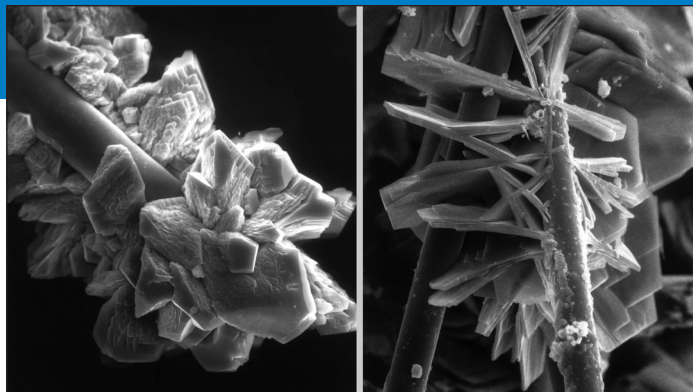


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Novel Characterization Techniques and
Advanced Cementitious Materials:
Tribute to James J. Beaudoin

SP-312

Editors:
Mohammad Pour-Ghaz, Aali R. Alizadeh, and
Jason Weiss



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Preface

With the recent quest for developing sustainable infrastructure materials, there is a need for more advanced material characterization techniques at different length scales that can provide insight to the nature and fundamental behavior of the new classes of cementitious materials as they are becoming available. These methods can be used to predict the mechanical properties, microstructural aspects, and long-term performance of different cementitious systems. Examples of these novel techniques that have been recently used for material characterization include nuclear magnetic resonance spectroscopy, nano- and micro-indentation, X-Ray tomography, and atomic force microscopy. Recently, major progress has also been made in the development of novel cement-based systems such as C-S-H/polymer nanocomposites and self-healing materials. This Special Publication aims at providing a treatise on the current research in the areas related to innovative characterization methods and analytical techniques used in the cement and concrete research, as well as the development of novel basic and composite cementitious materials. This Special Publication is developed to honor the significant contributions made by Dr. James J. Beaudoin over the past four decades to the advancement of cement and concrete science. Dr. Beaudoin, a Researcher Emeritus, Fellow of the Royal Society of Canada, and Fellow of the American Ceramic Society, has authored more than 500 publications, including five books, 20 book chapters, encyclopedia contributions, more than 270 research journal papers, 17 patents, and numerous discussions and book reviews. He is the recipient of numerous prestigious awards, including the Della Roy Lecture Award on applications of nanotechnology in cement science (American Ceramic Society, 2005), the Wason Medal for Materials Research (American Concrete Institute, March 1999) and the Copeland Award (American Ceramic Society, 1998). The papers included in this Special Publication were presented in two sessions in ACI Fall 2014 Convention, Oct 26-30, 2014.

Editors

Mohammad Pour-Ghaz, Aali R. Alizadeh, and Jason Weiss

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EVALUATION OF AN ACCELERATED CHARACTERIZATION METHOD FOR POZZOLANIC REACTIVITY

Saamiya Seraj, Maria C.G. Juenger
The University of Texas at Austin

Synopsis: Concerns about the future availability of traditional supplementary cementitious material (SCM) sources, like fly ash, have prompted the search for a wider variety of materials that could be used as SCMs in concrete. An important criterion for an SCM is pozzolanic reactivity, which is its ability to react with calcium hydroxide in the presence of water to form calcium silicate hydrate (C-S-H). ASTM criteria for SCMs address pozzolanic reactivity indirectly by measuring the compressive strength of SCM containing mortars, or more specifically the strength activity index (SAI). More direct methods of assessing pozzolanic reactivity include measuring the reduction of calcium hydroxide (CH) in cementitious pastes through methods like thermal gravimetric analysis (TGA). However, both direct and indirect tests to evaluate pozzolanic reactivity take a considerable amount of time due to the slow nature of certain pozzolanic reactions. Alternatively, the Chapelle test, which measures the amount of CH fixed by the SCM in solution at high temperatures, can serve as an accelerated test method for screening out potential SCMs. In this paper, the accuracy of the Chapelle test for measuring pozzolanic reactivity is evaluated for a variety of SCMs with different physical and chemical characteristics by comparing it with more traditional test methods like SAI and CH measurement through TGA.

Keywords: Chapelle Test, Concrete, Pozzolans, Reactivity, SCMs

AUTHOR BIOGRAPHY:

Saamiya Seraj received her Ph.D. from the University of Texas at Austin in 2014. Her Ph.D. research was focused on natural pozzolans, which included evaluating the effect of these materials on concrete strength, durability and mixture workability, as well as understanding the hydration chemistry of the natural pozzolans in cementitious systems.

Maria C.G. Juenger is a professor in the Department of Civil, Architectural, and Environmental Engineering at the University of Texas at Austin. Her teaching and research focus on materials used in civil engineering applications. Trained as a chemist and materials scientist, she primarily examines chemical issues in cement-based materials. These include: hydration chemistry of portland cement and supplementary cementitious materials; the development of microstructure in cementitious systems; and chemical deterioration processes in concrete.

1.0 INTRODUCTION

Supplementary cementitious materials (SCMs) are very important to the concrete industry due to the benefits they provide in terms of sustainability, economy, and long-term concrete durability. According to ASTM International, SCMs are inorganic materials that can contribute to the properties of cementitious mixtures through hydraulic and/or pozzolanic activity (ASTM C 125, 2014). As such they are often used as a partial cement replacement in concrete. Some of the traditional SCMs, like fly ash, are industrial by-products, which make them cheaper and more sustainable to use in concrete mixtures than ordinary portland cement, whose worldwide production is responsible for 5% of the global anthropogenic CO₂ emissions (Humphreys and Mahasenan, 2002). However, due to existing and evolving environmental regulations (EPA, 2014a-c; Heidrich et al., 2013; Sear, 2009; Barnes and Sear, 2006), there has been a considerable amount of concern regarding the future availability of traditional SCM sources like fly ash. This has prompted the search for alternative materials that could replace traditional SCMs in concrete and provide similar strength and durability benefits.

One of the most important criteria when qualifying new materials as SCMs is to look at their pozzolanic reactivity, which is their ability to react with calcium hydroxide (CH) in the presence of water to form calcium silicate hydrate (C-S-H). Understanding the pozzolanic reactivity is crucial as it gives an indication of the strength and durability benefits that can be derived from the use of the SCMs. ASTM C 618, the standard specification for fly ash and natural pozzolans, measures pozzolanic reactivity indirectly by looking at strength activity index (SAI), which is the ratio of compressive strength between the SCM containing mortar and the control mortar with no SCMs (ASTM C 618, 2012a; ASTM C 311, 2011b). More direct methods of assessing pozzolanic reactivity include measuring the reduction of calcium hydroxide in cementitious pastes over time through quantitative x-ray diffraction (XRD), thermal gravimetric analysis (TGA) and chemical titration methods like the Frattini test (Tironi et al., 2013; Donatello et al., 2010). However, both direct and indirect tests to evaluate pozzolanic reactivity take a considerable amount of time (7 – 28 d) due to the slow nature of pozzolanic reactions in cementitious pastes. Although there are faster tests that evaluate pozzolanic reactivity by measuring electrical conductivity of solutions containing pozzolans and lime, previous literature has shown these tests to be unreliable. A detailed review of the problems associated with electrical conductivity tests can be found in a journal article by Velazquez et al. (2014).

The Chapelle test, which is the focus of the current paper, is a quick test from the French standard, NF P 18-513, Annexe A (2010), designed to measure the pozzolanic reactivity of metakaolin. The Chapelle test accelerates the pozzolanic reaction by using high temperatures, and measures the amount of calcium hydroxide that can be fixed (consumed) by the SCM in a saturated lime solution during a 16 h time period. Although the Chapelle test has been used in previous literature to measure the pozzolanic reactivity of metakaolin, zeolites and fly ashes (Paiva et al., 2012; Taylor-Lange et al., 2012; Ninov et al., 2011; Perraki et al., 2005; Antiohos et al., 2005; Kostuch et al., 1993), very little research has been conducted to evaluate the accuracy of the Chapelle test to predict pozzolanic potential. As such, the current study has compared the results of Chapelle testing on different SCMs to values derived from more traditional methods of evaluating pozzolanic reactivity like SAI and TGA. Since the Chapelle test is conducted at elevated temperatures for a non-cementitious system, comparing the results to other test methods, which are performed at ambient temperatures for a cementitious system, can give valuable insight as to whether the Chapelle test can reliably predict the pozzolanic performance of an SCM in concrete. Furthermore, since the Chapelle test was originally designed for metakaolin, a variety of SCMs have been used in the current research to observe whether the test can be reliably used for a range of materials with different physical and chemical characteristics.

2.0 MATERIALS AND METHODS

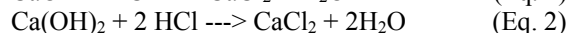
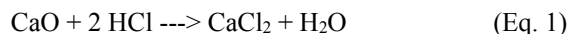
2.1 Materials

In the current study, the pozzolanic reactivity of 11 different SCMs was tested. The SCMs were sourced in the US from Texas, Idaho and Nevada. The 11 SCMs represent a broad range of physical and chemical characteristics, and consist of three pumices, three zeolites, expanded perlite, vitric ash, metakaolin, calcined shale and fly ash. The X-ray fluorescence (XRF) oxide compositions of the SCMs are presented in Table 1 and were analyzed according to ASTM

D 4326 (2011). The particle size distributions of the SCMs were also measured to observe whether the Chapelle test was sensitive to differences in particle size, when the chemical composition of the SCMs was identical. The particle size distributions of the SCMs were analyzed using a laser scattering particle size distribution analyzer and are presented in Figure 1. Along with the SCMs, inert quartz filler was also evaluated in the Chapelle test to observe the resulting CH fixed values produced by the test when a non-reactive material was tested. One cement was used for all the mixtures and it was an ASTM C 150 (2011) Type I portland cement sourced in Texas, USA. The sand used for all mortar mixtures was standard graded sand from Ottawa, Illinois, which met all the requirements of ASTM C 778 (2012). The calcium oxide (CaO) used in the Chapelle test was analysis grade, with a purity of 97%. Before testing, the CaO is heated to a temperature of 900°C to ensure that calcium hydroxide and calcium carbonate is not present. The CaO is then stored in the desiccator until tested. The sucrose used in the Chapelle test was of 99.7% purity.

2.2 Chapelle Test

According to the instructions in NF P 18-513, Annexe A (2010), for the Chapelle test, 1 g (0.002 lb) of pozzolan, 2 g of (0.004 lb) CaO and 250 ml (0.066 gal) of deionized water were combined in a flask and stirred for 16 h at 85°C (185°F), using a stirring-heating pad. A blank test, without any SCM was also run. After 16 h, the solution was cooled to ambient temperature (23°C (73°F)) within 15 min, using a combination of running water and ice bath. Immediately after cooling, 60 g (0.13 lbs) of sucrose (in 250 ml (0.066 gal) of water) was added to the solution and stirred for 15 min. 200 ml (0.05 gallons) of the solution was then filtered using a P2 grade filter paper (1-5 µm (0.00004-0.0002 in)). Five drops of 0.1% phenolphthalein indicator (in a 50% ethanol solution) was added to 25 ml (0.0066 gal) of the filtrate, and titrated with 0.1 N hydrochloric acid (HCl). The titration reactions are shown in Equations 1 and 2 and have been reproduced exactly as written in the Chapelle standard (NF P 18-513, Annexe A, 2010):



Based on the titration reactions shown in Equations 1 and 2, the Chapelle standard provides a formula to calculate the amount of CH fixed by the SCM. The formula, shown in Equation 3, uses both the volume of HCl required to titrate the blank test (v_1) as well as the volume required to titrate the test with the SCM (v_2). Duplicate testing was conducted for each material to ensure repeatability and the error was found to be less than 10%, as stated in NF P 18-513, Annexe A (2010). Equation 3 has reproduced exactly as written in the Chapelle standard (NF P 18-513, Annexe A, 2010):

$$CH \text{ fixed} = 2 \times \frac{v_1 - v_2}{v_1} \times \frac{74}{56} \times 1000 \quad (\text{Eq. 3})$$

where *CH fixed* is the amount of calcium hydroxide consumed by the pozzolan, v_1 is the volume of HCl required to titrate the blank test, and v_2 is the volume of HCl required to titrate the test with SCM.

