Pergamon

Cement and Concrete Research 29 (1999) 893–898

CEMENT AND CONCRETE RESEARCH

Analysis of acid-soluble chloride in cement, mortar, and concrete by potentiometric titration without filtration steps

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Manuscript received 8 December 1998; accepted manuscript 1 March 1999

Abstract

A potentiometric titration procedure that makes use of Gran's method for end-point detection has been developed to analyze acid-soluble chloride in cement, mortar, and concrete, eliminating the filtration steps performed in habitual laboratory reference methods. The accuracy and reliability of the proposed analytical technique has been checked against a standard method, such as Volhard's, by analyzing duplicate samples of cements, mortars, and concretes with varied chloride contents.

Keywords: Chloride; Chemical analysis; Cement; Mortar; Concrete

Chloride analysis in fresh or hardened concrete and its raw materials is of great importance both in quality control and in durability assessments of existing structures, due to the steel corrosion promoter character of Cl^- ion.

Although there is not a total agreement about the Cl^- content threshold below which the risk of depassivation of steel would be assumable, normatives usually limit this concentration in fresh concrete and raw materials. For instance the maximum total Cl^- contents for reinforced and prestressed concrete in Spain are now established at 0.4 and 0.2% by weight of cement respectively [1,2]. This means that the critical Cl^- concentration range in concrete is located between approximately 0.025 and 0.1% by concrete weight, and any Cl^- analytical method should provide accurate and precise results mainly in this concentration range. Nevertheless chloride contents in real concrete exposed to aggressive environments may vary from $<0.01\%$ to more than 1%, which is more than two orders of magnitude. The practical concentration range for cements is usually limited to $<0.1\%$, due to restrictions imposed by normative [3]. There is also an ongoing controversy about the convenience of determining the acid-soluble or the water-soluble chlorides in concrete, but this work is only focused on Cl^- extracted by acid treatment.

In durability studies of large structures, normally a lot of samples must be analyzed and decisions on expensive repairs have to be taken on the basis of their measured chloride contents. This fact has led to a considerable effort to develop and improve analytical methods for laboratory [4–6] and field [7–10] determination of total Cl^- in concrete.

Reference laboratory methods for determining total Cl^- in cement and concrete [11–14] usually prescribe an extraction with hot nitric acid solution, followed by filtration to separate solid residues or precipitates. Cl^- analysis is performed on the resulting solution by Volhard's method [15] (i.e., a back titration with visual end-point detection) or by potentiometric titration with an $AgNO_3$ solution, determining the end point by the first derivative method [15]. Field methods [9,10] usually perform a direct Cl^- potentiometry on the resulting suspension of the acid digestion, without filtration, after an appropriate calibration of the ionic selective electrode (ISE) with synthetic solutions of known Cl^- concentration. The filtration step needs special labware and vacuum facilities to speed up the separation, so it is logically eliminated in field procedures.

Visual end-point detection in Volhard's method is sometimes difficult, especially when the test solution is strongly coloured, and requires experience to accurately detect the first permanent red colour. Among the methods based on ISE, direct potentiometries are known to be less accurate than potentiometric titrations [16], mainly due to the fact that the potential reading of an ISE for a given concentration of the indicated ion is dependent upon the ionic strength and composition of the solution. These latter conditions may vary considerably for the resulting solutions of the acid digestion of different concrete samples, for instance, when the aggregate composition is changed. Potentiometric titrations need

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PII: S0008-8846(99)00063-0

an end-point detection procedure. The first derivative method [15], based on finding the maximum difference in potential readings between successive titrant additions, has two known drawbacks: a large number of points (potential volume) has to be taken, especially in the vicinity of the end point; and the potential readings tend to be unstable near the end point because Cl^- concentrations are very low, reaching values well below the lower detection limit of Cl^- ISE.

Clemeña et al. [5] reported the advantageous use of Gran's method [17] for end-point determination based on a plot of a mathematical function of the potential readings against the volume of titrant added (see Appendix for details). These authors applied the method to the potentiometric titration of acid-soluble Cl^- in concrete with filtration of the solid residue. In this procedure only a small set of data points have to be taken in the region past the equivalence point, where the ISE potentiometric response is highly stable. So the data collection is easier and faster than in the first derivative method.

