The role of metakaolin in the protection of concrete against the deleterious action of chlorides

O papel do metacaulim na proteção dos concretos contra a ação deletéria de cloretos

Abstract

The objective of this study is to evaluate the protective capacity of concretes produced with metakaolin in relation to the transportation and penetration of chlorides. Thus, from a commercial concrete of fck equal to 30 MPa, more two other concretes were produced by replacing 10% of cement by metakaolin, by weight. In one of them, it was kept the same water/binder of the initial reference mix design (w/b = 0.60), and in the other concrete the compressive strength remained fixed. In all three mixes, the same range of concrete consistency was maintained, with a slump equal to (100 + 10) mm. The front of chlorides in the cement matrix was evaluated by spraying a solution of silver nitrate, after an attack of 8 weekly cycles of wetting and drying using a solution containing chlorides. To obtain an indicative of the internal structure of the concretes, it was carried out the test of water absorption by immersion, which permitted an evaluation of the concrete open porosity, as well as it was performed the analysis of concrete samples by means of XRD and SEM. These studies aimed to verify the potential of metakaolin in fixing chlorides in the form of Friedel’s salt, besides providing microstructural analysis of the concretes. It was concluded with this work that the incorporation of metakaolin decreases the diffusivity of chlorides to the extent that this mineral addition produces refinement of the concrete pore structure and also because it induces the formation of Friedel’s salt, which becomes it an effective agent in preventing the corrosion of reinforcement in chloride-rich environments.

Keywords: metakaolin, concrete, chlorides, Friedel’s salt, durability.

Resumo

O objetivo deste trabalho é avaliar a capacidade de proteção de concretos produzidos com metacaulim em relação ao transporte e penetração de cloretos. Para tanto, a partir de um concreto comercial de fck igual a 30 MPa, foram produzidos mais dois concretos substituindo-se 10% da massa de cimento por metacaulim, a saber: em um dos concretos manteve-se a mesma relação água/aglomerante do traço inicial de referência (a/ag = 0.60) e no outro manteve-se fixa a resistência à compressão. Em todas as três dosagens foi mantida a mesma faixa de consistência do concreto, com abatimento igual a (100 + 10) mm. A frente de cloretos na matriz cimentícia foi avaliada por meio da aspiração de solução de nitrate de prata, após ataque de 8 ciclos semanais de molhagem e secação em solução contendo cloretos. Foram, então, realizadas avaliações da porosidade aberta, a partir do ensaio de absorção de água por imersão, para se ter um indicativo da estrutura interna dos concretos, assim como se procederam análises de DRX e MEV em amostras de concreto. Estes estudos objetivaram verificar as potencialidades do metacaulim na fixação de cloretos na forma de sal de Friedel, além de propiciar as análises microestruturais dos concretos. Conclui-se com o trabalho que a incorporação de metacaulim diminui a difusividade de cloretos, na medida em que essa adição mineral produz refinamento da estrutura de poros do concreto e também porque ela induz à formação de sal de Friedel, o que a torna um agente eficaz na prevenção da corrosão das armaduras em ambientes ricos em cloretos.

Palavras-chave: metacaulim, concreto, cloretos, sal de Friedel, durabilidade.
Environmental concerns caused by the extraction of raw materials and CO₂ emissions in the production of Portland cement led to pressures to reduce the consumption of this constituent of concrete, combined with the need to increase its durability [1]. In this context, mineral additions, including metakaolin (MK), become obvious alternatives. This material was first incorporated in concrete in 1962, in the construction of Jupiá dam, in Brazil, being obtained by calcination of clay rich in kaolinite at temperatures between 650°C and 800°C [2]. This is a highly reactive pozzolanic material [3, 4], whose the silico-aluminous mineralogy typically portrays the following constituents and contents: 50%-55% of SiO₂ and 40%-45% of Al₂O₃.

Artkan et al. [5] state that the main advantage in the use of MK in concrete and cement is its high pozzolanic activity, which is the ability to react with Ca(OH)₂ produced during the hydration of Portland cement (PC), forming hydrated calcium silicates and aluminates. Being a very fine material, with 99.9% of particles with size less than 16 µm and an average size of about 3 µm, therefore presenting a high specific surface, metakaolin possesses the ability to accelerate the pozzolanic reaction [6, 7].