2.3 Strength Activity Index (SAI) and Compressive Strength Tests with Fixed w/c

The strength activity index (SAI) is the compressive strength ratio of SCM containing mortar cubes to control mortar cubes made with only cement. ASTM C 618 (2012a) requires the compressive strength of the SCM mortar to be at least 75% of the control mortar's compressive strength at either 7 or 28 d. The SAI test was conducted according to the instructions in ASTM C 311 (2011b), which further refers to ASTM C 109 (2012) for the molding, curing and testing procedures for the mortar cubes. According to the ASTM standard, the SCM mortar cubes had 20% of the cement by weight replaced with SCMs, and a variable water to cementitious ratio (w/cm) to ensure constant flow across samples. In order to ensure that the variable w/cm did not bias the results against SCMs that have a high water demand, a second set of mortar cubes were made with a fixed w/cm. The w/cm for mortars containing the zeolite SCMs, which have a high water demand, were set at 0.55, while the w/cm for the other SCM containing mortars were set at 0.5. Two different w/cm were used to avoid the use of superplasticizers that would add another variable to the compressive strength results. Control mortars with no SCMs were made for each of the w/cm. The average compressive strength for each sample was calculated using three mortar cube specimens. In certain cases, if the range of the compressive strength data from the three mortar cubes was greater than 8.7% of the average, the result that deviated most from the average was discarded, as instructed by ASTM C 109 (2012). The average was then calculated from two mortar specimens instead of three and the final range of the two samples was checked to confirm whether it was less than or equal to 7.6% of the average, as required by ASTM C 109 (2012). All the compressive strength data (SAI and fixed w/c) presented in this study were within the limits prescribed by ASTM C 109 (2012).

2.4 Thermal Gravimetric Analysis (TGA)

Using thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC), the progress of pozzolanic reactions can be monitored by measuring the decrease of calcium hydroxide in cementitious pastes over time. The paste mixtures had 50 g (0.11 lb) of cementitious material and 22.5 g (0.05 lb) of water, giving the mixtures a w/cm of 0.45. The control paste had 50 g (0.11 lb) of cement, while the SCM containing pastes had 20% of the cement by mass replaced with the SCM being tested. After mixing the pastes by hand for 2 min, they were cured at room temperature and 100% relative humidity, until they reached the desired test age, which was 7, 28 and 90 d for the current study. After curing, the samples were weighed and then broken into small chunks (approximately less than 10 mm (0.39 in) in length) that were stored in a vacuum desiccator for 14 ± 1 d. The samples were reweighed after being removed from the desiccator at 14 d, and the change in weight was recorded as the amount of water lost on drying. The samples were then crushed and sieved through a No. 325 sieve (45 μ m (0.00177 in) opening) to ensure uniformity during testing. The sieved samples were stored under vacuum in a desiccator until they were tested on a thermogravimetric analyzer, with both TGA and DSC capabilities. During the test, the chamber gas used was nitrogen and the samples were contained in alumina crucibles with lids. The weight losses of the samples were recorded as they were heated from 40°C (104°F) to 1000°C (1832°F), at a rate of 20°C/min (36°F/min). The measured weight loss was used to plot the TGA curve. The heat flow during this interval was recorded as well and was used to plot the DSC curves. Figure 2 shows a representative TGA/DSC plot. The DSC curve was used to pinpoint the exact temperatures between which the calcium hydroxide in the paste decomposed (labeled points A and B in Figure 2). Using those temperatures, the weight loss due to calcium hydroxide decomposition was calculated from the TGA curve. Finally, using molecular weights and the recorded weight change from water loss in the desiccator, the weight loss from calcium hydroxide decomposition was converted to the calcium hydroxide content per gram of cement in the paste. Duplicate testing was conducted for each sample to ensure repeatability. The error calculated from the range of the data was 0.01 g per g (0.000022 lb per lb) of cement or less.

3.0 RESULTS AND DISCUSSION

3.1 Results from Chapelle Test

The results from the Chapelle test are presented in Figure 3. The error bars represent the range of the data from duplicate testing. From Figure 3, it can be seen that Pumice-N had the highest CH fixed value in the Chapelle test, followed by Metakaolin-D and Zeolite-Z. The CH fixed values of Pumice-D and Pumice-S were significantly lower than that of Pumice-N, which had a finer particle size distribution. This indicates that despite the chemical composition of the pumices being similar, the Chapelle results were sensitive to differences in pozzolanic reactivity that results from a finer particle size distribution. As expected, the inert quartz had the lowest CH fixed value. It must be noted here that although inert, the value of the CH fixed for quartz is not zero. The non-zero value for the inert quartz could be a result of the quartz becoming more soluble at the higher temperature environment of the Chapelle test. The non-zero value could also be a result of the Chapelle solution being over saturated. While oversaturation is not a problem for reactive SCMs that consume the CH through the pozzolanic reaction, for inert materials some of the CH can precipitate and be removed during the filtration process. This might make it seem as though some of the CH was fixed by the quartz. The non-zero value of quartz establishes the need to find a threshold value for the CH fixed results, which must be crossed before an SCM can be considered to have pozzolanic reactivity.

3.2 Correlation of Chapelle Test Results with Compressive Strength

Results from the SAI and the fixed w/cm compressive strength testing are summarized in Table 2. Please note that the fixed compressive strength results are presented as a percentage of the control mortar made at the same w/cm, since the zeolite mortars were made with a higher w/cm than the rest of the mortars. Since strength of concrete is correlated to C-S-H growth, and CH is being depleted by the pozzolan to form C-S-H, we expected a correlation between strength gain and CH consumption. Comparison of the Chapelle results with the SAI results show that SCMs with a high amount of CH fixation in the Chapelle test (Pumice-N, Metakaolin-D and Zeolite-Z) have mortars with a 28 d SAI value of 100% or more. Additionally, similar to the Chapelle results, the SAI results of the Pumice-D and Pumice-S mortars were lower than that of the Pumice-N mortar, at both 7 and 28 d. However, the 28 d SAI result of Pumice-D was higher than that of the Pumice-S, whereas the Chapelle results for Pumice-D and Pumice-S show their respective pozzolanic reactivities to be similar. Since Pumice-D is finer than Pumice-S it shows that the SAI test might be more

sensitive to particle size differences than the Chapelle test. Correlation between the Chapelle test and the 7 and 28 d SAI test is presented in Figures 4 and 5. The coefficient of determination (R^2) value is higher for the correlation between Chapelle test and the 28 d SAI results compared to the 7 d SAI results. However, even the 28 d SAI correlation with the Chapelle test is not very strong, with the results for Zeolite-T and Zeolite-A showing the highest deviation from the linear trend line. It is interesting to note that despite failing the SAI test, Zeolite-T shows similar Chapelle values to Pumice-D, Pumice-S and Perlite-I (Figure 5). Additionally, Zeolite-A, which also failed the SAI test has similar Chapelle values to Vitric Ash-S and Shale-T, both of which has acceptable 28 d SAI values (Figure 5). The cause of the deviation is most likely the high w/cm that was used to make the SAI mortar cubes for these two zeolites that have a high water demand.

As such, the Chapelle results were next compared to the compressive strength results made with a fixed w/cm ratio. Pumice-N, Metakaolin-D and Zeolite-Z, which had high CH fixed values in the Chapelle testing showed an early reactivity in compressive strength results, with similar strength to the control mortar (of the same w/cm) at 7 d, and higher strength at 28 d. However, the SCMs that performed well in terms of long term compressive strength (90 d) were not clearly distinguishable in the Chapelle results from SCMs that had low compressive strengths even after 90 d of hydration. For example, the Pumice-D SCM, which had a 90 d mortar strength that was 16% higher than the control, had a similar CH fixed value to Zeolite-T, which had a 90 d mortar strength that was 20% less than that of the control. Similarly, the Vitric Ash-S, Shale-T and fly ash SCMs, all of which had 90 d mortar compressive strengths that were similar to or higher than the control, had CH fixed values that were similar to Zeolite-A, which had a mortar strength that was 30% less than that of the control. The correlation between the fixed w/cm compressive strength results and the Chapelle results are presented in Figures 6-8. The R^2 values, which get progressively worse with increase in time, also indicated that the Chapelle results correlate better with early age compressive strength (7 d) vs. long term compressive strength (90 d), when a fixed w/cm is used. From the R^2 values it can also be observed that despite fixing the w/cm, the correlation between compressive strength and Chapelle results does not improve. Similar to the SAI, the two zeolites, Zeolite T and Zeolite-A, were again observed to have the largest deviations from the linear trend line. This indicates that perhaps these two zeolites are not suitable to be evaluated using the Chapelle test. Zeolites have a negative framework, which is balanced by exchangeable cations in its pores (Snellings et al., 2012). It is possible that these zeolites are showing a higher CH fixed value in the Chapelle test because the calcium cations are being absorbed into the zeolite structure through cation exchange, instead of being consumed through pozzolanic reaction.

3.3 Correlation of Chapelle Test Results with TGA Results

Table 2 also presents the reduction in CH content of cementitious pastes measured using TGA. Since the initial production of calcium hydroxide could be different depending upon the filler effects experienced in an SCM-cementitious system (Lothenbach et al., 2011), the TGA data are presented as a reduction over time instead of an absolute value at a particular point in time. Figure 9 shows the correlation between the depletion of CH in pastes between 7-90 d and the results of the Chapelle test. The R^2 value shows that the Chapelle results are more strongly correlated with calcium hydroxide reductions measured using TGA than compressive strength. However, with an R^2 value of only 0.73, the correlation is still not strong enough to conclusively state that the Chapelle test is a reliable predictor of pozzolanic reactivity. It must be noted that the time range used for the TGA test does not take into account the CH reduction in the first week of hydration, since pozzolanic reaction is considered to be negligible in the first few days of hydration (Lothenbach et al., 2011). For future research, however, the CH reduction should be measured from the start of hydration to measure any early reactions.

4.0 CONCLUSIONS

The current study has compared the results of Chapelle testing on a variety of SCMs to values derived from more traditional methods of evaluating pozzolanic reactivity like SAI and TGA, to assess whether the Chapelle test can reliably predict the pozzolanic potential of SCMs and their performance in cementitious mixtures. It was observed that the Chapelle test was good at identifying pozzolans with a high early reactivity, but poor at distinguishing SCMs that contributed more to long term strength. Additionally, using pumices of an identical composition but different particle size distribution, it was found that the Chapelle test was sensitive to the differences in pozzolanic reactivity

that result from a finer particle size distribution. However, the degree of sensitivity was more enhanced in the traditional methods of measuring pozzolanic reactivity like SAI and compressive strength than the Chapelle test. The Chapelle results correlate more strongly with the TGA data, which show reductions of CH in pastes over time, rather than with the compressive strength results. This could be because the underlying mechanism of CH reduction in TGA and CH fixation in the Chapelle results are the same, despite the Chapelle test being conducted in a non-cementitious system at elevated temperatures. However, the compressive strength of mortars depends not only on the pozzolanic reaction but other factors such as proper molding, compaction and finishing. Although the w/cm was fixed for the second set of compression cubes, a higher w/cm ratio was used for the zeolite mortars, which had a high water demand. Future research with the same w/cm for all mortar mixtures may improve the correlation between the Chapelle testing and compressive strength. However, it must be noted here that the compressive strength data were expressed as a percentage of the control at the same w/cm, and hence the use of the two different w/cm was not expected to have a major contribution to the poor correlation. Additionally, it was seen that the Chapelle test may not be suitable for SCMs like zeolites that can absorb calcium ions into their pores through cation exchange. Since the titration only measures the amount of calcium hydroxide left in the solution, the Chapelle test cannot distinguish between calcium ion adsorption and calcium ion depletion through pozzolanic reaction.

