A New Procedure Covering the Diagnosis of Hardened Structural Concrete in Service

Ferran Gomà[1], M.ª Teresa Pinheiro-Alves[2] and Mónica Vicente[3]

[1]*Polytechnical University of Catalonia, Avinguda Diagonal n.649, 08028 Barcelona, Spain.*
[2]*University of Évora, School of Science and Technologies, Apartado 94, 7002-554 Évora, Portugal, <tpa@uevora.pt>.*
[3]*Formicontrol Laboratory, Plaça Riera n.9, 08459 Sant Antoni de Vilamajor, Barcelona, Spain, <formicontrol@yahoo.com>.*

ABSTRACT

Nowadays, there are no effective chemical analysis methods to determinate the cement content on hardened concrete, which occurs because of the errors in the gravimetric determination of the soluble silica. By this fact, a new procedure is given for determining the soluble silica, which has a lower standard deviation compared with the existing methods. This new method allows also obtaining more accurate results on the water/cement ratio.

INTRODUCTION

Since the cement began to be used on the fabrication of concretes, many were made. Currently, the main objective is to fabricate concretes with the less cement contents, keeping or improving their behaviour. This occurs because of its high cost of manufacture and high quantities of CO_2 released to the atmosphere on its fabrication, making it a non-sustainable material. To maintain the same content of the binder, the cement contents reduction on the concrete implicates their substitution by other materials, like mineral admixtures, which are more sustainable for the environment. Despite these aspects, the concrete remains as the most used material on construction, letting us do any kind of structure, which is justified by his high versatility.

The "big boom" of the construction on concrete structures began after the Second World War. Many of those structures and others built after, doesn't have project specifications, which complicates rehabilitation works. Because of the climate changes and the natural resources needed to fabricate concrete is important to rehabilitate the older constructions. To do that, is important to know the concrete specifications.

Nowadays, in almost every developed country exists a decrease of the volume of new construction and the increase of rehabilitation works. By these facts, more reliable methods need to exist to determinate the materials used on those constructions. One of those cases is the determination of Portland cement content on hardened concrete.

Currently, the amount of cement and the water/cement ratio are standardised in ASTM C 1084:2002 and the BS 1881-124:1988. The procedures of these two standards do not have operational validity because of their errors in the gravimetric determination of the soluble silica. These errors are still unknown and, because of this, they give standard deviations that are too high. A new procedure is given for determining the soluble silica with a standard deviation that is three times lower than any other existing method. This method for silica determination has a lower standard deviation. It has been applied to determine the soluble silica in concrete in order to obtain the amount of cement with operational validity, together with the water/cement ratio.

From all the methods that have been employed in the silica determination, the safest and most approximate is the chemical gravimetric method. This has not yet been improved by any of the alternative chemical or physical techniques, like automated image analysis techniques [Elsen et al 1995; Wong & Buenfeld 2009]. The best procedures employed in the chemical gravimetric method for the determination of silica are those included in the standards ASTM C 114 and EN 196-2:2005. These methods provide precision values of 0,16%. The application of the silica determination to establish the cement content in hardened concrete from the determination of the soluble silica in an acid medium is affected by the same errors of the general method on which it is based and also involves a high standard deviation value. Variation in cement content ASTM C 1084:2002, 71 Kg/m^3, and BS 1881-124:1988, 50–60 Kg/m^3. The statistical deviations found in the determination of soluble silica in joint testing by ASTM and BS standards have turned out to be too high for obtaining operational results for the determination of the cement content in concrete. However, this reality was for the first time criticised by Neville [Neville 1999; Neville 2003] that said the results obtained for the water/cement ratio have not been technically operational, nor were other alternative methods.