The objective of this work is to determine if the elimination of the filtration step in acid soluble Cl^- analysis of cement and concrete is compatible with a highly accurate method such as a potentiometric titration. This elimination would be desirable for simplifying laboratory procedures, reducing the risk of yielding erroneous results due to incomplete filtration or to insufficient washing of precipitates. The accuracy of an analytical method is likely to be largely controlled by the separations involved [15]. Furthermore the obviation of the filtration step would help the automation of the analysis. The solid residue present in the resulting suspension of the acid digestion of concrete may affect the ionic activity (free concentration) in solution, for instance, by ionic adsorption. In case this interference is produced it would affect greatly the potential readings in the near end-point region, where the concentrations of Cl^- and Ag^+ ions are very low. Taking this consideration into account, the best choice for the end-point detection procedure would be Gran's method, which implies taking the relevant data in the past end-point region. Further advantages and drawbacks of this latter method are discussed in detail later. The accuracy and reliability of the proposed potentiometric titration without filtration step has been assessed by comparisons with the standard Volhard method [11,12].

1. Experimental

1.1. Cement samples

The analyzed cement samples were provided by several Spanish cement manufacturers, together with their own measured Cl^- contents (Table 1); these analytical results were obtained mainly by X-ray fluorescence (XRF) unless otherwise stated. Each cement sample was analyzed in this work at least twice by the proposed potentiometric titration procedure and by Volhard's method [11]. The analytical results presented are the average of the obtained values.

1.2. Mortar and concrete samples

Two series of mortar specimens ($4 \times 4 \times 16$ cm) were prepared by mixing distilled water, a Spanish ordinary portland cement, and a calcareous sand (C) for the first and a siliceous sand (S) for the second series. The maximum size of the aggregates was 2 mm. The mass proportions of water, cement and sand were: 270:450:1350 [water/cement (w/c) ratio 0.6] for C mortars and 225:450:1350 (w/c 0.5) for the S mortar series. NaCl (pro analysis [p.a.]) was admixed into the specimens to produce the following Cl^- contents: 0, 0.010, 0.025, 0.050, 0.100, 0.150, 0.200, 0.400, and 0.625% by mortar weight. Cement contents and w/c ratios were kept constant for the series. The initial chloride content of the cement was 0.019% and those of sands were 0.005% (C) and 0.0005% (S). After wet curing in a 98% relative humidity chamber for 28 days, powdered mortar samples (about 100 g) were obtained by dry drilling on several points of each specimen. Some salt leaching was observed (white spots on the metallic base) for the specimens with highest Cl^- contents. The powdered samples, without further grinding, were kept in plastic containers until analysis.

Powder concrete samples were obtained from cores taken from real structures exposed to a marine environment. These concrete samples were all analyzed by the proposed potentiometric titration procedure and some selected samples were also analyzed by Volhard's method.

Each mortar and concrete sample was analyzed at least twice by each of the methods mentioned in the preceding paragraph. Their reported analytical results are the average of the obtained values, expressed always as percent Cl^- by total weight.

1.3. Equipment and reagents

The potentiometric titrations were performed with a high impedance millivoltmeter (2002) and an electronic burette (2031) both from Crison (Barcelona, Spain), an Ag^+-S^{2-} ISE (Orion Research Inc. 9416, Boston, MA, USA) and a double junction Ag/AgCl reference electrode. All solutions were prepared with distilled water and p.a. reagents.

1.4. Determination of the ISE slope

The ISE slope (i.e., its potential variation by Ag^+ concentration decade) must be known to apply Gran's method (see Appendix). Its value should be close to the Nernstian value (59 mV/decade at 25°C). The experimental slope was determined before each analysis session in a 50 mL portion of 0.5 M $NaNO_3$ solution whose pH was adjusted to 2 with concentrated HNO_3. To this solution, nine successive additions of a standardized 0.01 M $AgNO_3$ solution were made so that the ISE potential readings would be within of the range between 310 and 365 mV. The Ag^+ concentrations reached in solution due to these additions varied between approximately $7 \cdot 10^{-5}$ and $6 \cdot 10^{-4}$ M, with the particular ISE and reference electrode used in our laboratory. Nevertheless it should be taken into account that the practical

