Reuse of coal mining waste to lengthen the service life of cementitious matrices

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Abstract

A chloride-induced accelerated corrosion test was conducted on steel bars embedded in mortar specimens prepared with thermally activated coal mining waste (ACMW). ACMW was observed to prompt two opposite effects: a delay in chloride ion penetration and a reduction in the critical chloride content needed to initiate corrosion. Service life predictions based on the findings revealed that adding 20 % or 50 % ACMW to cement improved reinforcement corrosion resistance. Optimal results were observed for 20 % replacement, in which the mean reinforcement section loss was 21 % lower than in OPC.

Keywords

Coal mining waste, blended cement, corrosion, chloride resistance, service life, corrosion rate

1. Introduction

The use of supplementary cementitious materials (SCMs) is indisputably one of the most efficient and widespread methods for reducing the cement industry's environmental footprint. Nonetheless, worldwide demand for cement has risen exponentially in recent decades, whilst the availability of conventional SCMs such as blast furnace slag and fly ash is expected to

decline [1]. That would generate a need for alternative SCMs, including burnt, especially metakaolin-like, clay (in turn the result of heating kaolinite clays), which have become an option of interest given their general availability and good pozzolanicity [2,3]. Unfortunately, however, the severe environmental impact and higher cost of exploiting natural kaolinite deposits than other SCMs [4] lessen cement manufacturers' propensity to use the material. New lines of research undertaken in recent years to address these drawbacks focus on the pursuit of alternative sources of kaolinitic materials. In keeping with cement industry practice, particular attention has been lent to the reuse of industrial by-products, which are both environmentally beneficial and cost-effective. Against that backdrop, industrial waste such as paper sludge [5], coal mining waste [6–8] and sewage sludge [9] has been proposed as a raw material for recycled metakaolinite.

The millions of tonnes of clayey waste generated yearly by coal mining are presently stockpiled in spoil heaps, with serious detriment to air quality, soils, surface and groundwater, deteriorating the landscape and reducing biodiversity in the surrounds [10–13]. Given the huge volumes involved, valorising such by-products in the cement industry is an approach well worth exploring for the enormous environmental, economic and social benefits involved. Earlier studies, many conducted by some of the present authors, verified that if thermally treated this waste constitutes an excellent supplementary cementitious material, in terms of both pozzolanicity and the physical and mechanical performance of blended cement matrices [8,13–20].

Significant gaps nonetheless persist in the scientific understanding of the durability of these new eco-efficient binary cements. One of the most common causes of reinforced concrete decay is reinforcement corrosion induced by chloride ion penetration in the matrix [21,22]. The passivated layer forming on the surface of steel bars thanks to the highly alkaline pore solution in concrete protects them from corrosion. This protective layer may be destroyed in

the presence of a certain threshold chloride ion content, however, raising steel susceptibility to corrosion [23–25]. A study recently conducted by the authors showed that blended mortars prepared with activated carbon waste exhibit higher resistance to chloride penetration than OPC [26]. That notwithstanding, whilst low infiltration rates in the cementitious binder are imperative to preventing chloride-induced corrosion, adding SCMs entails significant physical and chemical changes in the concrete interfacing with the steel that may affect corrosion behaviour in the latter [27]. The impact of additions on reinforcement corrosion must therefore be determined for a full understanding of how the presence of chlorides affects blended cement matrix behaviour.

The effect of adding activated carbon waste on reinforcement corrosion was studied here by performing accelerated chloride-induced corrosion tests. Corrosion onset times and the amount of chlorides needed to initiate the process in the samples studied were calculated. The method was applied to blended mortar specimens with replacement ratios of up to 50 % by binder weight. The findings were used in service life studies of each type of mortar analysed.

