

# Determination of the selectivity coefficient of a chloride ion selective electrode in alkaline media simulating the cement paste pore solution

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## A B S T R A C T

The measurement of the free chloride concentration in the pore solution of cement paste or concrete is of interest for assessing the probability of corrosion of the steel reinforcements embedded in concrete. This determination is performed through leaching or pore-pressing methods or through embedded potentiometric sensors into the hardened cementitious material. The potentiometric determination of chloride in cement paste pore solutions is limited by hydroxide ion interference, due to the high alkalinity of such media. The potentiometric selectivity coefficients,  $k_{Cl^-,OH^-}$ , are determined for a chloride ionic selective electrode in alkaline solutions simulating the electrolyte present within the pore network of cement paste and concrete. This is done using a fixed interference methodology, with least-squares non-linear curve fitting for obtaining the selectivity coefficients together with other relevant electrode parameters. The limit of detection of the Cl<sup>-</sup> ISE, due to OH<sup>-</sup> interference, varies with pH. For the pore solution corresponding to an ordinary Portland cement paste or concrete, this limit can be set between  $3 \times 10^{-3}$  m, and  $7 \times 10^{-3}$  m, i.e., approximately below a chloride concentration value of  $1 \times 10^{-2}$  molal. Taking into account these limits of detection the free Cl<sup>-</sup> concentrations able to depassivate the steel, can be adequately determined by potentiometric measurements with calibrated ISEs in the expressed pore solutions of Portland cement concretes, without significant influence of OH<sup>-</sup> interference. Nevertheless, this effect can prevent the adequate measurement of low free Cl<sup>-</sup> concentrations, below the corresponding limit of detection value.

### Keywords:

Potentiometry  
Ionic selective electrode  
Sensor  
Selectivity coefficient  
Chloride  
Cement paste pore solution

## 1. Introduction

Chloride into reinforced concrete is known to be a main responsible of steel corrosion. For this reason the chloride (Cl<sup>-</sup>) contents of the concrete raw materials are strictly specified to be under low safe values from the point of view of reinforcement corrosion. Nevertheless, these ions can ingress into concrete when exposed to a marine environment or to interaction with de-icing salts during the service life of structures. This ingress eventually leads to chloride contents high enough to depassivate and corrode the embedded steel. A widely accepted value for the chloride content corrosion threshold is 0.4% Cl<sup>-</sup> relative to cement mass in concrete [1], although the actual threshold value may be dependent on several circumstances [2].

Cementitious hydrated phases are able to bind or fix a portion of the Cl<sup>-</sup> ions present in concrete, but the rest of them remain dissolved in the concrete inner pore solution. This latter portion, sometimes called as the "free chloride", is that considered to be able to corrode the steel. For this reason there have been efforts

to develop methods for determining the Cl<sup>-</sup> concentration of the concrete pore solution. Three types of methodologies have been used for such purpose: leaching methods [3,4], based on the interaction of concrete with water and analysis of the leachates; the pore-pressing technique [5–9], based on the application of high pressures to samples of the cementitious materials allowing to extract small portions of liquid that can be analyzed; and finally the use of embedded sensors in concrete allowing to monitor the "free chloride" content in concrete on-site [10–16].

Direct potentiometry is an appealing non-destructive analytical technique for the determination of the Cl<sup>-</sup> contents of the solutions obtained by leaching or pore-pressing methods, especially for the latter technique due to the small amount of the obtained liquid samples. Furthermore, the on-site monitoring of Cl<sup>-</sup> contents in concrete is based on potentiometric sensors [10–16], whose working system is that of a Cl<sup>-</sup> ionic selective electrode (ISE). It has been also demonstrated that it is possible to determine the activities of chloride ions in synthetic [17,18] or real [19] cement paste pore solutions by potentiometric measurements, but these determinations have a limitation due to the high alkalinity of the pore solution, which shows pH values around 13, or even higher [5,19]. In these conditions the potentiometric response of a Cl<sup>-</sup> ISE can suffer

interference from hydroxide (OH<sup>-</sup>) ions, especially at low Cl<sup>-</sup> concentrations [20]. This interference has not been quantified before for the case of cement paste pore solution, although abnormally high Cl<sup>-</sup> activity coefficients were obtained potentiometrically with synthetic and real cement paste pore solutions at Cl<sup>-</sup> concentrations below approximately 0.01 m, due most probably to OH<sup>-</sup> interference [17–19].

Selectivity coefficients  $k_{ij}$  are in common use as the quantitative parameter determining the effect of the interfering ions on the potentiometric ISE response [20]. Selectivity coefficients are generally defined with reference to a model electrode response equation, the Nikolskii–Eisenman equation:

$$E_{obs} = E^{\circ} + \frac{RT}{z_i F \log e} \log \left( a_i + \sum_{j \neq i} k_{ij} a_j^{z_i/z_j} \right) \quad (1)$$

where  $E_{obs}$  is the potential difference measured,  $E^{\circ}$  is a term including all contributions independent of activities  $a$ , and  $z$  is the ion charge. Subscript  $i$  stands for the primary ion and subscript  $j$  stands for the interfering ions.