Table 1
Analyzed Cl^- contents for the cement samples

Type of cement	Denomination following ref [3]	Potentiometric titration (% Cl^-)	Volhard's method (% Cl^-)	Manufacturers analysis (% Cl^-)
Portland	I/45	0.019	0.020	0.016
	I/35	0.007	0.005	0.011
	I/45 SR-MR[a]	0.015	0.016	0.017
	I-B/55[b]	0.023	0.023	0.024
Portland with blast furnace slag	II-S/35 A	0.016	0.013	0.014[e]
Portland with pozzolan	II-Z/45 A	0.020	0.016	0.019
Portland with pozzolan	II-Z/35	0.020	0.019	0.02
Portland with fly ash	II-C/35 A	0.012	0.009	0.015
Portland with limestone	II-F/35 A	0.034	0.039	0.032
Portland blended	II-B/45 A[b]	0.020	0.017	0.021
Blast furnace slag cement	III-1/45 SR-MR[a]	0.046	0.045	0.036[e]
	III-1/35 SR-MR[a]	0.070	0.071	0.07[e]
	III-2/35 SR-MR-BC[c]	0.045	0.044	0.04[e]
	III-2/35 SR-MR-BC[c]	0.072	0.075	0.08[e]
Pozzolanic cement	IV/35A	0.034	0.030	0.033
Composite cement	V/35	0.035	0.034	0.029
	V-B/20[b]	0.014	0.014	0.015
Calcium aluminate cement	VI	0.002	0.001	0.008
Unknown	EI/5394[d]	0.005	0.007	0.001
	EI/5494[d]	0.048	0.048	0.046
	ATILH 1994 [d]	0.001	0.003	0.000
Portland raw mix		0.015	0.013	0.013

[a] Sulfate and sea-water resistant.
[b] White cement.
[c] Sulfate and sea-water resistant and low-heat cement.
[d] Special denominations (non normative).
[e] Analyzed by Volhard's method.

work potential range would be dependent upon the nature of the ISE and reference electrode used. A linear regression of the measured potentials against the logarithm of Ag^+ concentration yielded the slope of the electrode.

1.5. Potentiometric titrations

The starting cement, mortar, or concrete samples were dried at 110°C and weighed with 0.1 mg precision (2 g). They were treated with 25 mL of diluted HNO_3 (4.4 M) avoiding losses; after the effervescence ceased, the suspension was heated with continuous agitation until it boiled for 1 min. The resulting suspension, once cooled to room temperature, was partially neutralized with 2 M NaOH up to a pH of 2 (controlled with a pH meter and pH combination electrode).

After immersion of the ISE and reference electrode, nine successive additions of a standardized 0.01 M $AgNO_3$ solution were made, registering the potential after each addition. The first point was taken when the measured potential was about 310 mV and the last one at about 365 mV. These potentials correspond to the same Ag^+ concentration range used when determining the ISE slope (see later section).

The Cl^- content of the suspension and hence that of the analyzed sample, was determined by linear regression of the obtained Gran's plot (see Appendix).

1.6. Volhard's method

The analyses were performed following the standard methods described in previous works [11,12], whose experimental procedures are similar to that of BS 1881, Part 6 [13], but with filtration of the suspension instead of using nitrobenzene to coagulate the precipitate.

2. Results and discussion

The results of chloride analysis performed on the studied cement samples are shown in Table 1, together with the Cl^- contents determined by each manufacturer. A good agreement is observed between the results obtained with both techniques used in this work, potentiometric titration without filtration steps, and Volhard's method: the maximum difference found between values reported in the third and fourth columns in Table 1 is 0.005% Cl^-. The chloride contents measured through these latter methods also correlate well with the manufacturers' data (mainly obtained by XRF): the maximum difference found between values reported in the third, fourth and fifth columns in Table 1 is 0.010% Cl^-. The agreement found between results obtained with methods of essentially different character, such as titrations and XRF, may be accepted as indicating the absence of large determinate errors [15]. It is worth noting that ASTM recommendations [14] for qualifying a test method for chloride analysis in cement, establish a maximum allowable bias of 0.02% between duplicate analysis of the same sample for at least 77% of the analyzed Standard Reference Materials (SRM), and twice this value (i.e., 0.04%) for the remainder, in the case of analyzing more than seven SRM. Also as shown in Table 1, the accuracy and reliability of the proposed potentiometric titration is independent of the nature of the cement tested, and the method is also applicable to Cl^- analysis in portland cement raw material mixes.