2. Materials and methods

2.1. Materials

The chemical composition of the coal mining waste (CMW) used in this study furnished by Socied Anónima Vasco-Leonesa from an open-pit mine in the Spanish province of Leon is given in Table 1. Its mineralogical composition, identified by X-ray diffraction and quantified with Rietveld refinement [19,28], included quartz (37 %), mica (25 %), calcite (17 %), kaolinite (15 %), dolomite (5 %) and feldspar (2 %). This kaolinite-base waste was milled in a ball grinder to a particle size of under 90 µm prior to its conversion to a metakaolinitic pozzolan by kiln heating at the optimal conditions, i.e. 600 °C for 2 h [8]. The chemical composition of the resulting activated coal mining waste (ACMW) is also given in Table 1.

The blended cements were prepared using a CEM I 52.5 R ordinary portland cement (OPC) furnished by Italcementi Group, which had the chemical composition listed in Table 1. The two materials were blended in an automatic mixer to ensure uniformity. Three blended cements were prepared, replacing OPC with ACMW at ratios of 10 % (ACMW10), 20 % (ACMW20) and 50 % (ACMW50).

A water-reducing admixture added to the blended cements to obtain materials with a slump similar to that exhibited by the OPC mortar, Sikament-FF, was supplied by SIKA (Madrid, Spain). The aggregate used was standardised sand with a maximum particle size of 2 mm and a minimum silica content of 98 %.

2.2. Methods

2.2.1 Specimen preparation

The mortar specimens were prepared as specified in European standard EN 196-1 [29], with a water/binder ratio of 0.5. The water-reducing admixture used was added during mixing at 0.4 % for ACMW10, 0.8 % for ACMW20 and 1.3 % for ACMW50 by binder weight.

2.2.2. Integral accelerated test

The ‘integral’ accelerated method set out in Spanish standard UNE 83992-2:2012 EX [30] was used to test the bars for corrosion. Further to those guidelines, one 6 mm diameter ribbed B500 SD bar each was embedded transversally in the centres of the six 7 cm cubic specimens prepared per type of mortar. The bars, approximately 9 cm long, were pre-treated with an acid solution to ensure a clean surface. The length of the bars in contact with the mortar was limited to ~5 cm by wrapping the rest in insulating tape (Figure 1).

A tank containing 0.6 M NaCl and 0.4 M CuCl₂ was set on top (one of the sides parallel to the longitudinal axis of the bar) of the humidity chamber-cured specimens (98 % RH for 28 d). A copper electrode in the solution was connected to the negative pole of a power source. The

anode was a steel grid lying under the bottom of the specimen, connected to the positive pole of the source and to the specimen across a wet sponge. The system was stored on a plastic grid in a basin with distilled water to keep the sponge constantly moist. A 12 V current was applied to induce chloride ion migration through the specimen. The source was periodically disconnected, allowing the system to lie at rest for 30 min for full depolarisation. The specimens were then set in a Faraday shield and connected to an electrochemical cell with three electrodes: a reference Ag/AgCl electrode in the chloride ion solution, a working electrode connected to the steel bar and an auxiliary electrode connected to the bottom grid. The daily corrosion potential (E_{corr}) of the bar relative to the Ag/AgCl electrode was recorded on an Autolab PGSTAT204 potentiostat, while electrical (R_e) and polarisation resistance (R_p) were found using the linear polarisation technique [31]. The corrosion rate (I_{corr}), expressed in $\mu\text{A}/\text{cm}^2$, was subsequently calculated with Equation 1:

$$I_{corr} = \frac{B}{R_p \cdot A} \quad (1)$$

where B is the proportionality constant determined from the Tafel slopes and A the geometric area of attack. Here the value of B was taken as 26 mV [32] and the mean exposed bar area was 9.15 cm^2 .

The electrical field was applied until I_{corr} exceeded $0.1\text{--}0.2 \mu\text{A}/\text{cm}^2$, the value deemed to denote corrosion onset [31]. The power source was then disconnected, although the electrochemical parameters continued to be measured until they stabilised.

The specimens were subsequently split vertically in two along the plane containing the steel bar. One of the resulting fragments was coated with an AgNO_3 solution to visualise the chloride penetration front. Mortar samples at the interface with the steel bar were extracted from the other fragment.

2.2.3. Determination of total chloride content

The total chloride concentration in the accelerated corrosion-tested mortar samples was found as specified in European standard EN 14629 [33], drying the ground samples for 24 h at 40 °C and extracting the chloride ions by nitric acid digestion. The content was determined by titration with 0.05 M AgNO₃ using a Mehtrom 888 Titrand potentiometric titrator.