It is possible to obtain from literature [20] numerical values for the  $k_{Cl^-,OH^-}$  of ISEs based on solid AgCl membranes, which are approximately  $10^{-2}$ . Nevertheless, several authors [20–24] lay stress on the fact that the measured values of the selectivity coefficients of a given ISE, and even its preference for a given species, may be dependent on the procedures and experimental conditions used for their determination. This is especially true in cases where the ISE does not exhibit Nernstian response for both the primary and the interfering ions [22,25]. It has been considered also interesting to determine the  $k_{ij}$  values under conditions as close as possible to the practical work of the electrode, i.e., using test solutions with compositions and ionic strengths similar to those of real samples [26]. Nevertheless, experimental conditions and protocols have been described recently for obtaining unbiased, thermodynamic selectivity coefficients that are independent of experimental conditions [25,27].

Taking into account the precedent considerations, and the potential interest of the application under study, it is convenient to check if the special conditions imposed by the nature of the concrete inner electrolyte, i.e., high alkalinity and ionic strength [5], may change the selectivity properties of Cl<sup>-</sup> ISEs. It is also likely that such extreme conditions have not been studied in routine determinations of selectivity coefficients. The objective of this work has been to obtain the values of  $k_{Cl^-,OH^-}$  for a Cl<sup>-</sup> ISE in alkaline solutions simulating the electrolyte present within the pore network of cement paste and concrete. This determination would allow to quantify in a more reliable way the limitation of the potentiometric determinations of chloride activities due to OH<sup>-</sup> interference in such media.

Different experimental methods can be used to determine  $k_{ij}$  values [22,24,25,27]. The fixed interference (FI) method implies using test solutions with a constant interfering ion concentration while the primary ion concentration is varied. An interesting variation [28] of the FI method uses a single solution of the interfering ion and the primary ion activity is varied by means of small additions, with the electrodes continually in contact, and measuring the cell potential after each addition. This procedure, apart of other advantages [28], reproduces rather closely the working conditions of a Cl<sup>-</sup> sensor embedded in a cement paste matrix, i.e., permanently exposed to a fixed high OH<sup>-</sup> activity and progressively exposed to increasing Cl<sup>-</sup> activities, as these last ions penetrate the concrete cover of the sensor.

Several general recommendations for the determination of selectivity coefficients [24] have been taken into account in this work: the concentrations are defined on a molality ( $m$ ) base, and

the ionic activity coefficients and liquid-junction potentials of the reference electrode have been calculated.

## 2. Experimental

### 2.1. Electrochemical cells

The potential of a Cl<sup>-</sup> ion selective electrode (Ingold type 15 213 3000) was measured versus a KCl saturated calomel reference electrode (Russell type CR5). The reference electrode contacted the Cl<sup>-</sup> test solution through a Luggin capillary in order to avoid possible test solution contamination. Thus, the electrochemical measuring cell may be expressed as:



Test solutions were maintained at a temperature of  $25.0 \pm 0.1$  °C in a thermostated jacket vessel, stirred and bubbled with N<sub>2</sub> to avoid carbonation.

### 2.2. Test solutions and measuring procedure

The expressed pore solutions of cement pastes, mortars and concretes, have been shown to be mainly composed of alkaline hydroxides (especially KOH and NaOH in a lesser proportion), with other species (SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, AlO<sub>2</sub><sup>-</sup>, SiO<sub>2</sub>, etc.) being present in much-lower concentrations [5,6]. The OH<sup>-</sup> concentration of the expressed pore solutions of cement mortars and concretes is high (0.04–0.55 M) [29–31], while this concentration may be even higher, up to 0.7 M, for pore solutions obtained from pure Portland cement pastes [5]. Given all these facts we have chosen four fixed levels of OH<sup>-</sup> concentration to measure the  $k_{Cl^-,OH^-}$  of the Cl<sup>-</sup> ISE: 0.035 m, 0.1 m, 0.3 m and 0.5 m. For the sake of simplicity the alkaline solutions were prepared using only KOH. Ca(OH)<sub>2</sub> was not used for these solutions since the Ca<sup>2+</sup> concentrations found in cement paste pore solutions are very low [5].