Despite the weak correlation between Chapelle tests and traditional methods of pozzolanic reactivity measurement, it is important to remember that the Chapelle test takes less than 24 h, while some of the traditional test methods can take up to a week or a month to produce results. As such, the authors of the current study are of the opinion that the Chapelle test can serve as a quick screening tool for new SCMs, especially if the materials have an early reactivity. However, more work needs to be done to standardize the test. Although the error was found to be less than 10% in duplicate testing, the authors observed minor changes in cooling rate and filter paper to have a big effect on the results produced. Also, since quartz has a non-zero value in the Chapelle test, more testing needs to be done to establish a threshold value for the CH fixed results, which must be crossed before an SCM can be considered to have pozzolanic reactivity. The use of a non-siliceous inert filler that will not react at higher temperatures could perhaps be used to correct for CH precipitation from oversaturation.

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References

- Antiohos S, Maganari K, Tsimas S. Evaluation of blends of high and low calcium fly ashes for use as supplementary cementing materials. *Cement & Concrete Composites*. 2005; 27: 349–356
- ASTM C 109. Standard test method for compressive strength of hydraulic cement mortars (using 2-in. or [50-mm] cube specimens). ASTM International. West Conshohocken, PA; 2012.
- ASTM C 125. Standard terminology relating to concrete and concrete aggregates. ASTM International, West Conshohocken, PA; 2014.
- ASTM C 150. Standard specification for portland cement. ASTM International. West Conshohocken, PA; 2011.
- ASTM C 311. Standard test methods for sampling and testing fly ash or natural pozzolan for use in portland-cement concrete. ASTM International. West Conshohocken, PA; 2011b
- ASTM C 618. Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. ASTM International. West Conshohocken, PA; 2012a.
- ASTM C 778. Standard specification for standard sand. ASTM International. West Conshohocken, PA; 2012.
- ASTM D 4326. Standard test method for major and minor elements in coal and coke ash By x-ray fluorescence. ASTM International. West Conshohocken, PA; 2011.
- Barnes DI, and Sear LKA. Ash utilisation from coal-based power plants. Report COAL-R-274, Hatterrall Associates, UK Quality Ash Association. 2006. Accessed on September 20th, 2014 from:
<http://www.ukqaa.org.uk/wp-content/uploads/2014/02/AshTech-2006-Barnes-Sear.pdf>
- Donatello S, Tyrer M, Cheeseman CR. Comparison of test methods to assess pozzolanic activity. *Cement & Concrete Composites*. 2010; (32): 121–127
- Heidrich C, Feuerborn HJ, Weir A. (2013). Coal combustion products: a global perspective. 2013 World of Coal Ash (WOCA) Conference. Lexington, KY; 2013 Accessed on September 20th, 2014 from:
<http://www.flyash.info/2013/171-Heidrich-Plenary-2013.pdf>
- Humphreys K, and Mahasen M. Towards a sustainable cement industry, Sub-study 8: Climate Change. 2002. Accessed on September 20th, 2014 from:
http://www.wbcsdcement.org/pdf/battelle/final_report8.pdf
- Kostuch JA, Walters GV, Jones, TR. High performance concrete incorporating metakaolin: a review. *Concrete* 2000. E & FN Spon, New York; 1993: 1799-1811
- Lothenbach B, Scrivener K, Hooton RD. Supplementary cementitious materials. *Cement and Concrete Research*. 2011; 41: 1244-1256
- NF P 18-513, Annexe A. Détermination de la quantité d'hydroxyde de calcium fixé (essai Chapelle modifié). 2010: 16-19
- Ninov J, Doykov I, Dimova L, Petrov B, Brakalov L. On the kinetics of pozzolanic reaction in metakaolin–lime–water system. *Journal of Thermal Analysis and Calorimetry*. 2011; 105: 245-250
- Paiva H, Velosa A, Cachim P, Ferreira VM. Effect of metakaolin dispersion on the fresh and hardened state properties of concrete. *Cement and Concrete Research*. 2012; 42: 607–612
- Perraki T, Kakali G, Kontori E. Characterization and pozzolanic activity of thermally treated zeolite. *Journal of Thermal Analysis and Calorimetry*, 2005; 82 (1): 109-113

Sear LKA. Coal fired power station ash products and EU regulation. Coal Combustion and Gasification Products. 2009; 1: 63-66. Accessed on September 20th, 2014 from:
<http://www.ukqaa.org.uk/wp-content/uploads/2014/02/CCGP-Journal-Dec-2009.pdf>

Snellings R, Mertens G, Elsen J. Supplementary cementitious materials. Reviews in Mineralogy & Geochemistry. 2012; 74: 211-278

Taylor-Lange SC, Riding KA, Juenger MCG. Increasing the reactivity of metakaolin-cement blends using zinc oxide. Cement & Concrete Composites. 2012; 34: 835–847

Tironi A, Trezza MA, Scian AN, Irassar EF. Assessment of pozzolanic activity of different calcined clays. Cement & Concrete Composites 2013; 37, 319–327

US EPA. Coal combustion residuals - proposed rule. 2014-a. Accessed September 20th , 2014 from:
<http://www.epa.gov/epawaste/nonhaz/industrial/special/fossil/ccr-rule/index.htm>

US EPA. Clean Air Interstate Rule (CAIR). 2014-b. Accessed September 20th, 2014 from:
<http://www.epa.gov/cair/index.html>

US EPA. Cross-State Air Pollution Rule (CSAPR) - basic information. 2014-c. Accessed September 20th, 2014 from:
<http://www.epa.gov/crossstaterule/basic.html>

Velázquez S, Monzo JM, Borrachero MV, Paya J. Assessment of the pozzolanic activity of a spent catalyst by conductivity measurement of aqueous suspensions with calcium hydroxide. Materials. 2014; 7: 2561-2576

Tables and Figures

Table 1: XRF oxide composition of SCMs

Material Name	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)	Na ₂ O (%)	K ₂ O (%)
Pumice-N	68.9	12.7	1.0	1.0	0.5	0.1	4.0	4.9
Pumice-D	69.4	12.4	1.1	0.9	0.4	0.0	3.8	5.2
Pumice-S	68.9	12.2	1.2	1.4	0.3	0.1	5.1	4.4
Perlite-I	70.3	12.8	1.2	0.9	0.1	0.1	4.7	4.7
Vitric Ash-S	64.7	11.3	0.9	3.3	1.4	0.3	3.7	5.6
Metakaolin-D	51.7	35.2	2.0	0.6	0.5	0.1	0.1	1.4
Shale-T	65.4	14.6	5.7	2.4	2.3	0.4	1.1	2.9
Zeolite-Z	65.3	10.9	2.4	2.5	0.6	0.1	0.5	4.8
Zeolite-T	62.2	11.9	1.1	2.2	0.6	0.1	1.0	1.7
Zeolite-A	59.5	12.9	2.2	5.1	0.8	0.3	3.1	2.6
Fly Ash	52.1	23.1	4.0	11.6	2.1	0.5	0.4	0.7

Table 2: Summary of SAI, fixed w/c compressive strength and TGA data (1 g = 0.0022 lb)

Material Name	SAI (%)		Fixed w/cm compressive strength (% of control)			Reduction in CH content from 7-90 d (g/g of cement)
	7 d	28 d	7 d	28 d	90 d	
Pumice-N	99	119	101	138	154	0.08
Pumice-D	82	93	80	102	116	0.04
Pumice-S	81	83	68	91	97	0.03
Perlite-I	86	94	75	96	116	0.06
Vitric Ash-S	72	83	77	94	104	0.02
Metakaolin-D	94	111	101	123	111	0.04
Shale-T	72	81	73	90	99	0.01
Zeolite-Z	71	100	94	112	114	0.05
Zeolite-T	47	61	69	74	80	0.02
Zeolite-A	60	64	67	69	70	0.02
Fly Ash	---	---	67	109	119	0.02

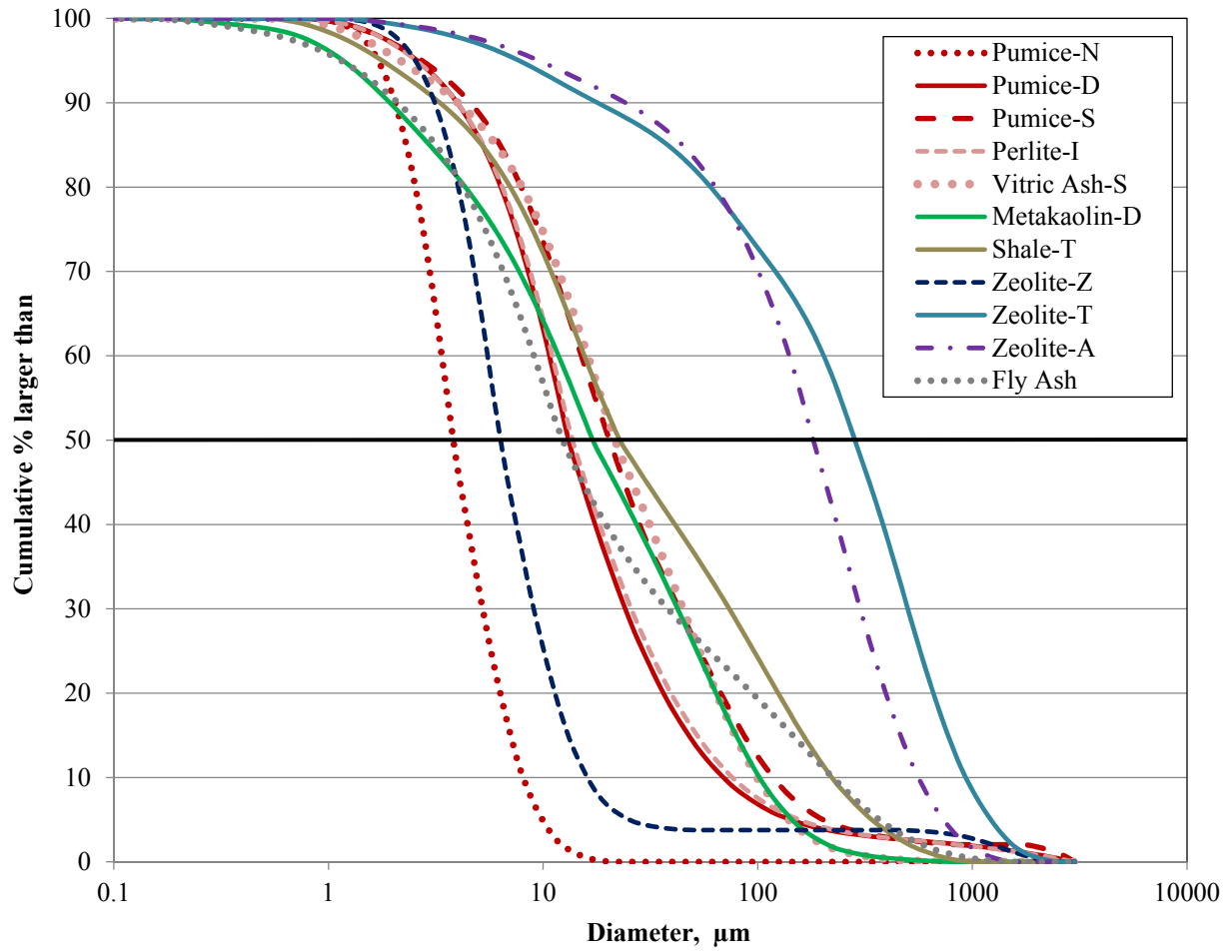


Figure 1: Particle Size Distribution of SCMs (1 μm = 0.00004 in)