The incorporation in the concrete of “superfine” MK particles results in a micro-filler effect, thus improving the packaging of the cement matrix. Thus, the use of MK in cement pastes leads to a refinement of the pore structure [5, 8].

The partial replacement of PC by MK increases compressive strength of the concrete. Li and Ding [9] observed that the maximum strength gain happens for a replacement of 10%. Kim et al. [10], in turn, detected that the improvement in the mechanical properties did not vary much for MK rates between 10% and 15%, but had a decrease in resistance for MK rate of 20% or higher, which indicates that there is an optimal replacement range. In the referred work, the authors concluded that the best replacement rate was 10%, in order to obtain a good relation between the cost of metakaolin and the performance improvement achieved. Additional information on optimum levels of substitution is conveyed by Oliveira and CASCUDO [11], and Galvão and CASCUDO [12].

According to these authors, the optimal content of a mineral admixture to be used in concrete (in replacement to the cement) is defined by its fineness, so that the finer the material, the lower is its optimal content. According to the cited studies, the optimum levels of different metakaolins varied in a range of 8% to 20%, and the fineness of the MK was the key feature towards the determination of optimal rate.

Regarding the durability of structures, the entry of chlorides in concrete, which brings as a consequence the serious problems of corrosion of steel reinforcement, occurs essentially by three transport mechanisms: absorption, permeability and diffusion, occurring solely or in combination [13-17]. There is still a fourth mechanism of transport, the ionic migration [13, 14, 18-20], motivated by applied external electric fields, however this mechanism is rather unlikely in service situations, but it is present on accelerated methods of chloride penetration or to determine the apparent diffusion coefficient in migration tests [21].

Diffusion is then considered as the main transport process of chlorides through the concrete. According to Fick’s laws, the rate of diffusion is proportional to the concentration gradient and inversely proportional to the diffusion coefficient. The diffusion of chlorides through the concrete mainly depends on the microstructure of the concrete or mortar and on the fixing ability of these ions, and this is one factor that substantially reduces the rate of chloride transport [26-28]. For mixtures in which the binder is ordinary Portland cement, the main chloride binding mechanism is Friedel’s salt formation as well as that of the aluminate compunds [29]. The PC anhydrous compound that is faster to react chemically with chlorides is tricalcium aluminate (C₃A). The product of this reaction is known as Friedel’s salt (Fs) and its chemical formula is: 3CaO.Al₂O₃.CaCl₂.10H₂O. Thus, a PC with a higher content of C₃A is recommended to ensure the integrity of the steel of reinforced concrete exposed to environments rich in chlorides [30].

In mixtures with supplementary cementitious materials such as MK, it is believed that the binding capacity is a function of the content of aluminates [28]. A recent study by Talero et al. [30] demonstrated that Friedel’s salt formation in mixtures of PC and pozzolan is mainly related to the content of reactive alumina in each pozzolan. It has been shown that the rate of Fs formation due to the presence of reactive alumina is much greater than that relating to C₃A, thereby enabling rapid formation of Fs in the first case, and slow formation of Fs resulting from the cement C₃A. Along this line, Bothe et al. [31] have prepared a series of pastes containing Friedel’s salt in equilibrium with other compounds including Al(OH)₃, Ca(OH)₂ and 3CaO.Al₂O₃.6H₂O. The solid phase extracted from one of the preparations and analyzed by X-ray diffraction revealed a pure Cl-AFm phase as shown in the diffractogram in Figure 1.
1. These authors then concluded that the formation of Friedel’s salt in presence of C₃AH₆ acts as a binding agent of the chlorides excess, thus corroborating the various studies cited.

Besides the chemical action of chloride binding as Friedel’s salt, MK also produces a physical protection mechanism, since it contributes to the refinement of the pores of the concrete hardened cement paste. With the refinement, the pores become less interconnected and more tortuous, which makes the penetration of chlorides more difficult [21]. This is reflected in considerable gains in terms of performance against reinforcement corrosion [32].

In this scenario, the goal of this work is to improve understanding of the overall mechanism of protection provided by the presence of MK in concrete, with respect to the action of chlorides. This objective can be divided into stages, beginning with a review of the role of MK in the Cl⁻ penetration, passing through an assessment of the internal structure of concrete with MK, and finally, verifying the binding mechanism of chlorides in the form of Friedel’s salt.