The test solutions series were: KOH 0.035 m + NaCl, KOH 0.1 m + NaCl, KOH 0.3 m + NaCl, and KOH 0.5 m + NaCl. The approximate Cl<sup>-</sup> molalities in these series were as follows:  $10^{-5}$  m,  $5 \times 10^{-5}$  m,  $10^{-4}$  m,  $5 \times 10^{-4}$  m, 0.001 m, 0.005 m, 0.01 m, 0.05 m, 0.1 m, 0.3 m, 0.5 m and 1 m. Each series was obtained as follows: a volume of 50 ml of KOH  $m_{KOH}$  ( $m_{KOH}$  standing for KOH molality of the corresponding series) were taken. The Luggin capillary was also filled with KOH  $m_{KOH}$  solution. A micropipette was used to do the following sequence of additions to the test solution: 4 additions (0.025, 0.1, 0.15 and 1 ml) of KOH  $m_{KOH}$  + NaCl 0.02 m, 4 additions (0.05, 0.45, 0.6 and 5 ml) of KOH  $m_{KOH}$  + NaCl 0.5 m and 4 additions (0.9, 3.5, 4 and 12 ml) of KOH  $m_{KOH}$  + NaCl 4 m.

After each addition the electrochemical potential of the cell (2) was measured. The test solution pH was also measured after each addition using a high pH glass electrode (Radiometer pHG211, pH measuring range 0–14). The pH electrode was calibrated with standard solutions of pH 11.0, 11.5, 12.0, 12.5 and 13.0 [32].

The densities of all solutions used to prepare test solutions were measured weighing thermostated samples of 5 ml (taken with micropipette). All solutions were prepared using analytical-grade reagents and ultrapure water (Millipore Academic).

### 2.3. Theoretical chloride activities

In real situations, cement matrices are porous media partially saturated with water. The solution filling the pore (i.e., pore water) locally approaches thermodynamic equilibrium with the different constituents of the cement matrix. The resulting pore water solution may be saturated with respect to some matrix constituents,

resulting in deviations from ideal dilute solution behavior and species activity coefficients significantly different from unity.

Chloride activities in the test solutions were calculated using the Pitzer model. The calculations were carried out with the computer program PHRQPITZ [33], which was developed for the calculation of chemical equilibria in solutions of high ionic strength using the Pitzer model in the temperature range 0–60 °C. A data base of Pitzer interaction parameters is also provided, and the program is accompanied by an interactive input code, PITZINPT.

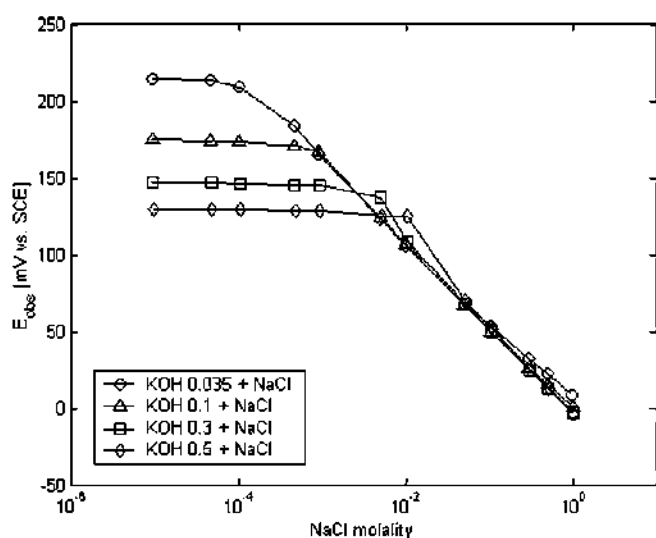
### 3. Results and discussion

The densities measured on KOH + NaCl solutions used to prepare test solutions are shown in Table 1. These data together with the addition volumes (see Section 2) are needed for the accurate calculation of the NaCl ( $\text{Cl}^-$ ) molalities of the test solutions.

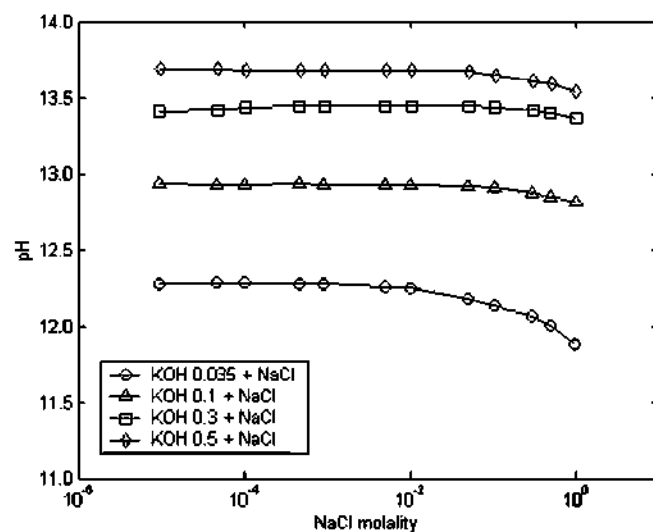
Fig. 1 shows the electrochemical potentials measured on cell (2) versus NaCl molality for all test solution series. Measured cell potentials range from –5 to 220 mV versus SCE approximately. The interfering effect of  $\text{OH}^-$  on the potential response can be appreciated in Fig. 1. At high chloride concentrations the potential varies approximately in linear form with the logarithm of chloride concentration. At low chloride concentration there is no response of cell potential to chloride concentration, i.e., potential remains constant while chloride molality varies. This curve shape agrees with the Nikolskii–Eisenman model. It is interesting to note in Fig. 1 that the chloride concentration range where chloride is not detected expands to higher values as KOH molality increases, showing a higher  $\text{OH}^-$  interference.