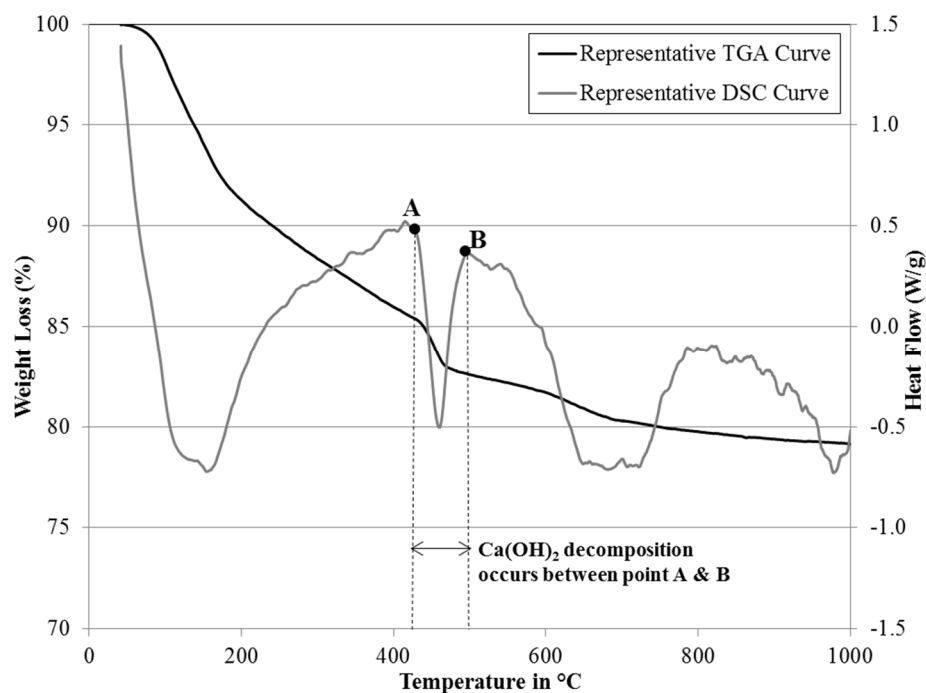


Figure 2: Representative TGA and DSC curves (500 °C = 932 °F; 1 g = 0.0022 lb; 1 W = 0.0013 hp)

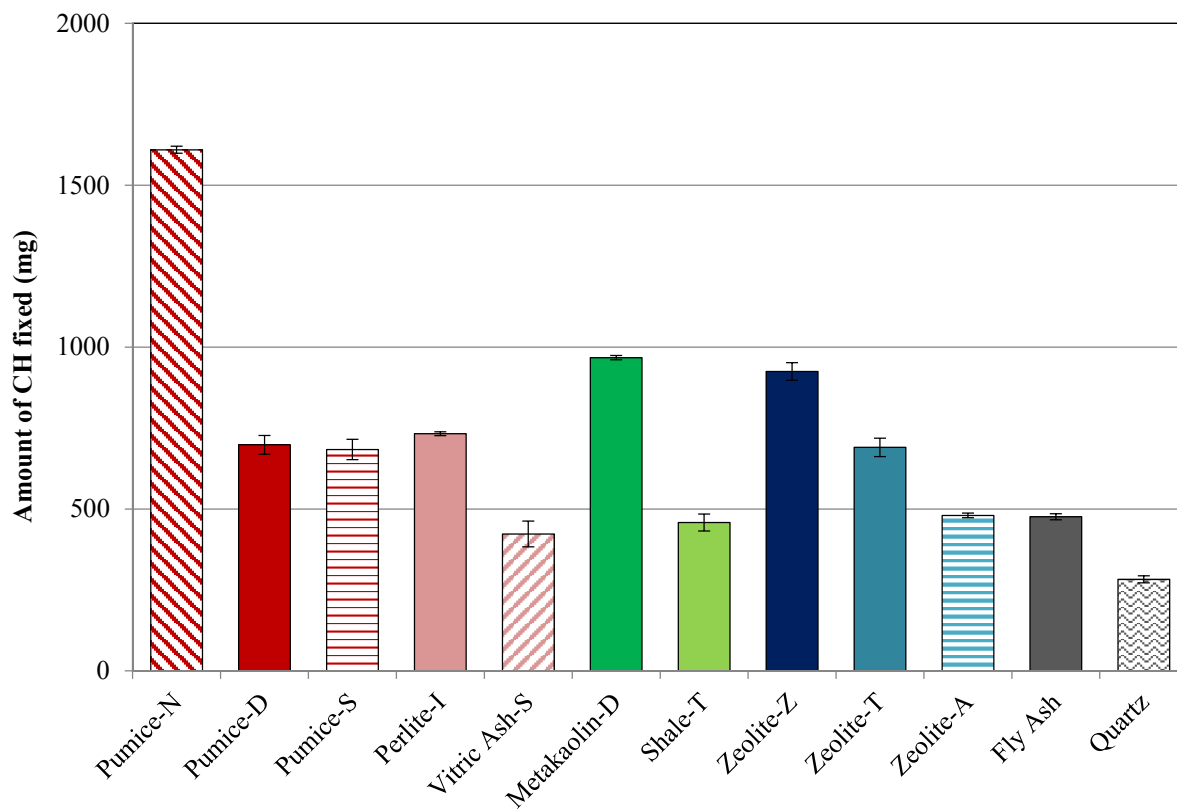


Figure 3: Results from Chapelle Testing of SCMs/Quartz (1000 mg = 0.0022 lb)

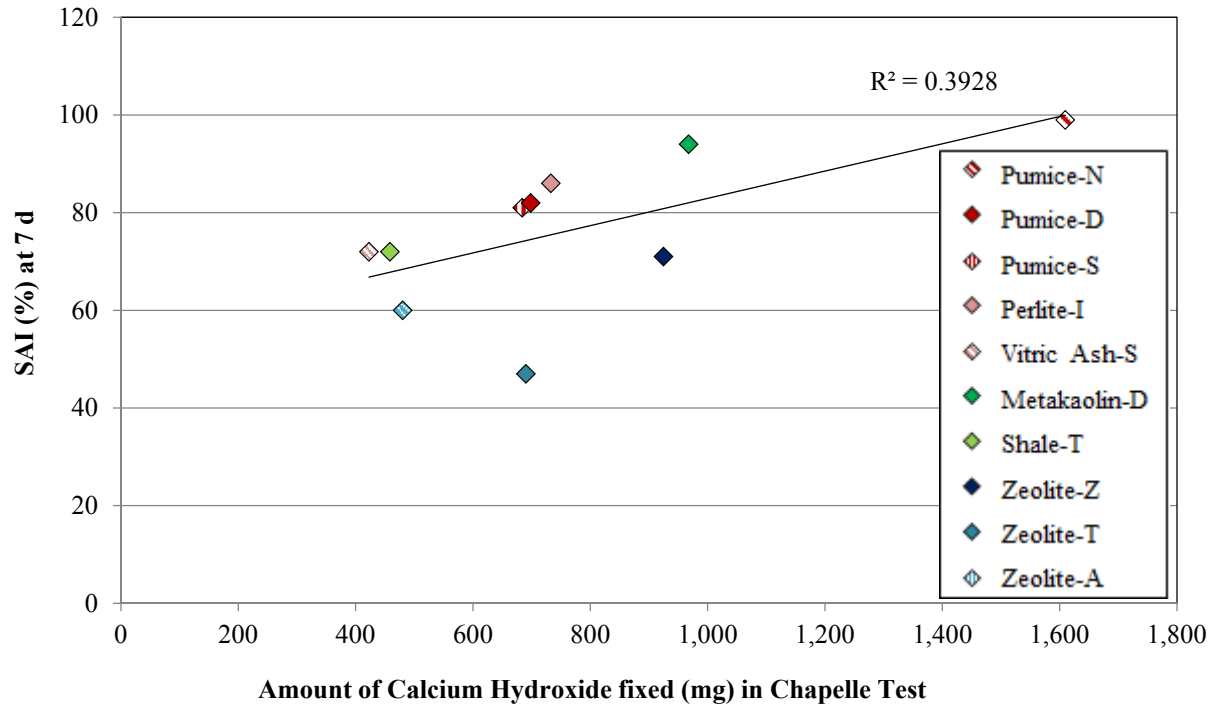


Figure 4: Correlation between 7 d SAI and Chapelle Results (1000 mg = 0.0022 lb)

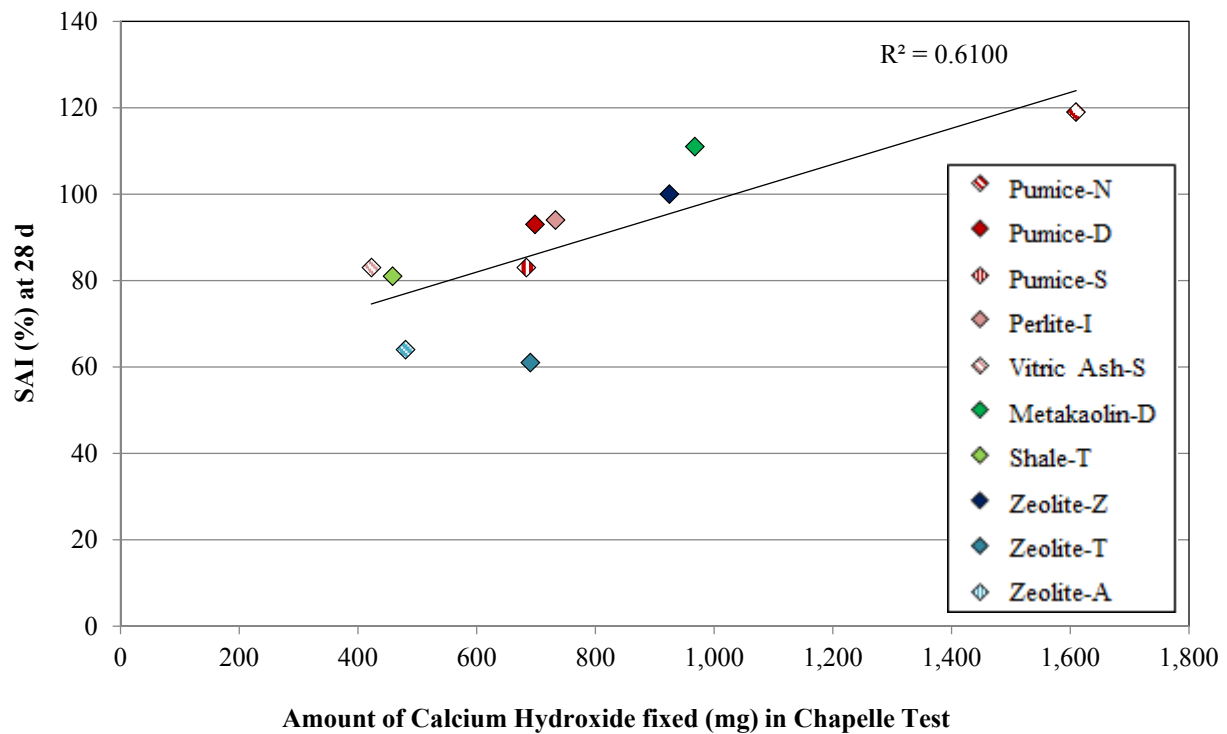


Figure 5: Correlation between 28 d SAI and Chapelle Results (1000 mg = 0.0022 lb)