It is also an aim of this work to analyze the effect of the presence of MK in concretes in the same range of strength, checking how the reduction of binder and the increase of water/binder ratio, compensated by the presence of MK, interfere with durability parameters associated with chlorides.

2. Materials and experimental program

To evaluate the effect of the presence of metakaolin in concrete regarding the action of chlorides, an experimental program involving the conception of three different concrete mixes was elaborated. In addition to the reference concrete, two other mixtures were prepared by replacing 10% of cement by metakaolin. In one of them, it was performed an increasing in the water/binder ratio (w/b) in order to achieve mechanical strength similar to that of the reference mixture, enabling considerations in terms of the effect of porosity in the progression of chlorides into the cementitious matrix (analysis of mixtures at the same strength level). In another mixture, the same w/b ratio of the reference concrete was maintained, which means a level of strength higher to the concrete with metakaolin.

2.1 Materials

2.1.1 Cement

The Portland cement used was a Brazilian standardized cement, CP V ARI-RS, characterized by giving a high resistance in the early stages of concrete curing and by possessing sulfate resistance. Chemical and physical characterization of the cement is shown in Tables 1 and 2.

2.1.2 Metakaolin

A highly reactive metakaolin (MK) produced by the company Metacaulim do Brasil Indústria e Comércio Ltda. was used. This material is characterized by containing a high alumina content, as well as by having a high particle fineness and a high specific surface, as can be seen in Tables 1-3.

### Table 1 – Chemical characterizations of cement and metakaolin obtained by X-ray fluorescence (XRF)

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Cement CP V-ARI RS (%)</th>
<th>Metakaolin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>26.24</td>
<td>57.81</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.57</td>
<td>34.97</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.58</td>
<td>1.72</td>
</tr>
<tr>
<td>CaO</td>
<td>47.98</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>5.63</td>
<td>0.54</td>
</tr>
<tr>
<td>SO₃</td>
<td>5.30</td>
<td>0.03</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>1.36</td>
<td>1.88</td>
</tr>
</tbody>
</table>

### Table 2 – Physical characteristics and pozzolanic activity of binders used

<table>
<thead>
<tr>
<th></th>
<th>Cement CP V-ARI RS</th>
<th>Metakaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>3.11</td>
<td>2.57</td>
</tr>
<tr>
<td>Specific surface area (m²/kg)</td>
<td>411 (Blaine)²</td>
<td>19 430 (BET)</td>
</tr>
<tr>
<td>Chapelle modified</td>
<td>–</td>
<td>907 mg Ca(OH)₂/g</td>
</tr>
</tbody>
</table>

1. ABNT NBR NM 23: 2001 (Cimento Portland e outros materiais em pó – Determinação da massa específica);
2. ABNT NBR NM 76: 1998 (Cimento Portland – Determinação da finura pelo método de permeabilidade ao ar);

### Table 3 – Physical properties of MK and recommended limits

<table>
<thead>
<tr>
<th></th>
<th>Determined value</th>
<th>Limits of NBR 15894 (33)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineness¹ (residue at # 45 µm)</td>
<td>6.5%</td>
<td>&lt; 10.0%</td>
</tr>
<tr>
<td>Specific gravity² (kg/dm³) – SG</td>
<td>2.57</td>
<td>–</td>
</tr>
<tr>
<td>Apparent density (kg/dm³) – AD</td>
<td>0.62</td>
<td>–</td>
</tr>
</tbody>
</table>

1. ABNT NBR 15894-3: 2010 (Metacaulim para uso com cimento Portland em concreto, argamassa e pasta – Parte 3: determinação da finura por meio do peneira 45 µm);
2.1.3 Aggregates

Table 4 presents the main characteristics of the used aggregates. Figure 2 displays particle size distribution curves for a better view of the distribution of aggregates in the mixtures carried out.

2.1.4 Plasticizer and superplasticizer admixtures

To keep the slump (obtained by the Abrams cone) within the defined values, it was used a plasticizer admixture of delayed setting (PR), which performed as a strength accelerator, due to its high capacity in reducing the water of concrete (Sikament® 815). Another admixture, a superplasticizer based on polycarboxylate - N SP-II (Sika ViscoCret® 6500), was also employed in order to disperse the MK before inclusion in the mixture, thus obtaining a homogeneous mixture. The characteristics of density and pH of the admixtures used are shown in Table 5.