**Table 1**  
Densities measured on KOH + NaCl solutions.

$m_{\text{NaCl}}$	Solution density in $\text{kg}/\text{m}^3$			
	KOH 0.035 m + NaCl	KOH 0.1 m + NaCl	KOH 0.3 m + NaCl	KOH 0.5 m + NaCl
0	1008.7	1006.9	1018.5	1017.6
0.02	1002.1	994.2	1010.5	1015.7
0.5	1023.6	1012.0	1034.4	1040.1
4	1135.5	1142.0	1151.3	1160.7



**Fig. 1.** Measured electrochemical potential. Circle: KOH 0.035 m + NaCl series, triangle: KOH 0.1 m + NaCl series, square: KOH 0.3 m + NaCl series, diamond: KOH 0.5 m + NaCl series.



**Fig. 2.** pH measured in test solutions versus NaCl molality. Circle: KOH 0.035 m + NaCl series, triangle: KOH 0.1 m + NaCl series, square: KOH 0.3 m + NaCl series, diamond: KOH 0.5 m + NaCl series.

Measured pH values are shown in Fig. 2 versus NaCl molality of test solution for all four series. Values range from 11.9 to 13.7. The pH remains approximately constant within a series. A slight pH decrease is seen at high chloride concentrations, especially for the lowest KOH molality series. pH can be considered constant at chloride concentrations lower than 0.01 m, with the following values measured for each series: pH 12.3 for KOH 0.035 m + NaCl series, pH 12.9 for KOH 0.1 m + NaCl series, pH 13.4 for KOH 0.3 m + NaCl series, and pH 13.7 for KOH 0.5 m + NaCl series.

Assuming a Nikolskii–Eisenman response (1) for the  $\text{Cl}^-$  ISE, being  $\text{Cl}^-$  the primary ion and  $\text{OH}^-$  the interfering ion, the measured potential difference of cell (2) can be expressed as:

$$E_{\text{obs}} = E_{\text{ISE}}^0 - S \log(a_{\text{Cl}^-} + ka_{\text{OH}^-}) - E_{j1} - E_{j2} - E_{\text{ref}} + N \quad (3)$$

where  $E_{\text{ISE}}^0$  is the ISE standard potential, which is taken here as the standard potential of the redox couple  $\text{AgCl}/\text{Ag}$  (i.e., 0.22233 V, versus SHE [34]),  $E_{\text{ref}}$  is the reference electrode potential (i.e., 0.2412 V, versus SHE [34]),  $k$  is the selectivity constant quantifying interference of  $\text{OH}^-$  on  $\text{Cl}^-$  ISE potentiometric response.  $E_{j1}$  is the liquid-junction potential between internal SCE electrolyte (i.e., saturated KCl,  $\beta$ -phase) and Luggin capillary solution (i.e., KOH  $m_{\text{KOH}}$ ,  $\alpha$ -phase).  $E_{j2}$  is the liquid-junction potential between Luggin capillary solution ( $\beta$ -phase) and test solution (i.e., KOH  $m_{\text{KOH}}$  + NaCl  $m_{\text{NaCl}}$ ,  $\alpha$ -phase). Junction potential may be calculated using the Henderson equation [35]:

$$E_j = \phi^\beta - \phi^\alpha = \frac{\sum_i \frac{z_i |u_i|}{z_i} (c_i^\beta - c_i^\alpha)}{\sum_i |z_i| u_i (c_i^\beta - c_i^\alpha)} \left( \frac{RT}{F} \right) \ln \frac{\sum_i |z_i| u_i c_i^\alpha}{\sum_i |z_i| u_i c_i^\beta} \quad (4)$$

here  $z_i$ ,  $u_i$ , and  $c_i$  are the respective charge, ionic mobility, and molar concentration of ionic species  $i$  in solution. In applying Eq. (4), we have assumed the common practice of substituting ionic mobilities with equivalent ionic conductivities at infinite dilution  $\lambda_i^\circ$  [35]. The sum of the two junction potentials calculated through (4) is plotted in Fig. 3 for all test solution series studied. It ranges from –13 to 1 mV. Measured cell potentials range from –5 to 220 mV, thus junction potential is not a negligible contribution in Eq. (3). Junction potentials remain approximately constant within a series for chloride concentrations lower than 0.01 m, but their absolute values increase sharply at higher chloride concentrations.