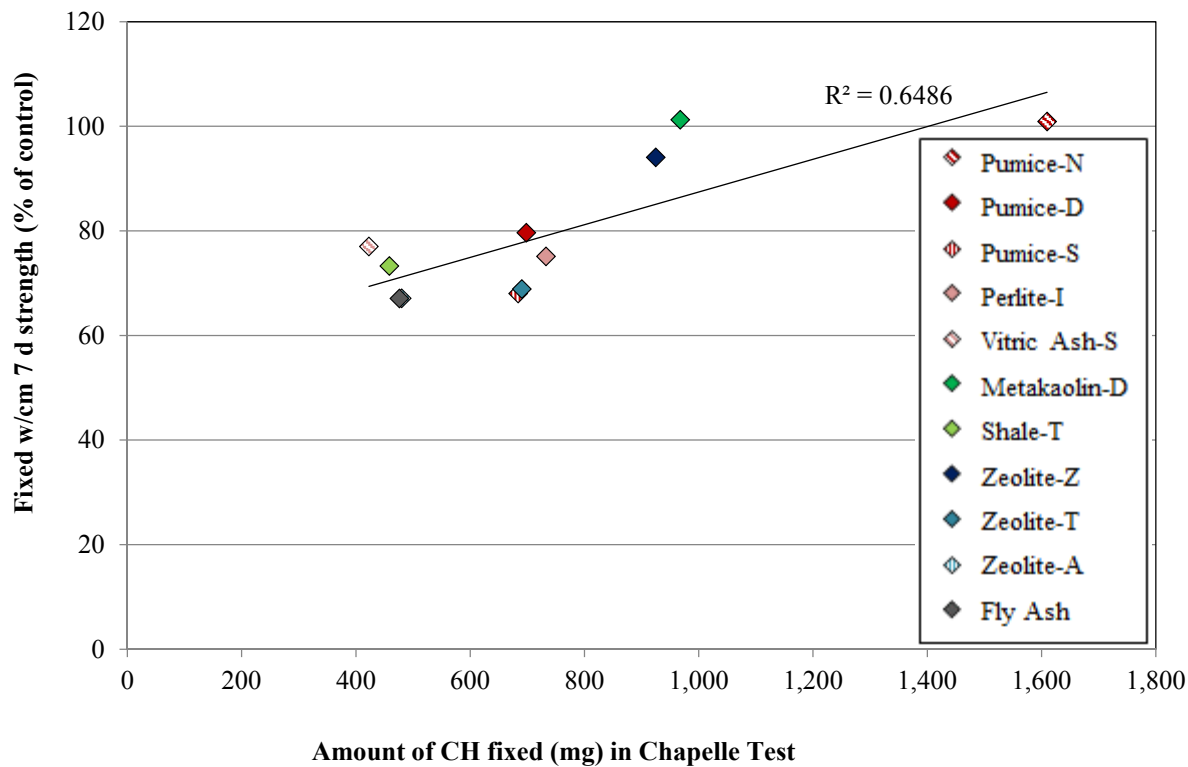


Figure 6: Correlation between 7 d strength (fixed w/cm) and Chapelle results (1000 mg = 0.0022 lb)

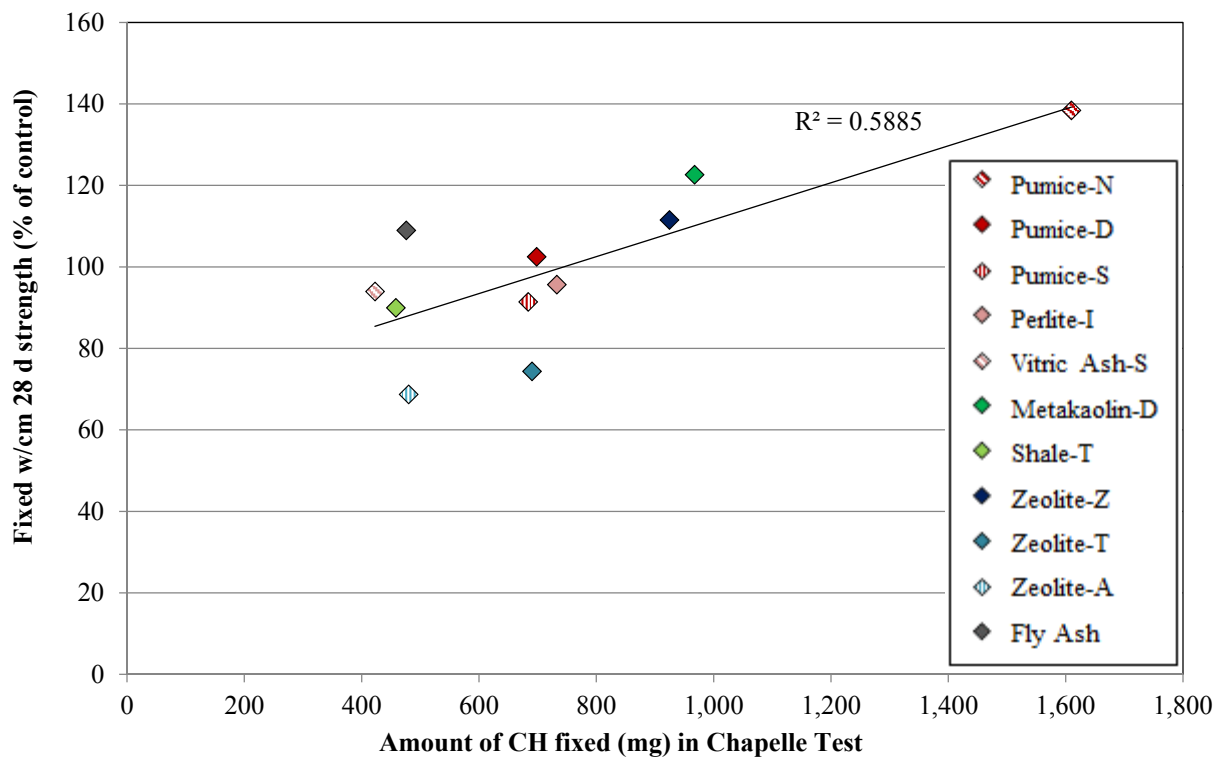


Figure 7: Correlation between 28 d strength (fixed w/cm) and Chapelle results (1000 mg = 0.0022 lb)

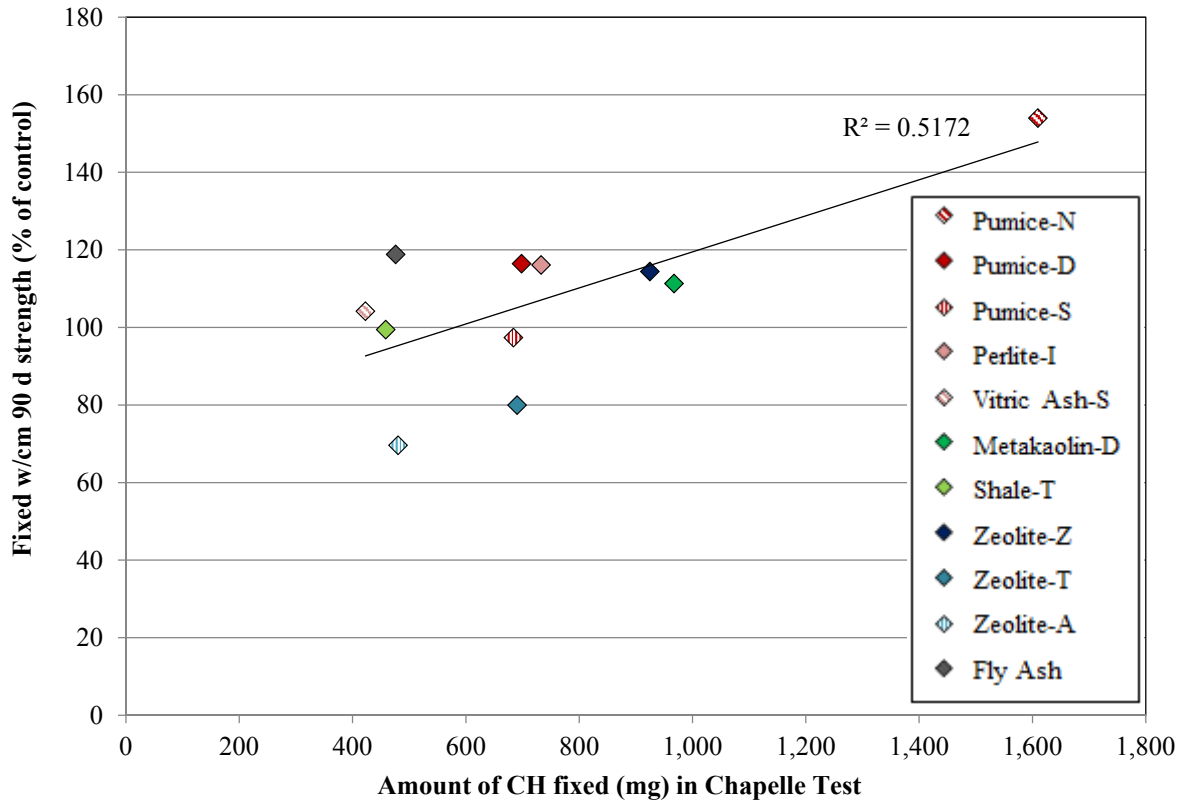


Figure 8: Correlation between 90 d strength (fixed w/cm) and Chapelle results (1000 mg = 0.0022 lb)

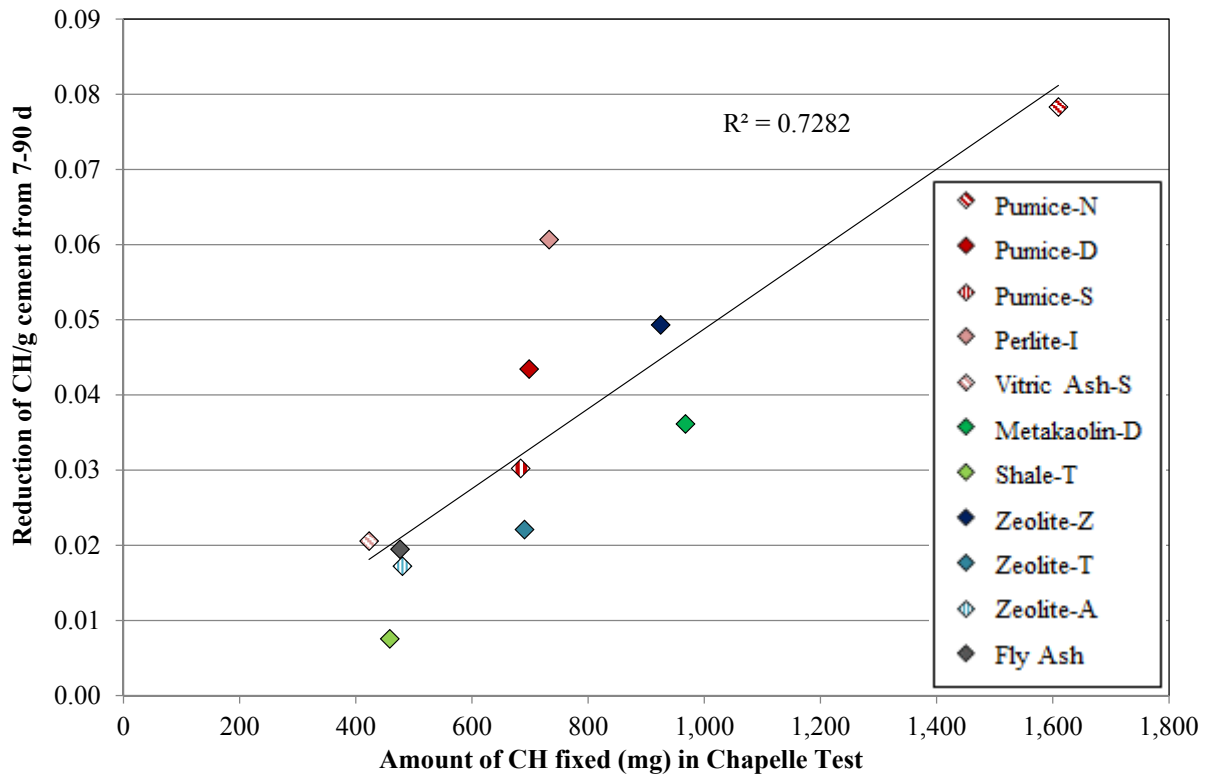


Figure 9: Correlation between TGA results and Chapelle results (1000 mg = 0.0022 lb)