2.1.5 Studied concretes

The reference concrete used was obtained using a commercial mix proportion usually produced by a ready mix concrete company in the city of Goiania, in Brazil. This concrete mix was formulated by the method of concrete mix design of IPT-EPUSP-IBRACON [34]. The base or reference formulation (Mref) was a concrete of fck = 30 MPa, with w/c ratio = 0.60 and slump equal to (100 ± 20) mm. From this base concrete, two new formulations were obtained. The first (M1) just replacing 10% of cement by MK, in mass, and keeping the same w/b ratio of Mref; and the second (M2) by replacing 10% of cement by MK, in mass, but increasing the w/b ratio in order to maintain the compressive strength of the concrete with MK similar to that of the reference concrete. Details of the concrete mixtures are shown in Table 6.

For the experimental study, cylindrical test specimens of 10 cm in diameter and 20 cm in height were prepared. 24 hours after casting, these cylindrical test specimens were de-molded, identified and placed in tanks filled with lime saturated water, according to ABNT NBR 9479: 2006 [35]. The test specimens remained under these conditions for 27 days, totaling thus 28 days of moist cure, except for the case of specimens tested at 7 days, which were removed from the curing tank at this age, a few hours before testing.

2.2 Methods employed

An experimental campaign was carried out in order to obtain...
data on the behaviour of concrete with metakaolin in the presence of chlorides and also to assess the influence of the chosen pozzolan on the mechanical performance of concrete. Except for the compressive strength test, all other analyses were performed after the age of 90 days. Between 28 and 90 days, the test specimens were stored in a laboratory environment, protected from solar irradiation, wind and outdoor humidity. For other testing procedures, X-ray diffraction (XRD) and scanning electron microscopy (SEM), 4 test specimens were reserved, by type of concrete. Of this total, 2 test specimens were submitted to chloride attack and 2 were not attacked, so that samples for these two tests (XRD and SEM) were obtained from these test specimens. In the microscopy analysis, samples were obtained by two different ways: by breaking or by cutting. In the first case, the samples were approximately reduced to cubes with 1 cm sides, taking care to preserve the fractured face (effective face for analysis on which the electron beam was focused); in the second case, when element mapping was performed (as commented below, in subsection 2.2.4), the samples were cut (with the same previous size), and then impregnated and polished for the analysis of concrete cover profile. In the XRD analyses, the samples were extracted in a similar way to that performed for microscopy, but at the end they were ground, so that the analysis could be done with the samples in powder form.

2.2.1 Compressive strength

Compressive strength tests were conducted at ages 7, 28 and 90 days, using three cylindrical test specimens of each studied situation in terms of axial compression, following the procedure of standard ABNT NBR 5739: 2007 [36].

2.2.2 Chloride attack

After 90 days of an initial standardized cure, as previously described, a chloride attack was undertaken in the three series of concrete under study. Two test specimens in total were designated by type of concrete for that attack, with subsequent analysis of the front of chlorides (section 2.2.5) and mineralogical and internal structure evaluation (post attack), by X-ray diffraction and scanning electron microscopy (sections 2.2.3 and 2.2.4). This attack consisted in submitting the test specimens to the contact with a solution of sodium chloride 10% (by weight), by performing 8 weekly cycles of wetting and drying (cycles consisting of 3 days of immersion, followed by 4 days of air drying in a laboratory environment whose relative humidity ranged from 10% to 30% during the test).

2.2.3 X-ray diffraction (XRD)

From the cylindrical test specimens, as previously mentioned, smaller samples were cut, which were subsequently sprayed with care to separate the coarse aggregate from the mortar of concrete samples. These samples were then analyzed in the Philips X-Pert Pro X-ray diffractometer, in the Materials Laboratory of the Department of Geosciences, and in the Rigaku PMG-VH X-ray diffractometer (with radiation CuKα = 1.5405 Å), in the XRD Laboratory of the Department of Ceramics and Glass Engineering, both at the University of Aveiro in Portugal. This technique was performed to detect the presence of Friedel’s salt, besides the expected products of cement hydration.

