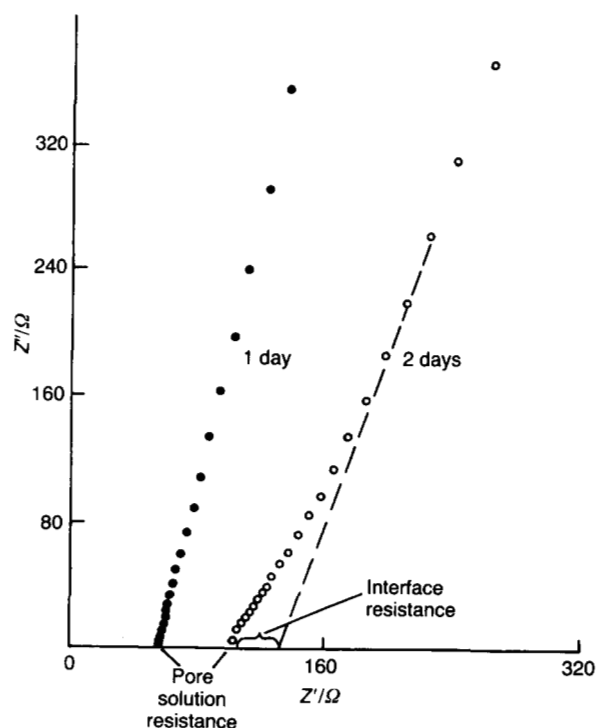


Fig. 2. Expanded view of the high-frequency region of the response for iron in BFS-OPC pore solution at 1 and 2 days

hydrating slag, then later stages of BFS hydration may well provide further electrochemical activity in or near the interfacial region. This factor suggests that further studies should be conducted on the long-term electrochemical performance of steel in BFS-containing concretes.

We accept that the degree of aeration of electrolyte will be an important variable. The availability of oxygen may well be reduced in BFS cement pastes, but our measurements indicated that rest potentials were not sufficiently low to promote anaerobic corrosion (< -750 mV (SHE)) even in samples submerged in electrolyte. It may be of interest, however, that in the report by Naish *et al.*²³ on steel corrosion under anaerobic conditions, the sample embedded in the BFS-containing matrix was the only one exhibiting a distinct corrosion product (magnetite) layer.

Finally, we agree that the gas-liquid interface level on partially immersed steel samples is likely to be an area of enhanced corrosion activity for the reasons given by Dr Polder and Dr Bakker. Unfortunately, the description of this observation in the Paper was incomplete. In a comparison with a corresponding cell for OPC where slight corrosion was observed at the interface in the OPC cell, corrosion in the BFS-OPC cell caused the electrode to break at the gas-liquid interface.

We are grateful to Dr Polder and Dr Bakker for pointing out the typographical error in the caption to Table 2. Units of current used are $\mu\text{A}/\text{cm}^2$. In addition, the potentiodynamic polarization scans were obtained over the range -1000 to 1000 mV against SHE, not -1500 to 560 mV as indicated in the Paper.