A numerical study of polarization tests applied to corrosion in reinforced concreteJ. Marchand ¹, S. Laurens ², Y. Protière ¹, E. Samson ¹¹ SIMCO Technologies Inc., 2666, Boulevard du Parc Technologique, Québec (QC) G1P 4S6 CANADA² Université de Toulouse; UPS, INSA; LMDC; 135, Avenue de Rangueil 31077 Toulouse Cedex 4; FRANCE

Abstract: The evaluation of steel corrosion in reinforced concrete is commonly carried out using techniques like half-cell potential (HCP) and linear polarization resistance (LPR) measurements. The latter is however the subject of interrogations concerning the relevance of the method and the actual steel area polarized by the external current I_{ce} applied from a surface counter-electrode. To control the path of the polarizing current I_{ce} towards a specific steel area, a current-confining device (guard-ring) is used in some LPR instruments, which imposes an additional current I_{gr} around the counter-electrode. The impact of this guard-ring on LPR measurements is deduced from the uniform corrosion assumption. However, previous works have shown that the polarizing current spreading in macrocell corrosion systems is more complex and does not verify the uniform corrosion hypothesis. This paper presents the results of a 2D numerical study providing new insights on the theoretical impact of a guard-ring in case of galvanostatic pulse measurements performed on a macrocell corrosion system. The polarizing and confining currents are spread in a similar way over the macrocell system. In the case of an anodic polarization, both I_{ce} and I_{gr} are collected by the active steel area. In the cathodic direction, both I_{ce} and I_{gr} are spread over the passive areas. Consequently, numerical results show that the assumed confining effect cannot be achieved in presence of corrosion macrocells and it is actually impossible to define a specific polarized area. Moreover, since polarizing and confining currents have similar distributions, the confining current fully contributes to the system polarization, while it is not considered in LPR measurement analyses.

Keywords: finite element analysis, guard ring, linear polarization, localized corrosion, modeling, reinforcement corrosion

About the author

Dr. Marchand co-founded Service d'Expertise en Matériaux (S.E.M.) Inc. in 1989 and SIMCO Technologies Inc. in 1997. He is an internationally recognized expert in concrete mixture design, degradation mechanism analysis and durability modeling of concrete infrastructure exposed to aggressive environments. From 1992 to 2012, Dr. Marchand has led a productive academic career at Laval University, during which he held a Canada Research Chair and a NSERC Industrial Research Chair.

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INTRODUCTION

The nondestructive evaluation of steel corrosion in reinforced concrete is commonly carried out by using complementary half-cell potential [1-3] and linear polarization resistance [2,4] techniques. The relevance of the linear polarization resistance (LPR) is however the subject of interrogations pertaining to:

- the relevance of the measurement approach in case of macrocell corrosion systems,
- the actual steel area polarized by the external current I_{ce} applied from a surface counter-electrode (CE).

The theory typically used to analyze LPR measurements is actually based on a series of hypotheses, the main one being the uniform corrosion assumption. According to this assumption, the anodic and cathodic areas are defined as corrosion microcells located on adjacent locations and exhibiting a common electrochemical potential (corrosion potential E_{corr}). However, laboratory and field observations show that, in most cases, steel corrosion in reinforced concrete exposed to chloride-laden environment consist in macrocell (or localized) corrosion. Fig. 1 and Fig. 2 illustrate the localized nature of chloride attacks on steel embedded in concrete.

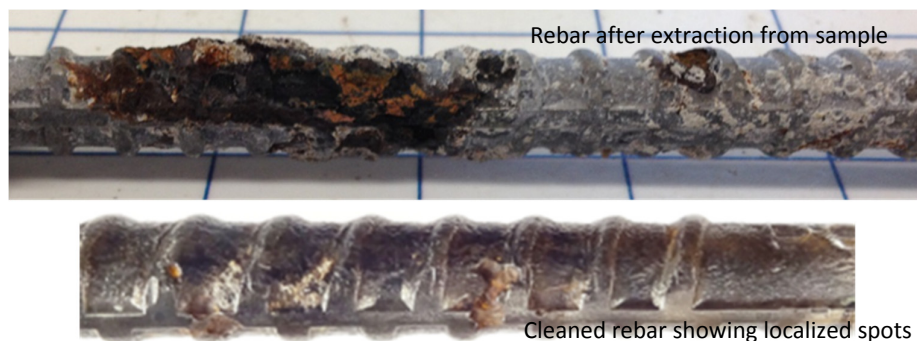


Fig. 1—Illustration of chloride-induced corrosion of reinforcing steel in concrete (localized attack)
(Data provided by authors)

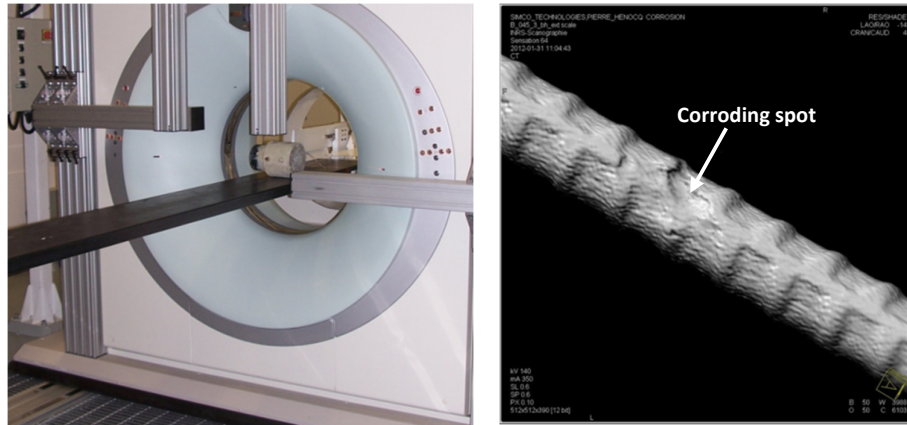


Fig. 2—Chloride-induced corrosion attack of reinforcing steel in concrete observed by X-ray tomography (Data provided by authors)

In cases of localized corrosion, anodic and cathodic areas are spatially separated, forming corrosion macrocells with different equilibrium potentials. This type of corrosion results in a potential gradient and a macrocell ionic current in the concrete volume. To date, LPR measurements performed on a macrocell corrosion system are not rigorously understood and the effect of macrocells on polarization measurements is simply assumed, but not yet demonstrated. Sagües and Kranc [5] reported the difficulties resulting from the presence of macrocells when measuring the polarization response of steel bars in concrete. Elsener [6] also discussed the implications of macrocells in corrosion monitoring. Despite these uncertainties, corrosion rate measurements in reinforced concrete still rely on the LPR concept, which is based on the microcell or uniform corrosion assumption.

The current approach to analyze LPR measurements is supported by the conclusions of the RILEM Technical Committee 154-EMC, which published in 2004 a technical recommendation on the subject [4]. This recommendation, based on the microcell assumption, is nowadays widely used to assess the corrosion rate of steel in concrete, while the same committee explicitly recognized the localized nature of steel corrosion in concrete in a former recommendation about on-site half-cell potential (HCP) measurements [1]. Indeed, as illustrated in the Fig. 3 excerpted from [1], the RILEM HCP recommendation promotes the detection of potential gradient to identify corrosion spots in reinforced concrete, meaning that the localized nature of the corrosion phenomenon is accepted. Moreover, this RILEM illustration clearly exhibits a local corrosion site exchanging macrocell current with surrounding passive steel areas. Therefore, corrosion engineers are encouraged by the RILEM committee to work with surface HCP mapping rather than HCP thresholds (Fig. 4).

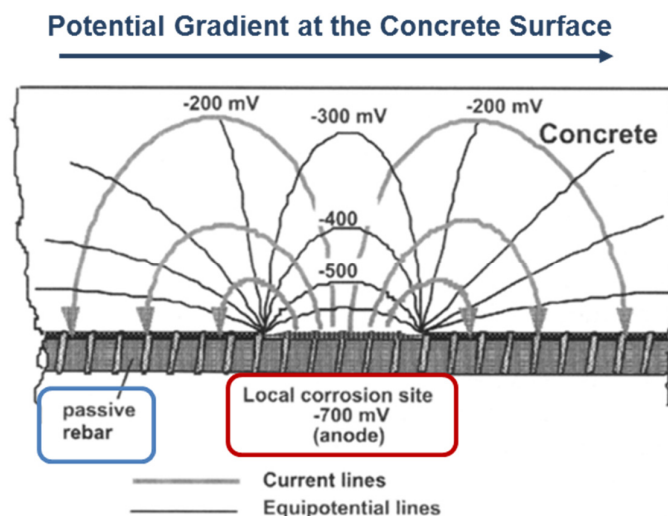


Fig. 3—RILEM TC 154-EMC illustration of a classical macrocell corrosion pattern in steel reinforced concrete justifying the recommended HCP protocol for on-site measurement and interpretation [1]
[Source: RILEM TC 154-EMC 2003]

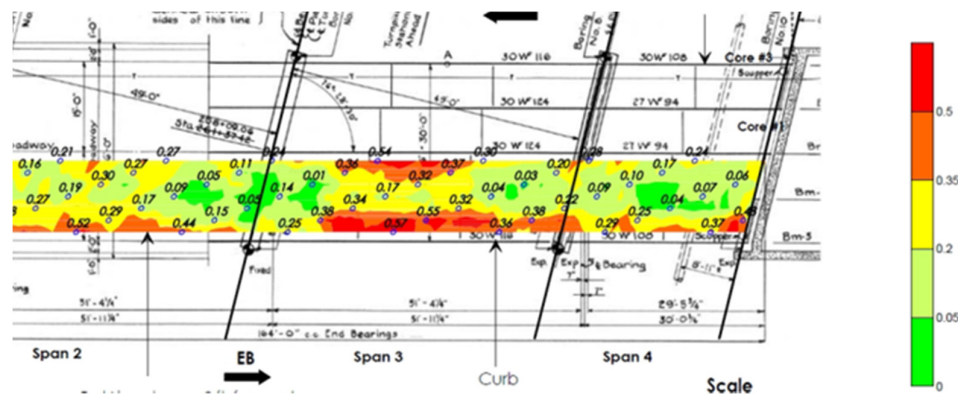


Fig. 4—Example of representation of HCP field measurement illustrating the localized nature of steel corrosion in concrete (Data provided by authors)

This short discussion highlights the duality of the paradigm involved in two publications authored by RILEM TC 154-EMC. Regarding HCP protocol, the committee clearly points out the localized (macrocell) nature of corrosion attacks in reinforced concrete to build the recommendation [1]. Then, the committee assumes uniform (microcell) corrosion to interpret LPR measurement for corrosion rate assessment [4].

From a physical point of view, this duality is not satisfactory and probably explains the lack of reliability of LPR measurements. In order to better understand the behavior of a macrocell corrosion system under polarization (LPR test), a series of 2D numerical simulations were performed. Simulation results provided original insight on a number of factors, such as (1) the distribution of the polarizing current over the macrocell system during the LPR measurement, (2) its interaction with the macrocell corrosion current and, finally, (3) the actual impact of the confinement device described in the RILEM technical document.

A CRITICAL DISCUSSION ON THE CURRENT APPROACH OF LPR MEASUREMENTS ON STEEL CORROSION SYSTEMS IN REINFORCED CONCRETE

Fig. 5 illustrates the current assumption regarding the behavior of the applied polarizing current during the LPR test in the presence of macrocells. This illustration is excerpted from the RILEM recommendation on LPR measurements established by the Technical Committee 154-EMC [4].