2.2.4 Scanning electron microscopy (SEM)

Fractured and cut samples were observed. The cut samples were impregnated with Araldite® epoxy resin and were subsequently polished to expose a regular surface, allowing the mapping of elements. In this case, the images were produced employing back-scattered electrons (BSE) detectors. The fractured samples, assessed by signs of secondary electrons (SE), were analyzed in LABMIC/UFG - Brazil (Multisuser Laboratory for High-Resolution Microscopy, at the Federal University of Goiás), by means of a JSM - 6610 scanning electron microscope, from JEOL brand, equipped with EDS, model NSS Spectral Imaging, from Thermo Scientific brand. The polished samples were analyzed at the Department of Ceramics and Glass Engineering, in the Microscopy Laboratory (at the University of Aveiro – Portugal), using a Hitachi SU-70 scanning electron microscope. In both analyses by SEM, 3 samples were fixed in each sample holder (one sample of each type of concrete). As there were 2 test specimens per type of concrete (attacked or not attacked), there were always 6 samples analyzed by SEM by type of concrete, both for fractured samples and for polished samples, and considering concrete attacked by chlorides or not.

2.2.5 Evaluation of the chloride front by means of spraying of silver nitrate indicator

After eight cycles of wetting and drying in a chlorides containing solution (after 90 days of initial curing), the cylindrical test specimens were splits by diametrical compression, according to ABNT NBR 7222: 2010 [37]. On the fractured faces of the test specimens (concrete exposed surface after its rupture), it was sprayed a solution of silver nitrate (0.05 M). The silver nitrate reacts with the chlorides in the concrete forming a whitish/silver compound, as a result.

<table>
<thead>
<tr>
<th>Concrete</th>
<th>Binder (CP + MK) (kg/m³)</th>
<th>Cement (kg/m³)</th>
<th>Mix proportion (by weight) binder:sand:stone</th>
<th>w/b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mref (100% PC)</td>
<td>330.0</td>
<td>330.0</td>
<td>1 : 2.42 : 3.16</td>
<td>0.60</td>
</tr>
<tr>
<td>M1 (90%PC + 10%MK)</td>
<td>327.0</td>
<td>294.3</td>
<td>(0.9:0.1) : 2.44 : 3.18</td>
<td>0.60</td>
</tr>
<tr>
<td>M2 (90%PC + 10%MK)</td>
<td>288.0</td>
<td>259.2</td>
<td>(0.9:0.1) : 2.88 : 3.58</td>
<td>0.68</td>
</tr>
</tbody>
</table>
The role of metakaolin in the protection of concrete against the deleterious action of chlorides

2.2.6 Index of voids (open porosity)

Voids index of samples obtained from the cylinders was measured to give an indication of the porous structure of the different concretes. This test allows evaluating the percentage of open pores, which are the pores that are communicable with the exterior, for the considered sample. Part of the procedures employed in this trial followed the recommendations of ABNT NBR 9778: 2009 [39], and 3 cylindrical test specimens of 10 cm diameter by 20 cm in height were used, at the age of 90 days, for each concrete mix proportion.

\[ \phi = \frac{W_{\text{sat}} - W_{\text{dry}}}{W_{\text{sat}} - W_{\text{sub}}} \times 100 \% \]  

In Equation 1, \( \phi \) represents the index of voids (open porosity), \( W_{\text{sat}} \) is the mass of the sample with saturated pores, \( W_{\text{dry}} \) is the mass of the dry sample and \( W_{\text{sub}} \) is the mass of the submerged sample with saturated pores.

3. Results and discussion

3.1 Compressive strength

Figure 4 shows the average compressive strength values (Rc) at 7, 28 and 90 days. It is confirmed that the mixture with 10\% of replacement of Portland cement by MK and in the same w/b ratio reaches higher strength values than those of the reference mixture (Mref) at all ages. In terms of the M2 mixture, although it does not equal the strength values of Mref, it could achieve similar values. In this way, a concrete in the same strength range, increasing the w/b ratio, was accomplished. This data allows us to evaluate the growth rate of the strength of the various mixtures. In the first seven days, the mixture with greater strength gain, on average, is M1. M2 has a slower increase of strength on account of the binder decrease. In terms of average strength, the concrete with the largest gains in growth is M1 mixture, probably due to the hydration of cement in conjunction with the pozzolanic reactions of MK and also due to the filler effect of this mineral addition, which represents a densifying effect on the concrete microstructure. The M2 mixture has a lower strength growth rate than Mref for the initial time segment, from 7 to 28 days.
days. This rate increases for the period from 28 to 90 days, achieving strength values near those of Mref.