Tables 2 and 3 show the comparative results of the analysis of acid-soluble chloride for the two prepared mortars series and for the concrete samples respectively. A good concordance is observed between the results obtained with both techniques, potentiometric titration without filtration steps and Volhard's method. The differences found for duplicate samples analyzed through both techniques are very low, especially in the critical concentration range between 0.01 and 0.1%, where the Cl^- content corrosion thresholds are usually located. Only for chloride concentrations higher than 0.15% by total weight, in the case of mortars, and higher than 0.4%, in the case of concretes, differences of about 0.010 and 0.020% between both techniques are found, and three samples of 29 (about 10%) showed differences between 0.020 and 0.030%. These latter samples correspond to the highest chloride contents both for mortars and concretes, which can be considered as excessive chloride concentrations from the point of view of reinforcement steel corrosion. The measured Cl^- contents for the two control mortar specimens (without admixed Cl^-) are in accordance with the sum of chlorides contributed by the mortar raw materials (see Experimental section). Another point of interest is the difference between the Cl^- concentrations found experimentally and those expected from the quantity of admixed NaCl in the cases of mortars with % Cl^- higher than 0.15%. These discrepancies may be ascribed to chloride leaching for the mortars with high Cl^- contents. It is also apparent from Table 2 that the different nature of aggregate (calcareous or siliceous) does not limit the applicability of the proposed potentiometric titration procedure without filtration.

Table 2
Analyzed Cl^- contents (as % by mortar weight) for the two series of mortars with increasing admixed chloride

	Calcareous aggregate		Siliceous aggregate	
Admixed chloride (% Cl^-)	Potentiometric titration (% Cl^-)	Volhard's method (% Cl^-)	Potentiometric titration (% Cl^-)	Volhard's method (% Cl^-)
0	0.008	0.012	0.005	0.005
0.010	0.015	0.013	0.009	0.009
0.025	0.025	0.022	0.025	0.025
0.050	0.051	0.048	0.044	0.046
0.100	0.106	0.105	0.085	0.083
0.150	0.150	0.131	0.137	0.138
0.200	0.198	0.199	0.145	0.127
0.400	0.392	0.365	0.381	0.378
0.625	0.542	0.531	0.536	0.560

The results shown for the specimens with admixed chloride have been corrected by subtracting the value found for the control specimens (0 admixed Cl^-).

Table 3
Analyzed Cl^- contents (as % by concrete weight) for the studied concrete samples

Potentiometric titration (% Cl^-)	Volhard's method (% Cl^-)
0.015	0.020
0.030	0.026
0.048	0.046
0.084	0.084
0.128	0.134
0.203	0.206
0.464	0.463
0.610	0.630
0.827	0.847
1.157	1.182
1.537	1.555

In dealing with analytical methods it is also important to know the precision attainable with a practical procedure, since it indicates the degree of uncertainty of the results obtained with the method. Table 4 shows the results of multiple analysis performed through the proposed potentiometric titration on different samples with varied Cl^- contents. Each sample has been analyzed at least four times. The standard deviations of results obtained with samples of Cl^- concentrations lower than 0.1% are always lower than or equal to 0.0025%, while for samples with higher chloride contents the standard deviations fall in the range between 0.005 and 0.007%, except for two samples that show higher deviations (0.018 and 0.045%). These two latter unusually high deviations are probably due to accidental errors. It is worth noting that no rejection of data has been performed for the results reported in this work. Taking into account the obtained standard deviations, the measured percent chlorides may be expressed by rounding to the nearest 0.001% for samples with Cl^- concentrations up to 0.1%, and by rounding to the nearest 0.01% for samples with higher Cl^- contents, if the experimental conditions are similar to those used in this work. The degree of precision attained with the proposed analytical method may be considered as satisfactory; although it seems that some improvement in precision may be obtained by a refinement of the experimental procedure to minimize accidental errors.

On the basis of the results obtained in this work it may be stated that acid-soluble chloride in cement, mortar, or concrete may be analyzed by potentiometric titration with end-point detection through Gran's method, obviating the filtration steps. The accuracy and reliability of the proposed method is at least similar to that of a laboratory reference procedure such as Volhard's method.