3. Results and discussion

3.1. Integral accelerated test

3.1.1. Variations in I_{corr} and corrosion onset time

The corrosion rate (I_{corr}) values for the six OPC mortars during application of the electrical field are shown in Figure 2a) and after disconnection from the power source in Figure 2b). At time=0, specimens OPC-1 and OPC-3 exceeded the 0.1-0.2 $\mu\text{A}/\text{cm}^2$ threshold for reinforcement depassivation. The steel bar in OPC-1 repassivated after the electrical field was disconnected, however, and when reconnected exhibited behaviour similar to that of the other samples. In contrast, the steel in specimen OPC-3 remained anomalously active throughout the experiment.

The other four OPC specimens behaved non-uniformly, with corrosion onset times of 150 h to 300 h of exposure to the electrical field. The I_{corr} values also fluctuated widely over time, with some samples having to be reconnected to the power source after exceeding the threshold value to prevent steel repassivation. Although the corrosion rate values observed after depassivation (Figure 2b)) covered a broad spectrum, they sufficed to verify stability.

The ACMW10 specimens followed a more uniform pattern (Figure 3), excepting sample ACMW10-1, in which a longer connection time and several connect-disconnect cycles were required to reach permanent depassivation. The permanent I_{corr} value observed for this specimen ranged from 3.5 $\mu\text{A}/\text{cm}^2$ to 7.5 $\mu\text{A}/\text{cm}^2$, which was much higher than the $<1 \mu\text{A}/\text{cm}^2$ generally recorded for the other samples. Corrosion onset was nearly identical in all the ACMW20 specimens (Figure 4), after approximately 200 h of exposure to the electrical field.

The effect of adding ACMW to the mortars was only clearly visible in the specimens with 50 % replacement. As Figure 5 shows, corrosion onset was substantially delayed in these specimens, with the exception of ACMW50-5, which exhibited anomalous behaviour. The reinforcement in one of the specimens, ACMW50-6, remained passivated throughout the experiment, with a corrosion rate far below the corrosion threshold.

In light of the scatter observed in the findings, in this study the parameters were calculated for a conservative 10 % likelihood of corrosion. The corrosion onset times calculated for each series of specimens at 10 % and 50 % probability are given in Table 2. Adding ACMW delayed corrosion onset, although no clear pattern could be ascertained for 50 % probability, possibly due to the wide scatter in the data. At 10 % likelihood, however, onset delay was clearly longer with rising ACMW content. These findings were consistent with those observed in similar studies with different types of blended cements, where corrosion onset was perceptibly retarded [31,34–38]. More specifically, the partial replacement of cement with metakaolin has been observed to lengthen the time to reinforcement depassivation [39–41]. That behaviour has generally been attributed to two factors: i) the refinement of the microstructure attendant upon the pozzolanic reaction; and ii) higher chloride binding capacity [42–44]. Recent research conducted by the present authors showed that chloride ion diffusion in mortars prepared with cements containing ACMW declined with rising cement replacement ratios. Those findings are consistent with the earlier results on longer onset times. Moreover, such behaviour was indeed proven to be induced by the change in the pore network and by the Friedel's salt forming in the reaction between chloride ions and the large store of hydrated aluminate phases present in the system [26].

3.1.2. Chloride penetration front and reinforcement corrosion

Figure 6 shows the chloride fronts in representative samples of each mortar type revealed by applying silver nitrate to the fracture surface of the specimens. At onset in the OPC samples,

the chloride ions had already penetrated the entire section of the specimen. In contrast, the chloride front was clearly visible in the specimens containing the pozzolan. In the ACMW10 samples, the front extended slightly beyond the position of the embedded steel, whereas for higher percentages (ACMW20 and ACMW50) the ions touched the steel surface locally only. These findings were consistent with the chloride diffusion resistance behaviour observed in the aforementioned studies [26], further to which chloride ions are more readily transported in OPC mortars.