EXPERIMENTAL INVESTIGATION

In order to determine the soluble silica, it should be insolubilised by progressive dehydration and evaporated to dryness, during which the silicic acids must be in a totally polymerised amorphous state. The current methods produce silica with unknown and not enough degree of polymerisation and, eventually, remain more or less the colloidal state. This polymerised silica, even in totally polymerisation state, is not completely insoluble in the acid dissolutions that are employed in the extraction operation of the cations and in the washings, so that a small, variable quantity, (1 to 2%) of resolubilised silica passes into the filtrate using current procedures. The determination of this solubilised silica is only partially recoverable for the same solubility reasons. The enormous amount of research work, over nearly a century, has gone into the gravimetric method in order to prevent the insolubilised silica passing into the filtrate operations without success. Up to now, none have been able to explain the causes of the solubility of this silica after its insolubilisation. Nor has it been established whether this passage of the silica into the solutions is in a colloid state or a true solution.

Demonstration of the Causes of the Errors

The analytical sample shown in the following Tables 1 and 2, is a homogenised sample from the Triassic Bunsdsandstein, which is sand with a high silica content of 78,5 % referred to the dehydrated sample at 110ºC. All results obtained from them, lower than 78,5%, are affected by negative errors.

The following Table 1 indicates that the temperature of 170ºC is the optimum value. If the temperature is higher than 200ºC, the silicates recombine to form soluble silicates and this means that higher temperatures cannot be employed. An additional treatment with anhydride acetic, gives a better results.

Table 1. Results as a Function of the Insolubilization Temperature

95ºC			110ºC			170ºC			240ºC		
1st SiO_2	2nd SiO_2	Total SiO_2	1st SiO_2	2nd SiO_2	Total SiO_2	1st SiO_2	2nd SiO_2	Total SiO_2	1st SiO_2	2nd SiO_2	Total SiO_2
76,7	0,90	77,6	78,2	0,13	78,3	78,1	0,20	78,3	77,3	0,39	77,7
77,2	0,70	77,9	78,2	0,05	78,3	78,0	0,22	78,3	77,3	0,31	77,6
77,5	0,53	78,0	77,7	0,40	78,3	78,2	0,35	78,5	76,8	0,50	77,3
76,6	1,10	77,7	77,4	0,52	77,9	77,8	0,20	78,1	77,5	0,38	77,9
77,2	0,58	77,8	77,5	0,60	78,1	77,6	0,26	77,9	77,6	0,40	78,0
76,7	0,82	77,5	77,6	0,63	78,2	77,9	0,30	78,2	77,1	0,45	77,5
X_i		77,7			77,7			78,2			77,7
σ		0,17			0,14			0,18			0,24
vc		0,22			0,19			0,23			0,31

X_i - average; σ - statistical deviation; vc - variation coefficient (%); 2ª SiO_2 - silica that passes into extraction and washings filtrates.

In the Table 2 we can see that the ASTM C 114 and BS 1881-124 results of the silica that passes into the dissolution are a function of the temperature and hydrogen ions concentration of the extraction and washing solutions. Above +5ºC, the effect of temperature and low hydrogen ion concentration of less than 4 M, produces a depolymerisation of the polysilicic acids effect resulting in soluble monomer acids. This effect is produced by a true dissolution and not by any colloidal effect.

The results of EN 196-2 show how the effects of high temperature and low pH prevail on the partial protector effect of the opposite colloid sign. The colloidal form of silica is destroyed when the polymerisation of the silica in the insolubilisation is carried out to completion. In order to achieve this state, the silica must be dehydrated, in an open atmosphere at a temperature of 170ºC under epiradiated heat for thirty minutes. The dry product must then be treated with anhydrous acetic acid and evaporated to dryness at the same temperature. These conditions have never been taken into account in any procedures and constitute an important point in the author's new method. The passage of the colloidal silica does no produce silica-molybdenum complexes, which means it cannot be recovered by the generalised colorimetry that is normally system employed. It is, therefore another cause of negative error. The effect of the colloids as a solution to the problem has become a very significant generalised error so that the standards have accepted this solution as valid and/or an alternative procedure.