The main advantage of the proposed potentiometric titration procedure, apart from the elimination of the filtration step, is the ease for data acquisition due to the stability of

Table 4
Reproducibility of measured Cl^- contents (as % by total weight) obtained with the proposed potentiometric titration without filtration for different samples

Sample	% Cl^-				Mean value (% Cl^-)	Standard deviation (% Cl^-)
Concrete	0.0138	0.0146	0.0154	0.0154	0.0148	0.0008
Cement I/45	0.0160	0.0180	0.0181	0.0184	0.0186	0.0013
	0.0187	0.0194	0.0198	0.0203		
Concrete	0.0294	0.0294	0.0302	0.0303	0.0298	0.0005
Concrete	0.0455	0.0473	0.0481	0.0489	0.0475	0.0015
Concrete	0.0804	0.0832	0.0856	0.0858	0.0838	0.0025
Concrete	0.1217	0.1282	0.1310	0.1315	0.1281	0.0045
Concrete	0.1976	0.1995	0.2033	0.2095	0.2025	0.0052
Concrete	0.4399	0.4624	0.4675	0.4840	0.4635	0.0182
Concrete	0.6024	0.6055	0.6151	0.6154	0.6096	0.0066
Concrete	0.7279	0.7358	0.7385	0.7418	0.7360	0.0059
Concrete	1.4871	1.5200	1.5290	1.5391	1.5367	0.0445
	1.6082					

ISE potential readings in the past end-point region. Its drawbacks are the necessity of obtaining the ISE slope and a more involved calculation than that performed in the first derivative method for end-point detection. Nevertheless, measuring the ISE slope before each session is an effective test for the electrode performance and for chloride contamination of labware or reagents, since the slope is rather sensitive to this type of contamination. So this determination may be considered as a helpful means of keeping quality control in the laboratory work. On the other hand, the calculation of Gran's function values from the raw experimental data and the linear regression of final plot may be easily performed with a programmable hand-held calculator or a computer. This last step may also be obviated using the commercially available Gran's plot papers.

3. Conclusion

The potentiometric titration procedure described in this work, which makes use of Gran's method for end-point detection, allows the elimination of the filtration steps in the analysis of acid soluble chloride in cement, mortar, or concrete. The accuracy and reliability of the proposed technique is similar to that of a laboratory reference procedure such as Volhard's method, for a Cl^- concentration range as wide as 0.01 to 1.5% by total weight.

Acknowledgments

This work has been financially supported by the Consellería d'Educació i Ciència de la Generalitat Valenciana through project GV-3224/95. We thank the following Spanish cement manufacturers for providing the analyzed cement samples: Compañía Valenciana de Cementos Portland (Sant Vicent del Raspeig, Alacant), Cementos Rezola (Arrigorriaga, Vizcaya), Cementos Asland (Villaluenga de la Sagra, Toledo), Lemona Industrial (Lemona, Vizcaya), La Auxiliar de la Construcción (Tenerife), Hornos Ibéricos Alba (Carboneras, Almería), and Cementos Molins (Sant Vicenç dels Horts, Barcelona). We also thank Professor Andrade for her advice and valuable comments.

Appendix: Mathematical treatment involved in Gran's plot method

Let us suppose a volume V_X of test solution with an unknown concentration C_X of Cl^- ion, which is being titrated with a standard solution with known concentration C_S of $AgNO_3$, using a Ag^+ ISE to follow the potentiometric titration. Since Ag^+ concentration is low during the whole titration, its activity coefficient is constant and the electrode potential reading, E, may be expressed as in Eq. (1):

$$E = E' + S \log C_{Ag^+} \tag{1}$$

where E' is a constant potential and S is the electrode slope whose value must be determined. After the equivalence point of the titration, when a volume V_S of titrant has been added E becomes [see Eq. (2)]:

$$E = E' + S \log\left[\frac{V_S C_S - V_X C_X}{V_S + V_X}\right] \tag{2}$$

Taking antilogarithms and rearranging Eq. (2) gives Eq. (3):

$$\begin{aligned}(V_S + V_X) \cdot 10^{E/S} &= V_S C_S \cdot 10^{E'/S} - V_X C_X \cdot 10^{E'/S} \\ &= BV_S - A \end{aligned} \tag{3}$$

where A and B are constants. A plot of the experimental function against V_S yields a straight line, whose intersection point with the x axis corresponds to the titrant volume equivalent to the quantity of Cl^- ion in the test solution. This volume may be obtained graphically with commercially available Gran's plot papers or by linear regression of the obtained data points.

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