The previous history of the electrode may affect its potentiometric response considerably. For this reason constant  $N$  and slope

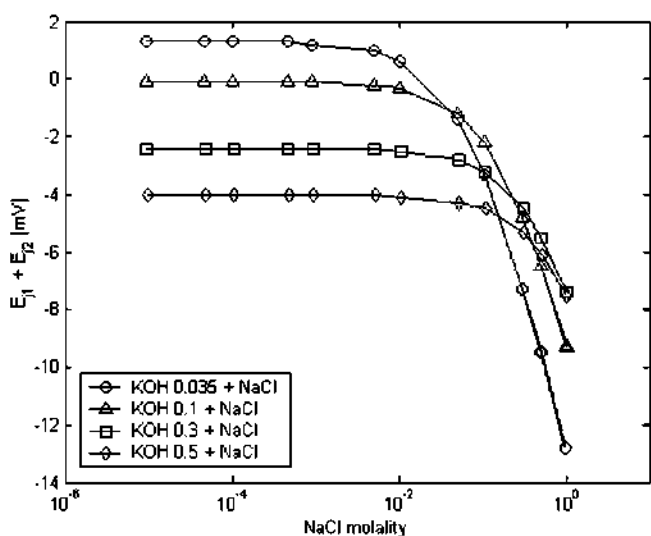


Fig. 3. Liquid-junction potential calculated for each series. Circle: KOH 0.035 m + NaCl series, triangle: KOH 0.1 m + NaCl series, square: KOH 0.3 m + NaCl series, diamond: KOH 0.5 m + NaCl series.

$S$  have been introduced in Eq. (3) to account for deviations from ideal ISE behavior. Their theoretical values are, respectively, 0 mV and 59.13 mV (i.e., Nernstian slope).

Chloride activities in the test solutions  $a_{Cl^-}$  have been theoretically calculated through Pitzer's model. The corresponding activity coefficients  $\gamma_{Cl^-}$  (defined in Eq. (5), where  $m_{Cl^-}$  is the chloride molality of test solution) are shown in Fig. 4.

$$\gamma_{Cl^-} = \frac{a_{Cl^-}}{m_{Cl^-}} \quad (5)$$

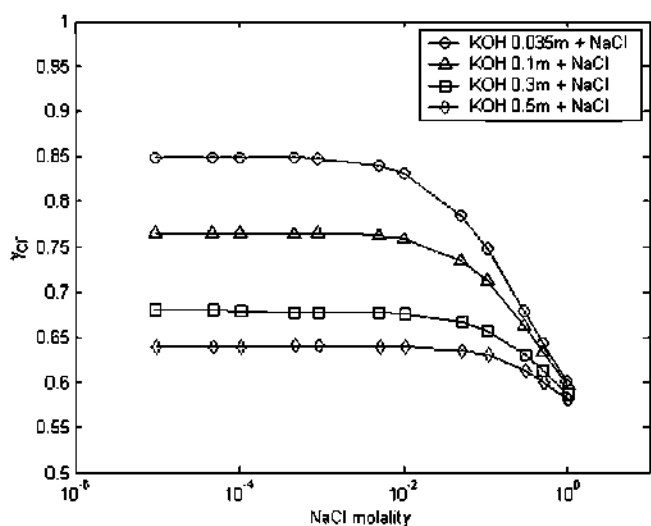


Fig. 4. Theoretical chloride activity coefficients calculated through Pitzer's model.

Table 2  
Fitting parameters of the measured cell potentials into Eq. (3).

	KOH 0.035 m + NaCl	KOH 0.1 m + NaCl	KOH 0.3 m + NaCl	KOH 0.5 m + NaCl	Averaged	Theoretical
$N$ (mV)	0.2	-5.2	-9.9	-13.0	-4.7	0.0
$S$ (mV)	61.44	64.32	69.07	75.12	64.39	59.13
$\log k$	-2.159	-2.065	-1.965	-1.807	-2.055	-2.032
$\sigma$ (mV)	2.5	3.4	4.7	5.8	4.5	-
$r$	0.9996	0.9991	0.9975	0.9949	0.9979	-

It can be seen in Fig. 4 that the higher the KOH molality, the lower the chloride activity coefficient due to higher ionic strength of the medium. Dependence of chloride activity coefficient with chloride concentration is low at low chloride molalities ( $m_{NaCl} < 0.01$ ), showing the low contribution of chloride to ionic strength under these conditions. Hydroxide activities have been calculated from experimental pH values according to Eq. (6):

$$a_{OH^-} = 10^{pH - pK_w} = 10^{pH - 14.0} \quad (6)$$

The measured cell potential differences have been fitted to Eq. (3) through a least-squares non-linear curve fitting. This is achieved by minimizing the standard deviation,  $\sigma$ , of the experimental values from best-fit curve.