It is clear, from these results, that there is benefit in replacing part of the cement by MK on the mechanical compressive strength, attaining 20% in gains of strength with a substitution of 10%. Increasing the w/b ratio (M2) by decreasing the binder content, it is possible with the addition of MK to achieve a mechanical strength of the same order of magnitude as that of a formulation containing only Portland cement. The projection made for the compressive strength of M2 was similar to that desired, although it resulted in slightly lower values compared to the reference concrete. Considering then small differences in compressive strength between M2 and Mref, the results presented in the following sections may be comparable from the point of view of the properties of concrete in the same strength range as was the intention of this work.

3.2 X-ray diffraction

The following results reflect the two diffraction tests performed in the samples of mixtures under analysis. Initial tests were performed on samples not attacked by chlorides (Mref, M1, M2) and on samples attacked by chlorides, called Mref_Cl, M1_Cl and M2_Cl. In a second phase, a new test of X-ray diffraction was performed, assessing this time only the outer part of the samples taken from cylindrical test specimens. This analysis aimed at obtaining a more defined peak of Friedel’s salt, allowing thus to relate and to compare the intensities of this peak among the 3 attacked samples. This would enable the determination of the role of MK as a potentiating agent (or not) in the formation of Friedel’s salt. From literature, according to Bothe et al. [31] and Balonis et al. [40], it is known that the most intense Friedel’s salt peak is at $2\theta = 11.39^\circ$.

The XRD patterns shown in Figures 5 and 6, corresponding to the first phase of analysis, showed the presence of the main peak of Friedel’s salt (Fs) in the samples attacked by chlorides (in Figure 6, it was limited the $2\theta$ range of variation of up to a maximum of $20^\circ$ for a better visualization of the main peak). Although also present in the sample without MK, the main peak indicative of Fs appears clearly more intense in samples corresponding to M1 and M2 mixtures, with metakaolin. As previously discussed, the precipitation of Friedel’s salt having only Portland cement in the concrete composition is possible but, as shown by Talero et al. [30], its rate of formation as well as the relevance of the precipitated compounds is much lower when compared to systems containing MK. This is a function of the much higher reactivity of the reactive alumina present in MK compared to the cement C3A, which is the phase that effectively reacts with the Cl$^-$ to produce Friedel’s salt. When the chlorides react with the cement aluminates (C$_3$A), Fs precipitates by slow formation and to a lesser extent, while in the reaction between the Cl$^-$ and the reactive alumina of MK, it is produced rapid formation Fs and to a much more significant extent.

In a second analysis, where samples of material from a more peripheral zone of the test specimens were used, therefore more attacked by chlorides, the peaks were even more distinct and prominent for samples with metakaolin, thus confirming the formation of crystalline chloroaluminate complexes (Figure 7). It is worth noting...
mentioning that the XRD technique is semi-quantitative, which means that more intense and sharp peaks give an indication not only of the presence of the compound in analysis (Fs), with greater safety and precision, but also give information of its occurrence in terms of quantity and relevance in the samples analyzed.

It follows, therefore, that the cement replacement by MK promotes the formation of Friedel’s salt in the presence of chlorides. This happens due to the high amount of reactive alumina present in MK, which leads the formation of calcium aluminates, increasing thus the fixation of chlorides. Calcium chloroaluminate is then formed by ionic exchange and replacement of OH- ions by Cl- ions. This result enhances, therefore, one of the important mechanisms of protection provided by metakaolin in concrete, with respect to chloride transport, since these ions chemically fixed in the form of stable compounds precipitated in the cement paste are harmless to reinforcement bars inside the concrete [13, 32].

3.3 Scanning electron microscopy

Mapping of elements was performed to determine the presence of calcium chloroaluminate compounds, as well as to verify the microstructure of the cement paste. EDS spectra were also obtained. In the sample from Mref it was chosen an area (Figure 8), where it was possible to observe a large concentration of Cl together with Al and Ca, which may indicate the formation of hydrated calcium chloroaluminate.