The steel bars extracted from the mortar upon conclusion of the experiment showed clear signs of pitting (Figure 7). The samples that exceeded the I_{corr} threshold at time=0 (OPC-3 and ACMW50-5) showed no sign of corrosion on the exposed surface of the steel, nor did the chloride penetration front reach the steel in those specimens.

3.1.3. Critical chloride content

The critical chloride content (Cl_{crit}), also known as the chloride threshold, is defined as the minimum concentration of chloride ions required near the reinforcement surface to depassivate the steel, inducing corrosion [42]. In this study, Cl_{crit} was taken as the total chloride ion content in the mortar samples extracted from the mortar-steel interface upon conclusion of the accelerated corrosion test. The values recorded are given in Table 3 together with the critical chloride concentration calculated for each mortar type at 50 % and 10 % probability of corrosion. The specimens exhibiting anomalous behaviour were disregarded in these calculations.

The distribution of the critical chloride values for each mortar type are plotted against the ACMW content in Figure 8. Despite the scanty uniform data distribution, the inclusion of ACMW clearly lowered the chloride threshold value, particularly at a replacement ratio of 50 %. Those findings were consistent with the behaviour depicted in Figure 6 , showing the

chloride front in specimens where corrosion was already under way, triggered in mortars ACMW20 and ACMW50, apparently, as soon as the front reached the reinforcement depth.

As noted earlier, ACMW blended matrices have been shown to bind chloride ions by forming Friedel's salt [26], thereby reducing the amount of free chloride ions in the system and with it the risk of corrosion [22,42]. The inference would initially be that the chloride threshold, expressed as total chloride concentration, would be higher with ACMW. The effect of pozzolanic additions on critical chloride content is still debated, however. Whilst some mineral additions foster chloride capture, thereby raising Cl_{crit} , the store of calcium hydroxide in cements with pozzolanic additions tends to be wholly or partially consumed, lowering pore solution alkalinity and system buffering capacity, which is known to reduce the chloride threshold [45–47]. Moreover, Friedel's salt may be unstable if pH declines, releasing chlorides into the pore solution and contributing to further lower the chloride concentration required to depassivate steel [42,48]. As a result, the inclusion of mineral additions has often been reported in the literature [38,46,49–52] to induce substantial declines in critical chloride content.

The results of the accelerated corrosion test at 10 % probability are summarised in Figure 9. These data suggest that adding ACMW induced two opposite effects on chloride resistance in mortars containing blended cements: i) a reduction of material permeability to chlorides; and ii) a decline in the chloride concentration needed at the mortar-reinforcement interface to initiate corrosion. On the sole grounds of those data, firm conclusions can scarcely be drawn about the impact of ACMW in preventing corrosion in this type of cement matrices. Rather, service life predictions are needed to conclusively address the issue.

3.2. Service life prediction

The service life of the material studied was calculated in accordance with the model proposed by Tuutti [53,54]. Further to that procedure, the process was divided into two stages: i)

initiation, or the time required to initiate the destruction of the passivated layer around the reinforcement; and ii) propagation, when corrosion proceeds actively [40,55]. As this study was designed for a marine environment, a 4 cm steel cover was entered in the model pursuant to the requirement for type IIIc exposure set out in Spain's structural concrete code EHE-08 [56]. The surface chloride concentration used was 2.67 % by cement weight, in keeping with similar studies conducted by Markeset [57]. The model was run for a 100 year period.

3.2.1. Initiation

The initiation period was determined by the rate at which chloride ions penetrating the system to the depth of the steel reached the threshold chloride concentration. The first stage was consequently modelled on the grounds of Fick's second law, which, using the error function and assuming a semi-infinite medium, can be solved as in Equation 2 [58]:

$$C_{x,t} = C_0 + (C_s - C_0) \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2)$$

where $C_{x,t}$ is the chloride concentration at depth x and time t , D is the diffusion coefficient for the material, C_s is the chloride concentration on the surface and C_0 in the starting material. Parameters C_s and D were assumed to be time-constant, whilst concentration C_0 was deemed to be negligible.