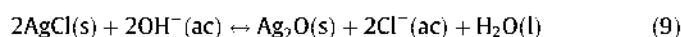
$$\sigma = \sqrt{\frac{\sum_{i=1}^n (E_i^{calc} - E_i^{exp})^2}{n - p}} \quad (7)$$

where  $E^{exp}$  are the experimentally measured values of cell potential difference,  $E^{calc}$  are the corresponding values calculated through (3),  $n$  are the number of data points fitted and  $p$  is the number of fitted parameters (fitted parameters are  $N$ ,  $S$  and  $k$ , i.e.,  $p = 3$ ).  $\sigma$  represents an average separation of the calculated potential values from the experimental ones, and thus it is a measurement of the goodness of the fitting. Parameter values that minimize  $\sigma$  have been found applying a simplex method (Nelder-Mead algorithm implemented in MATLAB software). Results are shown in Table 2. Fitting has been done in two ways. Firstly data from each series have been fitted independently, yielding one set of parameters for each KOH molality. Results are shown in the first four columns of Table 2. Secondly data from all four series have been fitted together, yielding a set of parameters that represent an average of the parameters sets previously calculated with the other approach, and being a set of parameters applicable to the full range of concentrations of  $Cl^-$  and  $OH^-$ . This set of averaged parameters is shown in fifth column of Table 2. Also, regression coefficients  $r$ , corresponding to the calculated potential versus experimental potential plots, are shown. Table 2 shows high correlation coefficients ( $r > 0.99$ ) and low  $\sigma$  values ( $\sigma < 6$  mV). It can be stated that the experimental values of the cell potential differences can be adequately fitted to the Nikolskii-Eisenman model (3). Experimental cell potentials and calculated ones using the set of averaged parameters, (fifth column of Table 2), are plotted against chloride activity in Fig. 5.

Theoretical parameter values are also shown for comparison in last column of Table 2. According to the literature [20,34], the theoretical value of  $k$  is given by:

$$\log k = pK_S(Ag_2O) - pK_S(AgCl) = -2.032 \quad (8)$$

where  $pK_S$  stands for the solubility product. Eq. (8) is applicable to  $Cl^-$  ISEs consisting on a  $AgCl$  or  $Ag_2S/AgCl$  membrane. It is assumed in (8) that, in presence of  $OH^-$ , silver activity near the surface (and hence electrode potential response) is determined by the exchange equilibrium:



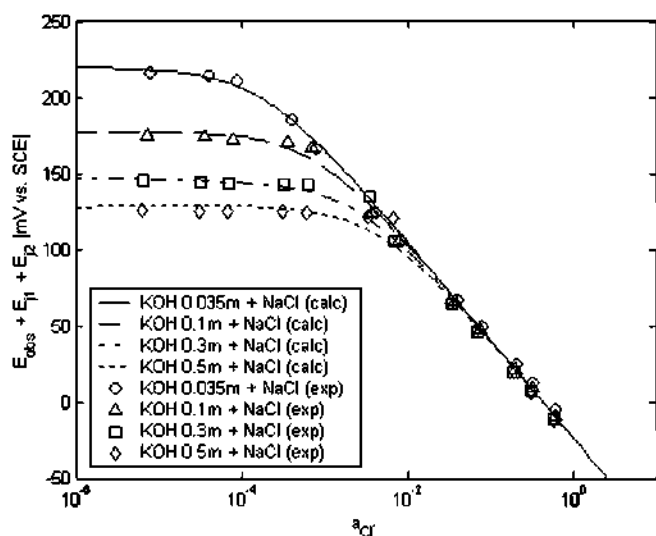


Fig. 5. Comparison of the experimental and calculated cell potentials versus chloride activity in test solutions.

Averaged parameters (fifth column of Table 2) are very similar to theoretical ones (sixth column of Table 2). A variation of parameters values with KOH concentration can be appreciated in Table 2.  $N$  decreases from 0.2 mV to  $-13.0$  mV when increasing KOH concentration from 0.035 m to 0.5 m.  $S$  increases from 61.44 mV to 75.12 mV, and  $k$  increases from  $6.9 \times 10^{-3}$  to  $15.6 \times 10^{-3}$ . The goodness of the fittings and the similarity between calculated and theoretical parameters diminishes slightly when changing KOH concentration from 0.035 m to 0.5 m.

The good agreement between the determined average value of the selectivity coefficient ( $8.8 \times 10^{-3}$ ) and its theoretical, thermodynamic value ( $9.3 \times 10^{-3}$ ), indicates that under these experimental conditions the ISE exhibits Nernstian response slopes for both the primary and the interfering ions [25]. For this reason it may be accepted that the measured values of  $k$  are not corrupted due to problems as primary ion contamination or co-extraction processes, and thus these values represent the unbiased selectivity coefficient  $k_{Cl^-, OH^-}$  [25]. Nevertheless, the slight separations observed for  $N$ ,  $S$  and  $k$  from their theoretical values, as the alkalinity of the test solutions is increased (Table 2), indicate that it is not possible to rule out the possibility of modifications of the AgCl membrane upon prolonged exposure to highly alkaline solutions. This possibility deserves further research, and if confirmed would imply the need to check periodically the behavior of  $Cl^-$  ISEs when extensively used in contact with such alkaline solutions.