References

1. WIEBENGA J. G. *Durability of concrete structures along the North Sea coasts of the Netherlands*. Special publication SP-65, American Concrete Institute, Detroit, 1980, pp. 437-452.
2. RAUPACH M. *Zur chloridinduzierten Makroelementkorrosion von Stahl in Beton*. Deutsche Ausschuss für Stahlbeton, **433**, Beuth Verlag, Berlin and Köln, 1992.
3. ALONSO M. C. *et al.* Relation between resistivity and corrosion rate of reinforcement in carbonated mortar made with several cement types. *Cem. Concr. Res.*, 1988, **8**, 687-698.
4. POLDER R. B. *et al.* Laboratory investigations of concrete resistivity and corrosion rate of reinforcement in atmospheric conditions. *Proc. CSIRO/RILEM Int. Conf. on Rehabilitation of Concrete Structures, Melbourne* (ed. D. W. S. Ho and F. G. Collins), 1992, pp. 475-486.
5. ARUP H. The mechanisms of the protection of steel by concrete. *Corrosion of reinforcement in concrete construction* (ed. A. P. Crane), Ellis Horwood, Chichester, 1983, pp. 151-158.
6. POLDER R. B. and LARBI J. A. *Investigation of concrete exposed to North Sea water submersion for 16 years*. Report 93-BT-R0619-02, TNO, Delft, to be published.
7. GONZALEZ J. A. *et al.* Corrosion rate of reinforcements during accelerated carbonation of mortar made with different types of cement. *Corrosion of reinforcement in concrete construction* (ed. A. P. Crane), Ellis Horwood, Chichester, 1983, pp. 159-174.
8. ANDRADE C. *et al.* Similarity between atmospheric/underground corrosion and reinforced concrete corrosion. *Corrosion of reinforcement in concrete* (ed. C. L. Page *et al.*), Elsevier, London, 1990, pp. 39-48.
9. HOLDEN W. R. *et al.* The influence of chlorides and sulphates on durability. *Corrosion of reinforcement in concrete construction* (ed. A. P. Crane), Ellis Horwood, Chichester, 1983, pp. 143-150.
10. LARBI J. A. *et al.* The chemistry of pore solution of silica-fume blended Portland cement pastes. *Cem. Concr. Res.*, 1990, **20**, 506-510.
11. LARBI J. A. Microstructure of the interfacial zone around aggregate particles in concrete. *Heron*, 1993, **38**, No. 1, 1-6.
12. SCHIESSL P. and RAUPACH M. Influence of concrete composition and micro-climate on the critical chloride content in concrete. *Corrosion of reinforcement in concrete* (ed. C. L. Page *et al.*), Elsevier, London, 1990, pp. 49-58.
13. SALVAREZZA R. C. *et al.* The electrodisolution and passivation of mild steel in alkaline sulphide solutions. *Corros. Sci.*, 1982, **22**, No. 9, 815-829.
14. ANGUS M. J. and GLASSER F. P. The chemical environment in cement matrices. *Mater. Res. Soc. Symp. Proc.*, 1986, **50**, 547-556.
15. PREECE C. M. *et al.* The influence of cement type on the electrochemical behaviour of steel in concrete. *Corrosion of reinforcement in concrete construction* (ed. A. Crane), Ellis Horwood, Chichester, 1983.
16. CAO H. T. *et al.* Corrosion characteristics of steel in blast furnace slag-Portland cement blends. *Proc. 9th Int. Congr. on the Chemistry of Cements, 1992*, pp. 309-315.
17. TORII K. *et al.* Carbonation and steel corrosion in concretes containing mineral admixtures under different environments. To be presented at Int. Conf. on Corrosion and Corrosion Protection of Steel in Concrete, Sheffield, July 1994.
18. PARROTT L. J. A study of carbonation-induced corrosion. *Mag. Concr. Res.*, 1993, **45**, No. 165, Dec.
19. MACPHEE D. E. *et al.* Corrosion characteristics of iron in BFS-OPC pastes. *Proc. Meeting on the Chemistry and Microstructure of Cements and Concretes, Aberdeen, 1993*. The Institute of Materials, London.
20. HANSSON C. M. Comments on electrochemical measurements of the rate of corrosion of steel in concrete. *Cem. Concr. Res.*, 1984, **14**, 574-584.
21. LUKE K. and GLASSER F. P. Selective dissolution of hydrated blast furnace slags. *Cem. Concr. Res.*, 1987, **17**, 273-282.
22. KONDO R. and OSHAWA S. Studies on a method to determine the amount of granulated blastfurnace slag and the rate of hydration of slag in cements. *Proc. Int. Congr. on the Chemistry of Cements, Tokyo, 1968*, **5**.
23. NAISH C. C. *et al.* *The anaerobic corrosion of carbon steel in concrete*. Nirex report NSS/R273, 1990.