In the samples relating to the mixtures M1 and M2 various NaCl crystals were observed. This may indicate the precipitation of chlorides in this form. In M1 it was not possible to observe the formation of chloroaluminate. In M2, in addition to NaCl crystals, there are Cl concentrations which may indicate some complex formation involving chlorides ions and the elements present in the cementitious matrix.

Mapping of elements in the sample M2 is shown in Figure 9, where it can be verified the occurrence of free chlorine and NaCl. On the images of Figure 9, it can be seen a higher concentration of Cl and Al in the presence of calcium, which may indicate the start of formation of chloroaluminate (there is also certain Na content). A subsequent new mapping was performed in sample M2, as shown in Figure 10, where close to an aggregate it is possible to verify the presence of a high concentration of Cl and Al, which may indicate the formation of chloroaluminate.

Analysis by SEM and EDS spectra indicate chloride ions fixed as Friedel’s salt. The most outstanding evidence of this was found in mix Mref, in which it was found the formation of lamellas comprising Cl, Al and Ca. In other samples, although the same elements as in Mref have not been detected, they were also observed occasional high concentrations of chlorine combined with aluminum concentrations, in addition to chlorine present in the above mentioned areas. This may indicate the
early of phases formation involving these elements, which may be Friedel’s salt.
Despite these initial evidences, it can be said that the results of scanning electron microscopy gave only preliminary indications on the mechanism of chloride binding, not allowing emphatic conclusions on the issue. It should be noted that the expectation concerning the precipitation of calcium chloroaluminate is relatively restricted within the universe of concrete samples, which in turn are small representations of the concrete volume of a test specimen. This means that the technique needs to have high sensitivity to identify small precipitated compounds, as was the case of XRD. Anyway, through the microstructural analysis of fractured samples (using images obtained from SE signals), the positive effects of densification of concrete can be observed, especially in aggregate-paste interface (Figures 11 and 12), caused by the presence of MK, which greatly contributes to the overall performance of concrete, especially in regard to the durability in marine environments.
3.4 Index of voids (open porosity)

The test results of the determination of open porosity (Figure 13) indicate a lower porosity of M1 when compared to Mref. The M2 concrete has a larger void index in comparison with M1 and Mref concretes. The lowest porosity value of M1 can be attributed to the presence of MK and its densifying effect applied to the cement pastes, as seen in the SEM analysis (Figure 12). The results are as expected: a greater compactness and a lower open porosity of concrete M1 due to the replacement of PC by MK, and a higher porosity of concrete M2 related to its higher w/b ratio.

As a result of lower porosity (case of concrete M1), the entry of chlorides into the cementitious paste is more difficult, as discussed in the analysis on the chloride front (presented in the section 3.5). The measure of the open porosity obtained from the test of water absorption by immersion is a limited result, because it refers to an absolute datum of the void index of concrete. This parameter is partially responsible for the resistance of concretes in relation to chloride penetration. With large differences in porosity between two concretes, it can be concluded on the greater or lesser capacity in resisting to the action of chlorides. However, when only minor differences occur, conclusions may not be drawn. In the present case, concrete M2 has a larger open porosity than concrete M1, as shown in Figure 13, but the difference is small as the concretes M2 and Mref are compared. However, when the penetration of chlorides was analyzed (section 3.5), the front of ions Cl⁻ of the reference concrete was more pronounced than that of concrete M2. Therefore, besides the data of total porosity (as determined in this section), it is also important to know the distribution of pores size, understanding if there was a refinement of pores. A higher volume of micropores (pores smaller than 50 nm), instead of macropores (greater than or equal to 50 nm), even if that means a higher total volume of pores, characterizes a system with a greater refinement of pores, which is always desirable in terms of durability. Greater refinement generally implies a lower amount of interconnected pores and more tortuous pores [21], which in practice means a less permeable cement paste to the transport of chlorides. This may in part explain why the penetration of chlorides in the concrete M2 was lower than in Mref, in spite of being the open porosity of M2 higher than that of Mref. A more precise analysis of this issue can be achieved by means of the results from the techniques of porosimetry by mercury intrusion or porosimetry by nitrogen adsorption.