The main difficulty of the ASTM C 114, EN 196-2 and BS 1881-124 lies in the small, variable and uncontrollable amount of silica that passes into filtrates of the soluble salts

extraction and the associated washing operations. The recovery of the silica that passes into the solution, when performed by colorimetry from the silica-molybdenum complexes is partial because the colloidal silica does not form silica-molybdenum complexes. The currents cited methods for determining the soluble silica in order to find the cement content do not recover the silica that passes into the filtrate.

Table 2. Results as a Function of Extraction and Washing Solutions Temperature and pH

ASTM C 114 & BS 1881-124		EN 196-2	
Extraction: 90ºC; $[H^+]$ = 1 to 3 M Wash with diluted acid at 90ºC		Extraction: 70-80ºC; $[H^+]$ = 4 M; 5 ml of polyethylene oxide solution at 2,5 g/l Without insolubilisation, only concentrated in steam water bath	
	Total SiO$_2$		**Total SiO$_2$**
	78,0		78,0
	77,8		77,9
	78,0		78,1
	78,1		77,7
	77,5		77,8
X_i	77,9		77,9
σ	0,21		0,13
vc	0,27		0,17

All procedures use high temperature near the boiling point and low hydrogen ions concentration. These are precisely worst conditions. The errors of the all analytics steps of the method have never been into account at the same time by any author. By this fact a new method for the determination of the soluble silica is presented below.

Gomà Method for soluble silica determination

The sample should be prepared for this determination by grinding in the usual way by following, for example, BS 1881-124 or ASTM C 1084 instructions, until an approximate analytical sub sample, about 25 g, is obtained. The entire remaining part should be ground so that it passes through a 75 μm sieve as an analytical sample.

Three or four g ± 0,001 of the analytical sample, dehydrated at 105ºC to be analysed is weighed and put into a small 25 ml beaker. Three to five ml of water is added to the sample and then stirred with a glass rod to form a slurry. This slurry, which warrants the total necessary dispersion state, is slowly poured "drop by drop" into 150 ml of dilute hydrochloric acid 1+9 dissolution, previously cooled to 0-1ºC in a 300 ml beaker with magnetic stirring. An ice-cube of distilled water is added to this beaker to prevent the temperature increasing during the 30-minute reaction of the sample. Under these conditions, no precipitated silica gel is formed in the reaction and is not necessary to recover it by 0,47 M Na_2CO_3 usual treatment. The liquid should then be immediately decanted through a

medium ash less filter and the residue washed with water cooled to 0-1ºC in equilibrium with ice.

The filtrate and washings should then be transferred into a porcelain dish of about 250 ml capacity. Twenty ml of concentrated hydrochloric acid is added and evaporated to dryness under epiradiator heat in such a way that the height from the bottom of the dish to the heat focus produces a temperature of 170 ± 5ºC in the dry material, as indicated on a thermometer placed at the bottom of the dish under dry conditions. The evaporation is carried out in a dustproof glass cabinet and left until complete insolubilisation is obtained. When dryness is obtained, it should be left to cool and 20 ml of concentrated hydrochloric acid carefully added and evaporated again to dryness. When dry state is reached, the dehydration operation should be continued for another thirty minutes. After this period of time, it should be left to cool until the temperature drops below 100ºC and then 20 ml of anhydrous acetic is added. The evaporation is continued under the epiradiator heat.

When it is completely evaporated, the dehydration operation is continued at the same temperature for another thirty minutes and then the dish is allowed to cool until it reaches room temperature. Silica prepared in this way is completely polymerized and is practically insoluble in a "cold", 0 to 3ºC, solution of hydrochloric acid at a concentration of 1:1.
Two distilled water ice cubes are added to the dish when cold and 15 ml of hydrochloric acid, 1:1, is added over the ice and it is left to digest for 20 minutes (Figure 1). The large silica particles are then broken up with a flat tip glass rod and the mixture is filtered through a medium texture ash less filter that has already been described earlier in this paper and then it is washed with cold water at 0-1ºC with ice in equilibrium, until chloride ions are eliminated. The silica that passes into the solution, under these conditions, is a minimum and constant quantity of less than 1 mg, which can be taken into account without any need to recover it.