According to this schematic representation, the polarizing current is primarily attracted by the local anodic area (active steel) while only a few streamlines are distributed over the cathodic (passive) area. This phenomenon is commonly referred to as self-confinement [6, 7], in which the polarizing current is attracted by a remote corroding area. Actually, this illustration depicts incorrectly the polarization response of a macrocell corrosion system. A first critical comment originates from the fact that the natural macrocell current exchanged between active (anodic) and passive (cathodic) areas is simply not considered here. As discussed by Sagües and Kranc [5], the existence of a macrocell creates a specific initial condition, which should be rigorously addressed in corrosion measurements.

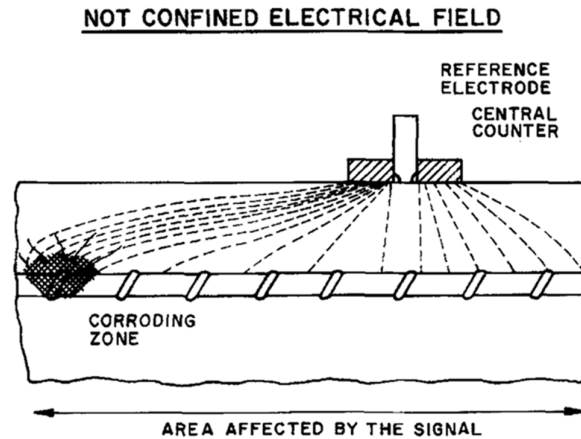


Fig. 5—Effect of a localized corrosion spot on LPR measurements without guard-ring according to RILEM TC 154-EMC 2004 [4]

In order to control the path of the polarizing current I_{ce} towards a specific steel area, a current-confining device is commonly used for on-site LPR instruments. Due to its annular geometry, the confinement device is often referred to as the guard-ring. In the field of reinforced concrete, the guard-ring concept has been developed by Feliu et al. [8, 9]. The basic principle consists in applying an additional current I_{gr} around the counter-electrode (CE). Fig. 6 illustrates the assumed effect of a guard-ring on the LPR measurements for cases of macrocell corrosion. The measuring system presented in the illustration refers to a commercial galvanostatic pulse device, which is composed of:

- a central reference electrode aimed at collecting the potential response of the corrosion system,
- an annular central counter-electrode (CE) applying the system perturbation (polarizing current I_{ce}),
- an external guard-ring (GR) applying an additional current I_{gr} aimed at confining the polarizing current I_{ce} ,
- two additional reference electrodes (S_1 and S_2) used to control the guard-ring current.

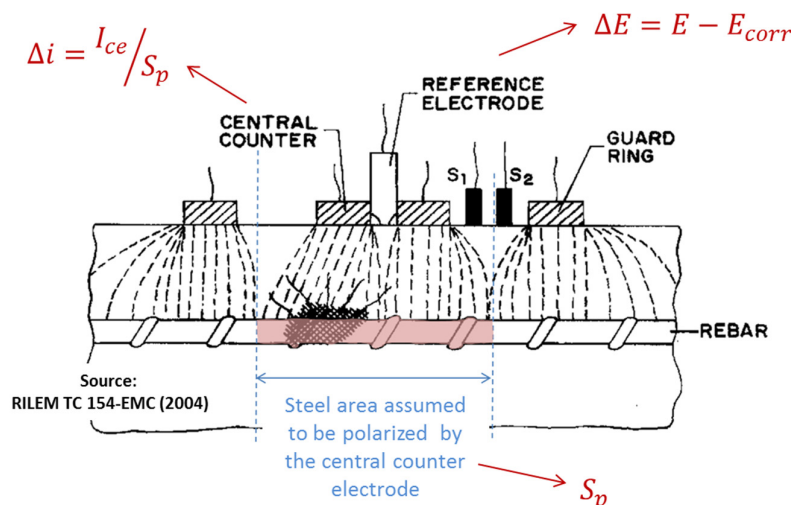


Fig. 6—Confinement effect induced by a guard-ring, as assumed in RILEM TC 154-EMC 2004 [4]

The additional reference electrodes S_1 and S_2 are involved in the measurement setup since the guard-ring current I_{gr} is controlled in order to keep a constant potential drop between S_1 and S_2 [9]. This confinement approach is referred to as modulated guard-ring. With this setup, it is assumed that the surface potential gradient is unchanged around CE and the polarizing current I_{ce} is flowing uniformly from CE towards the steel bar. Therefore, the steel area affected by the polarizing current is considered to be controlled and determined by the geometry of the surface measuring system, the polarized area being assumed to extend approximately within a virtual circle drawn in the middle of the space between the two annular electrodes CE and GR.

This illustration neglects the initial macrocell current exchanged between active and passive steel areas and wrongly depicts the response of the macrocell system to the externally applied polarization. The polarizing current I_{ce} is assumed to be confined in the controlled area (S_p) and to be spread uniformly over the steel surface. More surprisingly, it is assumed that the polarizing current streamlines (I_{ce}) are not affected by the local anode. Actually, there is no physical reason for I_{ce} to behave differently than what is presented on Fig. 5 and it should be primarily collected by the anodic area.

In the literature, difficulties relative to the guard-ring technique are often reported, based on either experimental or numerical works [7, 10-14]. Videm and Myrdal [10] concluded that measurements performed with a guard electrode did not correlate with potential mapping or visual inspection. Recently, original experiments have been carried out by Nygaard et al. [13] in order to understand the recurrent differences observed between measurements provided by two commercial LPR devices: Gecor 6® and Galvapulse®. The authors demonstrated that current confinement in LPR measurements is actually much more complicated to achieve than usually assumed.

Wojtas [11] performed numerical simulations of LPR measurements by using a simplified impedance network. The author found that a modulated guard-ring was actually unable to avoid lateral current spreading from the polarizing current and concluded to a significant underestimation of the corrosion rate in case of high corrosion activity. The latter conclusion regarding the underestimation of the corrosion rate in cases of high corrosion activity is reported in several works [7].

Andrade et al. [15] performed FEM simulations of LPR measurements trying to demonstrate the physical relevance of the modulated guard-ring technique. However, the authors still assumed uniform corrosion in their calculations, making the physical problem much simpler than it actually is. The physical relevance of the confinement technique in cases of uniform corrosion has already been demonstrated in several works. However, although it is recognized to be very frequent, the localized nature of the corrosion process is quite systematically neglected in numerical works aimed at simulating LPR measurements.

Relevant simulations of LPR measurements on macrocell corrosion systems reveal that the physical problem cannot be approximated by the uniform corrosion assumption. In the present paper, specific numerical experiments are presented in order to complement the scientific discussions about this issue. The numerical results are then discussed and confronted to some literature data.

NUMERICAL STUDY OF A CURRENT LPR DEVICE

Modeling and simulation background

2D numerical experiments were carried out by using the commercial finite element software Comsol Multiphysics® (v4.2). All the simulations were performed in steady-state condition, using the “Electric currents” option of the AC/DC toolbox. The simulations focus on current distribution in concrete. For the purpose of this paper, it was assumed that concrete resistivity is uniform. More details on the modeling and simulation background are given in [16].

In the concrete volume, local Ohm's law (Eq.1) and charge conservation (Eq.2) governs electrical phenomena:

$$\text{Eq. 1} \quad \mathbf{j} = -\frac{1}{\rho} \nabla E$$

$$\text{Eq. 2} \quad \nabla \cdot \mathbf{j} = 0$$

where:

- $\mathbf{j}$ is the local current density vector, in A/m² (A/in²),
- E is the electrical potential field, in V,
- ρ is the electrical resistivity of concrete, in ohm.m (ohm.in).

Electrical resistivity of concrete (ρ) is set at 50 ohm.m (1968 ohm.in), corresponding to a typical saturated material with a high chloride content. Providing appropriate sets of electrochemical parameters (Table 1), the electrochemical behavior of both active and passive steel-concrete boundaries is modeled by the Butler-Volmer equation (Eq.3):

$$\text{Eq. 3} \quad j_n = j_{corr} \left(\exp \left(\log(10) \frac{E - E_{corr}}{\beta_a} \right) - \exp \left(-\log(10) \frac{E - E_{corr}}{\beta_c} \right) \right)$$

Where:

- E_{corr} is the free corrosion potential (V/ref) of active or passive steel at equilibrium,
- j_n is the net current density in A/m² (A/in²) flowing normally through the metal-electrolyte interface due to polarization,
- j_{corr} is the exchange current density in A/m² (A/in²) which is the current in the absence of net electrolysis and at zero overpotential,
- β_a and β_c are respectively the anodic and cathodic Tafel coefficients (V/dec) of the uniform corrosion system.

Some variability may be observed in the literature regarding the values of the electrochemical parameters, which need to be considered in the simulations. However, electrochemical parameters involved in this work reflect the global orders of magnitude that may be found or deduced from literature data [17].

Table 1—Butler-Volmer parameters involved in numerical experiments

Butler-Volmer Parameter	j_{corr} A/m ² (A/in ²)	E_{corr} V/ref	β_a V/dec	β_c V/dec
Active steel area	10 ⁻¹ (6.45e-5)	-0.7	0.06	0.16
Passive steel area	10 ⁻⁴ (6.45e-8)	-0.1	0.4	0.16

The polarization tests were simulated as a galvanostatic step protocol, by applying a constant current I_{ce} of 50 μ A (positive or negative according the expected polarization direction). The guard-ring current I_{gr} was set equal to the polarizing current I_{ce} . Nevertheless, the values of both these currents do not affect the general qualitative conclusions achieved in this research work.

Preliminary simulation of LPR measurements on a uniform (microcell) corrosion system

Fig. 7 presents the result of a preliminary simulation involving a uniform corrosion state of the steel bar. Current streamlines and equipotential lines are plotted as grey and red lines, respectively. For this specific purpose, the entire steel boundary was modeled using the Butler-Volmer equation involving only “active steel” parameters.

In this case of uniform electrochemical state (active corrosion), the polarizing current appears to be effectively confined in a controlled area (comprised within the blue dashed lines). Due to the uniform nature of the corrosion process here (microcell corrosion), only the polarizing current I_{ce} (blue arrows) and the guard-ring current I_{gr} (black arrows) are flowing through the concrete volume (no macrocell current). The simulation presented here only involves anodic polarization, since the distribution of current lines is identical for the

cathodic polarization case (only the sign of current is changed). It has to be noted that the two-dimensional nature of the simulation artificially supports the confinement. Former results achieved on a three-dimensional uniform corrosion system showed that the confinement is dependent on geometrical considerations [18]. Nevertheless, the confinement of the polarizing current appears to be achievable in case of uniform electrochemical condition at the steel-concrete interface.