3.5 Analysis of the chloride front

The sprinkling of silver nitrate provides a readily measurable visual outcome, in which one can obtain an indication of the depth of the chloride front advancement. Table 7 shows the average values of the penetration of chloride front from the outer face of the cylinders. With these results, the improved performance of concretes containing metakaolin is demonstrated. In the first case, with MK replacing cement and at the same w/b ratio (M1) as that of concrete containing only Portland cement (Mref), a reduction of 20% in the Cl⁻ penetration was observed. Concerning the mixture M2, despite its higher w/b ratio (resulting in increased open porosity) and despite their lower contents of cement and total binders, it also attained an increased resistance to chloride attack when compared to the reference concrete, with a decrease of 10% in the penetration of chloride front. It is verified that, for this test, when the decrease in binder is compensated by an adequate replacement of cement by MK, there is no reduction in the resistance to the advancement of chlorides through the concrete structure. This is due to the fact that MK promotes a densifying effect in concrete when present in addition or in replacement of cement, as discussed in section 3.3 and illustrated in Figure 12; and also, as demonstrated in the XRD results (section 3.2), due to the fact that MK potentiates the formation of Friedel’s salt and the consequent binding of chlorides when these ions are propagating through the cement matrix. These two factors allow the avoidance or delay of the penetration of chloride ions and thus prevent them of reaching the reinforcement in the interior of concrete, causing its depassivation.

4. Conclusions

From the present work, the following conclusions can be drawn:

- From the accelerated wetting and drying test using a solution containing chlorides, the decreased penetration of the front of chlorides in concretes containing metakaolin was evident, especially when it was kept the same w/b ratio specified for the reference concrete with f<sub>c</sub> equal to 30 MPa.
- Analysis by SEM and EDS spectra provided indications of chloride binding under Friedel’s salt form. In Mref, clear evidences of the formation of layers consisting of Cl<sup>-</sup>, Al and Ca were found, but also in samples with metakaolin, punctual high chlorine concentrations in conjunction with aluminum concentra-
trations were detected, which may indicate the start of formation of Friedel’s salt.

- In the XRD analysis, the mechanism of chloride binding in the form of hydrated calcium chloroaluminate became clearer, with the observation of more pronounced peaks of Friedel’s salt in the concretes with metakaolin, especially in tests conducted in the surface layers of concrete.

- Measurements of void index of the concretes emphasize the reduction of open porosity of concrete with metakaolin in the same w/b ratio (M1) when compared to the reference concrete (Mref), a fact that became clear in the microstructural analysis of fractured samples, which showed a denser and more compact microstructure for M1. In this case, the reduction of porosity adds to the chloride binding mechanism in the form of Friedel’s salt to explain the better performance of this concrete regarding the attack of chlorides.

- For concrete M2, despite its higher w/b ratio and higher open porosity when compared to Mref, the results after 8 attack cycles in a 10% solution of NaCl showed a resistance to the Cl⁻ penetration higher than that of Mref (average penetration of chlorides front in M2 about 10% less than Mref). In principle, this is due to the action of chloride binding (Friedel’s salt), as seen in XRD tests, but there is probably an effect in terms of pores refinement.

As final considerations to this work, it can be stated with respect to current concretes, with $f_{cu}$ equal to 30 MPa, that the use of metakaolin as a partial substitute for cement demonstrates a very good potential in protecting these concretes against the action of chlorides, as it allows both the refinement of the structure of the cementitious matrix and the binding of chloride ions in the form of Friedel’s salt. Combining these two mechanisms, it is possible to produce a delay in the initiation of reinforcing steel corrosion, thereby increasing the service life of reinforced concrete structures.

The use of metakaolin also allows a decrease in the amount of binder in concrete while maintaining the same strength and the performance in terms of reinforcing steel protection with regard to its depassivation caused by chloride ingress. Thus, it can be concluded that for the same range of strength, the use of metakaolin brings benefits in terms of durability. It is possible, in this way, to create an economically and environmentally sustainable concrete by reducing the consumption of Portland cement. Clearly the benefits are even greater when the concrete incorporating metakaolin occurs by partial replacement of cement with a fixed w/b ratio. In this case, there is an effective reduction of porosity, followed by an increase in strength, which means lower rates of chloride transportation inside the concrete.

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6. References


The role of metakaolin in the protection of concrete against the deleterious action of chlorides