Fig. 1. Extraction

The filter with the silica is calcinated in a platinum crucible, at a temperature of 1.200ºC during forty minutes. Before calcination is due to confirm the constancy of weight of the crucible. It is then removed from the muffle oven and placed inside a desiccators which contains concentrated sulphuric acid or magnesium per chlorate or P_2O_5. After some seven or eight minutes, the crucible, if it is platinum, is already cold enough to be weighed

immediately on a balance. The silica obtained from these analytical treatments, coming from the concretes, is very pure and there is no need to determine its purity with sulphuric and hydrofluoric acids, unless there are additions containing iron in a significant quantity. This can be seen by the colour of the silica after calcination. In this case it is not white and it is necessary to obtain its exact value.

Comparative trials between Gomà's Method and BS 1881-124 on hardened concrete samples

Two concretes were prepared with the following specifications:

Concrete A - Cement CEM I-52,5 R; 300 kg/m^3; Cement:Fines:Coarse: 1,0:2,0:3,4; Aggregates: Fine and Coarse Mycritic Limestone; w/c = 0,6; Bulk Density 2.220 kg/m^3; Soluble SiO$_2$ Content of Cement 19,5%; Insoluble Residue 0,95%; Soluble SiO$_2$ Content of Aggregates 0,22%.

Concrete B - Cement CEM I-52.5 R; 230 kg/m^3; Cement:Fines:Coarse: 1,0:2,7:3,5; Aggregates: Fine, sand and Coarse, Granitic; w/c = 0,6; Bulk Density 2.190 kg/m^3; Soluble SiO$_2$ Content of Cement 19,5%; Insoluble Residue 87,0%; Soluble SiO$_2$ Content of Aggregates 0,25%.

These two concretes were analysed by the method from the BS 1882-124 and the Gomà's Method and compared.

RESULTS AND DISCUSSIONS

The results obtained for the two methods are the indicated in the following Table 3.

With the Gomà's method is possible to achieve values closer to the cement content of the fabricated sample than the ones obtained by the BS 1881-124 method, making it a better method. The smaller statistical deviation of the proposed procedure for the soluble silica determination leads to a significantly better approximation for obtaining the water/cement ratio in the hardened concrete making it possible to obtain the water/cement ratio with a true operational validity.

CONCLUSIONS

The following general conclusions can be drawn from the study provided in this paper:

- The effects of high temperature and low pH of the extraction and washings dissolutions are the causes of the wide variation in the existing methods for determination of the soluble silica;
- A better method for determination of the soluble silica was obtained, Gomà's Method;
- Gomà's Method allows obtaining more accurate results for the determination of the cement contents on hardened concrete;
- A more accurate result for the cement content also implicates a more accurate result for the water/cement ratio.

Table 3. Comparative Analysis Between Gomà's Method and BS 1881-124 on Hardened Concrete Samples

	Concrete A		Concrete B	
	BS 1881-124	Gomà's Method	BS 1881-124	Gomà's Method
SiO_2 aggregates (%)	0,11	0,22	0,18	0,25
SiO_2 cement (%)	19,3	19,5	19,3	19,5
Total SiO_2 concrete (%)	2,60	2,81	2,21	2,16
	2,44	2,89	1,90	2,18
	2,45	2,92	1,94	2,21
	2,36	2,87	1,98	2,27
	2,55	2,83	2,03	2,29
	2,63	2,78	2,14	2,24
	2,54	2,79	1,85	2,25
	2,51	2,81	2,17	2,20
	2,53	2,82	2,10	2,24
X_i	2,51	2,84	2,03	2,23
σ	0,08	0,04	0,12	0,04
vc	3,18	1,55	5,91	1,79
X_i of cement content (kg/m^3)	278	302	212	227
Max. cement content (kg/m^3)	292	312	233	238
Min. cement content (kg/m^3)	261	296	192	218

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