The quantity  $E_{obs} + E_{j1} + E_{j2}$  is plotted in Fig. 6 against  $a_{Cl^-} + k a_{OH^-}$  in a logarithmic scale. The averaged  $k$  value is used for calculating the data of Fig. 6. According to Eq. (3) straight lines should be obtained for such a plot. This is the case for the most diluted series KOH 0.035 m + NaCl, but the other series show an anomaly. Divergences from linearity are observed at monotonically increasing  $Cl^-$  activities, as KOH molality increases. This fact could also help to explain the divergence of calculated parameters from theoretical ones, for the fittings of experimental cell potentials to Eq. (3), as KOH concentration increases, see Table 2.

The experimental set-up implies measuring cell potential in a solution of constant KOH concentration and increasing NaCl concentration. Initially ISE potential is not able to respond to chloride activity due to the interference of hydroxide. At higher NaCl concentrations ISE responds to chloride activity and the effect of the interfering ion  $OH^-$  is negligible, see Fig. 5. It can be seen in Fig. 6 that the potential anomalies occur approximately at the chloride activity values at which the change of ISE response happen in

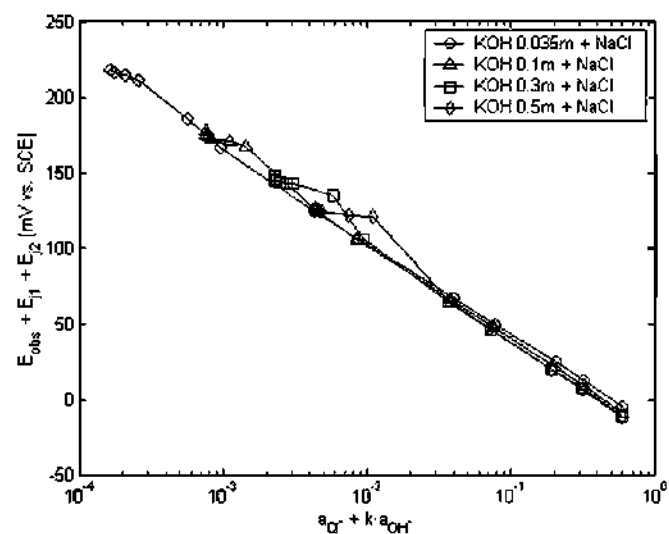


Fig. 6. Plot of  $E_{obs} + E_{j1} + E_{j2}$  versus  $a_{Cl^-} + k \cdot a_{OH^-}$ . See text for details.

Fig. 5. We can hypothesize that equilibrium (9) and hence potential response to chloride activity cannot be well established until certain chloride concentration is reached.

The limit of detection (LOD) of an ISE can be defined [21,28] as the chloride activity at which the observed cell potential deviates an amount  $S \log 2$  from the Nernstian response. Graphically LOD is given by the intersection of the Nernstian response (linear to  $\log a_{Cl^-}$ ) with the constant value of the Nikolskii-Eisenman response for low primary ion activity. Thus, the LOD values in this work are given by:

$$LOD = k \cdot a_{OH^-} \quad (10)$$

Thus, the limit of detection of the chloride ISE is dependent on the pH. The higher the alkalinity of the medium the higher the limit of detection for chlorides. Taking into account the pH measured and the averaged  $k$  value, the LOD for each series studied are the following activity values:  $2 \times 10^{-4}$ ,  $7 \times 10^{-4}$ ,  $2 \times 10^{-3}$  and  $4 \times 10^{-3}$ , respectively for the 0.035, 0.1, 0.3 and 0.5 m KOH series. The corresponding  $Cl^-$  molal concentrations are:  $2 \times 10^{-4}$ ,  $9 \times 10^{-4}$ ,  $3 \times 10^{-3}$  and  $7 \times 10^{-3}$ , respectively. Concentrations lower than these values cannot be accurately determined by potentiometric measurements.

The pore solutions of hardened ordinary Portland cement pastes [5,8,19] and concretes [29–31] have physico-chemical characteristics (pH and composition) similar to those of third and fourth solutions series in this work, i.e., KOH 0.3 m + NaCl and KOH 0.5 m + NaCl, respectively. Thus the relevant values of LOD for  $Cl^-$  ions in these solutions are between  $3 \times 10^{-3}$  m, and  $7 \times 10^{-3}$  m, i.e., approximately below 0.01 m  $Cl^-$ . This latter value is in fairly good agreement with the chloride concentrations below which the potentiometric determinations of  $Cl^-$  activities start to fail, due to  $OH^-$  interference, in synthetic [17,18] and real [19] cement paste pore solutions. Nevertheless, experimental difficulties may rise this LOD to even higher values [19,21].