The diffusion coefficients for the mortars studied, determined in earlier research [26], are listed in Table 4. Entering those values into Equation 2 yielded the chloride content over time at a given depth and a known surface concentration. The variation in chloride content over time at a depth of 4 cm is shown in Figure 10 for all the mortars studied.

The initiation period start time (t_i) was found by entering the critical chloride content values found with the accelerated corrosion test into the equations defining the curves in Figure 10. According to the results given in Table 4, initiation was clearly retarded in the ACMW20

mortars, whilst the AMCW50 mortars exhibited behaviour not significantly different from the OPC materials. In contrast, steel depassivation began earlier in the ACMW10 than in the OPC specimens.

3.2.2. Propagation period

Propagation is defined as progressive corrosion-mediated section loss in the reinforcement. Steel corrosion over time can be described by Equation 3 [59]:

$$P_{corr} = \alpha \cdot 0.0116 \int_0^t I_{corr}(t) dt \quad (3)$$

where P_{corr} is corrosion depth in mm and α the pitting factor, which represents the non-uniformity of damage to the reinforcement during corrosion. Since chloride-induced corrosion leads to local deterioration in steel, as shown in Figure 7, high α values are routinely used in such situations. In this study, a pitting factor of 10 was applied [60]. The function describing the variation in corrosion rate over time is required to calculate corrosion penetration, however.

Figure 11 plots the critical chloride content found for the accelerated corrosion-tested samples against the mean I_{corr} value for those samples after the electrical field was disconnected. According to Alonso et al. [61], the relationship between the log of I_{corr} and the log of Cl_{crit} is linear. As Figure 11 shows, the values for each mortar were not distributed in any specific pattern, in all likelihood due to the small volume of data. Nonetheless, when the results were assumed to constitute a single population, they followed a perceptibly linear upward trend. The data (at 50 % probability) were fitted to Equation 4:

$$\log I_{corr} = -0.861 + 0.625 \log Cl_{crit} \quad (4)$$

An analogous expression was calculated for 10 % probability of corrosion. Here also, the data for the samples with anomalous behaviours were excluded.

Inasmuch as chloride concentration over time was determined for each mortar using Fick's law, combining Equations 2 and 4 would give an expression describing the variation in corrosion rate over time after steel depassivation. P_{corr} could consequently be calculated from Equation 3. Corrosion penetration progress so estimated for each mortar is plotted in Figure 12. Further to those findings, the rate of steel bar deterioration clearly declined with rising ACMW concentration, as shown by the slopes on the curves in the figure. The loss of reinforcement diameter calculated for each type of mortar after 100 yr of exposure given by way of example in Table 5 shows that steel corrosion was from 13% to 21 % lower in ACMW20 and ACMW50 than in OPC. That notwithstanding, the overall behaviour exhibited by the ACMW20 mortars was deemed to be optimal, for they protected the steel more effectively at early ages due to their higher chloride threshold.

4. Conclusions

The following conclusions may be drawn from the results presented in this paper.

1. The accelerated corrosion test showed that adding ACMW induced a decline in the critical chloride content, a finding attributable to the reduction in the store of alkalis resulting from the pozzolanic reaction. The specimens with the highest ACMW content exhibited chloride threshold values up to 90 % lower than found in the OPC specimens.
2. At the same time, ACMW was experimentally shown to induce a general rise in corrosion onset time, which was more visible at higher replacement ratios. The explanation lay in the lower chloride diffusion coefficients in blended cement mortars and the concomitantly higher resistance to chloride ion penetration.
3. According to the Tuutti service life model, corrosion onset was retarded in the samples with a high ACMW content, especially in ACMW20. The corrosion propagation rate

also declined with rising amounts of ACMW, with 13 % to 21 % lesser reinforcement section loss in the mortars with the higher replacement ratios.

In short, the use of ACMW as an SCM at moderate or high replacement ratios has a generally beneficial impact on resistance to chloride ion-mediated corrosion. Inasmuch as the inclusion of ACMW at a replacement ratio of 50 % lowers the critical chloride content substantially, the ACMW20 mortars are deemed to exhibit the optimal overall behaviour.