It is also interesting to evaluate the impact of the  $OH^-$  interference upon the potentiometric determinations of free chloride content in cement paste or concrete pore solution, for assessments of the probability of corrosion of steel reinforcements. From practical engineering experience, and for non-carbonated ordinary Portland cement concretes (inner pH > 13), the steel corrosion risk is considered low for total  $Cl^-$  contents below 0.4% relative to cement mass in concrete, while this risk is considered high for  $Cl^-$  contents higher than 1% [36]. Table 3 shows the values of free  $Cl^-$  concentrations

**Table 3**

Chloride concentrations of expressed pore solutions obtained from ordinary Portland cement paste (CP) and concrete (C) samples contaminated at mixing with chloride salts at 0.4% Cl<sup>-</sup> ([Cl<sup>-</sup>]<sub>0.4</sub>) and 1% Cl<sup>-</sup> ([Cl<sup>-</sup>]<sub>1</sub>) levels.

Sample	Admixed salt	[Cl <sup>-</sup> ] <sub>0.4</sub> (mol/l)	[Cl <sup>-</sup> ] <sub>1</sub> (mol/l)	pH	Reference
CP	CaCl <sub>2</sub>	0.080 <sup>a</sup>	0.257 <sup>a</sup>	13.3 <sup>b</sup>	[8]
CP	NaCl	0.068 <sup>a</sup>	-	13.4 <sup>b</sup>	[8]
CP	NaCl	0.060 <sup>a</sup>	0.290 <sup>a</sup>	13.5	[19]
C (50 MPa)	NaCl	0.021	0.140	13.7	[29]
C (38 MPa)	NaCl	0.016	0.056	13.1 <sup>b</sup>	[30]
C (60 MPa)	NaCl	0.031	0.181	13.3 <sup>b</sup>	[30]
C (73 MPa)	NaCl	0.053	0.258 <sup>a</sup>	13.3 <sup>b</sup>	[30]

Data in parenthesis are the mean compressive strength values of concretes.

<sup>a</sup> Interpolated datum.

<sup>b</sup> pH value calculated from OH<sup>-</sup> concentration.

of the expressed pore solutions obtained from ordinary Portland cement paste (CP) and concrete (C) samples, which were prepared with different amounts of chloride salts dissolved in the mixing water. The values shown in Table 3 are those corresponding to 0.4% Cl<sup>-</sup> relative to cement mass, [Cl<sup>-</sup>]<sub>0.4</sub> and 1% Cl<sup>-</sup>, [Cl<sup>-</sup>]<sub>1</sub>.

It may be appreciated in Table 3 that for total Cl<sup>-</sup> contents between 0.4% and 1%, the measured free Cl<sup>-</sup> concentrations are between 0.016 M and 0.29 M. These values are higher than the safe LOD value of 0.01 m, see precedent paragraphs. This means that the free Cl<sup>-</sup> concentrations able to depassivate the steel, can be adequately determined by potentiometric measurements with calibrated ISEs in the expressed pore solutions of Portland cement concretes, without significant influence of OH<sup>-</sup> interference. This statement can be extended, in principle, to chloride sensors permanently embedded in Portland cementitious matrices. Nevertheless, in this latter case it must be taken into account that the OH<sup>-</sup> interference effect can prevent the adequate measurement of low free Cl<sup>-</sup> concentrations, below the corresponding LOD value, and this fact would count somewhat against the functional requirement of early detection of chloride ingress. The quantification of this latter effect is currently under research.

#### 4. Conclusions

The interference of hydroxide ions upon the potentiometric response of a chloride ionic selective electrode has been studied in alkaline solutions simulating cement paste or concrete pore electrolytes. The mixed potentiometric response of the Cl<sup>-</sup> ISE, to both Cl<sup>-</sup> and OH<sup>-</sup> ions, is described through the Nikolskii-Eisenman model. Selectivity coefficients,  $k_{Cl^-,OH^-}$ , together with other electrode parameters, have been determined for the ISE in KOH + NaCl solutions representative of the inner cement paste pore solution, using a fixed interference methodology, with least-squares non-linear fitting of the measured potentials to the model equation. A good agreement between experimental and theoretical values is found for all the electrode parameters, although a slight difference appears at high KOH concentrations. The limit of detection of the ISE varies with pH. This implies that for the studied media, and in the pH range from 11.9 to 13.7, chloride concentrations below  $2 \times 10^{-4}$  to  $7 \times 10^{-3}$  molal cannot be accurately determined by potentiometric measurements, due to the OH<sup>-</sup> interference. Taking into account these limits of detection, the free Cl<sup>-</sup> concentrations able to depassivate the steel, can be adequately determined by potentiometric measurements with calibrated ISEs in the expressed pore solutions of Portland cement concretes, without significant influence of OH<sup>-</sup> interference. Nevertheless, this effect can prevent the adequate measurement of low free Cl<sup>-</sup> concentrations, below the corresponding limit of detection value.

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