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Figure captions

Figure 1. Experimental procedure used for the accelerated corrosion test

Figure 2. Corrosion rate in reinforcement embedded in OPC: a) during exposure to an electrical field; b) after disconnection from the power source

Figure 3. Corrosion rate in reinforcement embedded in ACMW10 specimens: a) during exposure to an electrical field; b) after disconnection from the power source

Figure 4. Corrosion rate in reinforcement embedded in ACMW20 specimens: a) during exposure to an electrical field; b) after disconnection from the power source

Figure 5. Corrosion rate in reinforcement embedded in ACMW50 specimens: a) during exposure to an electrical field; b) after disconnection from the power source

Figure 6. Chloride penetration front (yellow dashes) relative to the embedded steel rebar (dotted red line) revealed by silver nitrate coating in samples a) OPC; b) ACMW10; c) ACMW20; d) ACMW50

Figure 7. Steel bar corrosion in mortars a) OPC, b) ACMW10, c) ACMW20; d) ACMW50

Figure 8. Box diagram of critical chloride content vs ACMW content

Figure 9. Variation in corrosion onset time (blue) and critical chloride content (red) versus ACMW content at 10 % probability of corrosion

Figure 10. Variation in chloride ion concentration at a depth of 4 cm in the mortars studied

Figure 11. Corrosion rate (shown on a logarithmic scale) versus critical chloride content

Figure 12. Corrosion propagation over time in mortars a) OPC; b) ACMW10; c) ACMW20; d) ACMW50

Table 1. Chemical composition (wt%) of starting materials

<i>Oxide</i>	<i>CMW</i>	<i>ACMW</i>	<i>OPC</i>
SiO ₂	49.79	56.63	20.80
Al ₂ O ₃	21.77	25.29	5.70
Fe ₂ O ₃	4.07	4.64	2.89
MnO	0.08	0.08	0.03
MgO	0.64	0.77	1.89
CaO	3.84	4.20	58.99
Na ₂ O	0.13	0.17	0.93
SO ₃	0.27	0.27	4.11
K ₂ O	2.74	3.09	1.36
TiO ₂	1.07	1.17	0.15
P ₂ O ₅	0.13	0.14	0.26
LoI ¹	15.18	3.09	2.79

¹ Loss on ignition

Table 2. Corrosion onset times (t_{corr}) for the binders studied, calculated assuming 10 % and 50 % probability of corrosion

Mortar	t_{corr} (h)	
	50 % probability	10 % probability
OPC	235	148
ACMW10	235	179
ACMW20	211	199
ACMW50	352	237

Table 3. Critical chloride content in the samples studied

Mortar	Cl_{crit} (% , cement)							
	<i>Specimen number</i>						50 % <i>probability</i>	10 % <i>probability</i>
	1	2	3	4	5	6		
OPC	2.12	1.29	exc ¹	2.30	1.03	2.85	1.92	0.96
ACMW10	exc ¹	0.81	0.93	0.91	0.21	0.65	0.70	0.32
ACMW20	0.92	2.61	1.09	3.57	0.85	0.91	1.66	0.18
ACMW50	0.32	1.13	0.49	n.d. ²	exc ¹	exc ¹	0.64	0.1

¹ anomalous behaviour, data excluded

² not detected

Table 4. Initiation period start time calculated for the mortars studied

<i>Mortar</i>	<i>D</i> x 10 ⁻¹² (m ² /s)	<i>t_i</i> (years)	
		50% <i>probability</i>	10% <i>probability</i>
OPC	20	9.8	1.5
ACMW10	12	1.7	0.9
ACMW20	4.7	22	1.6
ACMW50	2.7	6.9	2.2

Table 5. 100 yr diameter loss (mm) in reinforcement embedded in the mortars studied

<i>Mortar</i>	<i>P_{corr} (mm)</i>	
	<i>50% probability</i>	<i>10% probability</i>
<i>OPC</i>	7.5	9.9
<i>ACMW10</i>	7.7	9.6
<i>ACMW20</i>	5.9	8.6
<i>ACMW50</i>	6.3	8