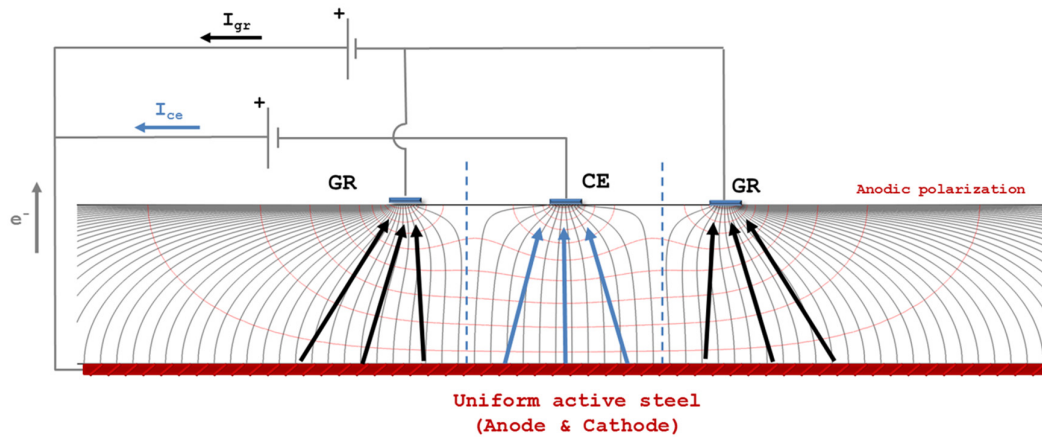


Fig. 7—FE simulation of a polarization test with guard-ring on a uniform corrosion system

Simulation of LPR measurements on a macrocell corrosion system

In a second series of simulations, a free macrocell corrosion system is modeled as illustrated in the Fig. 8. To simulate a single corrosion spot in the middle of rebar, a 2 cm-length anodic area is set between two large cathodic regions, by applying relevant Butler-Volmer boundary conditions according to Table 1: “Active steel” parameters at the corrosion spot and “Passive steel” parameters on the rest of the steel boundary. Fig. 9 presents the simulation result relative to the free corrosion system in terms of natural macrocell current exchanged between anodic and cathodic regions. In the figure, the potential field is represented by red equipotential lines. It can be observed that the computed potential field is significantly different from what was assumed by RILEM TC154-EMC (and illustrated in Fig. 3).

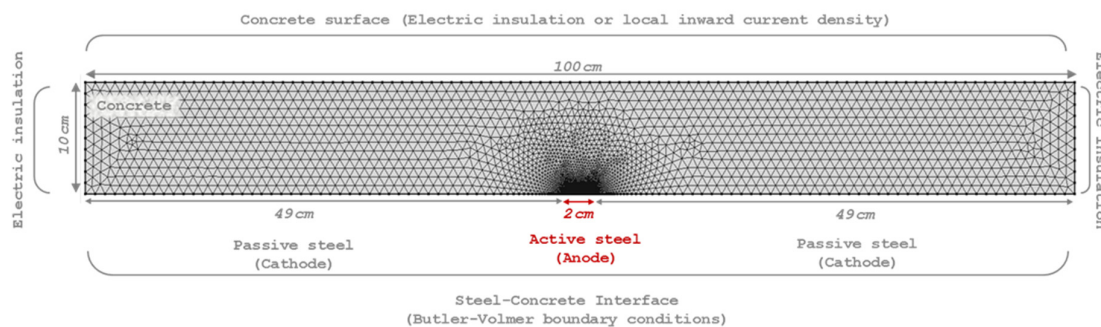


Fig. 8—2D finite elements model

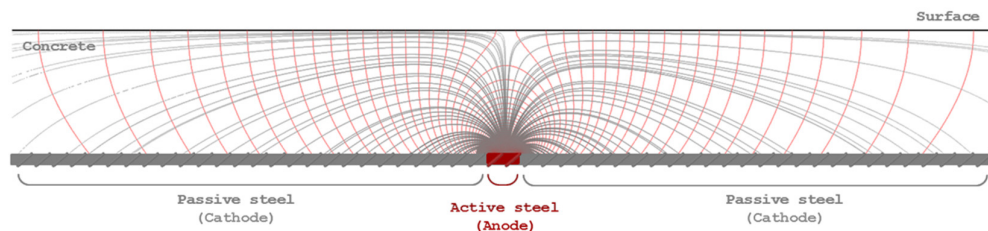


Fig. 9—FE simulation of a free corrosion system: macrocell current streamlines and potential field

The next step of the numerical experiment consists in applying an anodic polarization from a counter-electrode located above the anodic area (Fig.10). A guard ring is also used in the simulation. The current streamlines obtained by the numerical simulation are very different from the RILEM illustration presented in Fig. 6. The simulation clearly shows the effect of the applied currents I_{ce} and I_{gr} (blue and black arrows, respectively) on the natural macrocell current (red arrows), which is significantly affected during the test. To achieve the constraint on the potential field between CE and GR, the injected currents I_{ce} and I_{gr} are necessarily of the same nature (same algebraic sign), i.e. either positive or negative according to the polarization direction. Hence, in the case of an anodic polarization, electrons are extracted from the corrosion system by the way of both CE and GR. These electrons being produced at the anodic area, both the polarizing and confinement currents are spread over the small active steel region, exclusively. These numerical results provide a theoretical argument supporting the experimental observations of Nygaard et al. [13]. According to the simulation, there is no confinement of the polarizing current I_{ce} . Moreover, it is very unlikely that confinement can be obtained with such a setup, no matter the intensity of polarization currents. The second consequence, also mentioned by Nygaard et al. [13], is that the guard-ring current fully contributes to the system polarization, while it is not considered in the calculation of the polarization resistance as usually carried out.

Fig. 11 presents the simulation result for the case of a cathodic polarization of the macrocell system. In this case, both the polarizing and confinement currents are collected by the passive regions, which are able to consume electrons provided by the measurement device to the corrosion system. The natural macrocell current exchanged between anodic and cathodic regions is also affected by the cathodic polarization of the corrosion system. Actually, the cathodic polarization leads to a decrease in the natural macrocell current exchanged between anodic and cathodic regions. The same conclusion is achieved here compared to anodic polarization: the guarding appears to be physically unable to confine the counter-electrode current in a specific steel area. It also contributes to the system polarization.

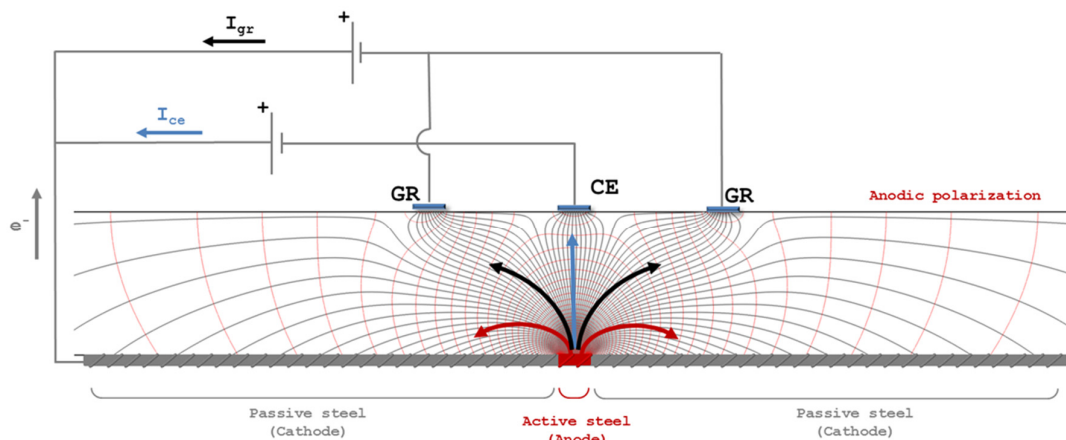


Fig. 10—FE simulation of current distributions for an anodic polarization test with guard-ring on a macrocell corrosion system: residual macrocell current (red arrows), I_{ce} (blue arrows) and I_{gr} (black arrows)

The numerical experiments presented above and based on basic theoretical laws provided unexpected results with respect to the general ideas commonly accepted in this research field. Focused on the spatial distribution of the currents (counter-electrode and guard-ring) involved in classical LPR measurements, this paper clearly show that a guard-ring does not work as assumed by many authors. Considering the additional complexity it induces in the polarization response of a macrocell corrosion system, it seems to be likely to avoid the use of such confinement devices.

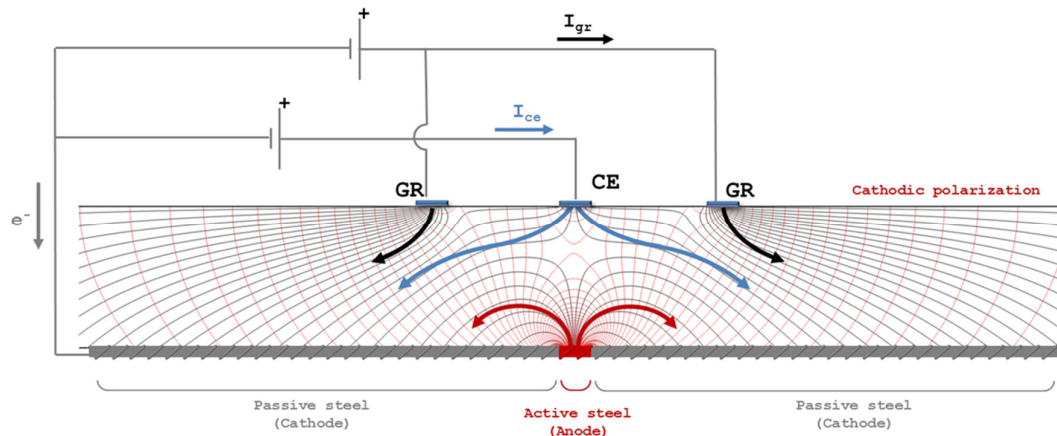


Fig. 11—FE simulation of current distributions for a cathodic polarization test with guard-ring on a macrocell corrosion system: residual macrocell current (red arrows), I_{ce} (blue arrows) and I_{gr} (black arrows)

It has to be noticed that this paper voluntarily does not address the problem of polarization resistance calculation. Indeed, it is impossible to describe by a simple scalar value the polarization undergone by the steel. Basically, it is a real three-dimensional physical problem and it is impossible to perform a 1D simplification as done in classical current measurements. Therefore, even the concept of polarization resistance shall be deeply revised in the case of macrocell corrosion and further research works in this field should be focused on this topic. At this stage, a peculiar attention was paid to the spreading of polarizing current over the entire macrocell system, which is the first step to build a relevant measurement protocol.

At last, several influential parameters (such as concrete cover, electrical resistivity, anode-to-cathode surface ratio, electrochemical properties of steel-concrete interface...) may modify the quantitative aspects of the results, but not the qualitative conclusions of the paper, i.e.:

- guard-rings should be simply avoided for on-site measurement protocols since they are physically unable to bring the expected confinement effect and moreover they contribute to the corrosion system polarization;
- the concept of polarized area is actually very difficult to define and probably meaningless;
- on-site protocols for corrosion measurements should be deeply revised in order to take into account the real macrocell nature of corrosion in reinforced concrete.

CONCLUSION

Whatever the polarization direction, the numerical solution of the corrosion problem shows the incapacity of the guard-ring technique to confine the polarizing current in a controlled area. Polarizing and guard-ring currents behave identically, since they are of the same nature. It was thus theoretically demonstrated that the guard-ring current fully contributes to the macrocell system polarization, while it is not considered in the calculation of the polarization resistance. Hence, in cases of macrocell corrosion, the use of guard-rings appears to bring even more complexity to corrosion measurements.

The numerical study also calls into question the actual relevance of the concept of polarized area. The macrocell nature of the steel corrosion process is recognized to be very frequent in reinforced concrete, and almost systematic in the case of chloride-induced corrosion. Hence, the corrosion system may not be considered only as the anodic region, but as the interaction between remote anodic and cathodic regions. Trying to isolate and measure a portion of such a corrosion system, which is the objective of using guard-rings, proved impossible. Such a protocol adds to the complexity of the analysis and further leads to erroneous interpretation of the system response.

Previous and current research works on corrosion measurement in steel reinforced concrete are actually guided by an underlying paradigm, which can be summarized by the microcell or uniform corrosion assumption. The

LPR theory is based on the Stern-Geary equation, which is relevant for uniform corrosion systems at free equilibrium. In such uniform systems, the equilibrium is totally determined by the Butler-Volmer equations of the two half-cells involved in the redox reaction. As Song concluded [19], the validity of Stern-Geary equation is limited to very specific corrosion cases. Actually, it may not describe the response of a macrocell system since it does not enclose the Ohm's law, which has a fundamental influence on the macrocell equilibrium.

The numerical results presented in this study show how advanced analyses can improve our understanding of the complex corrosion phenomena in reinforced concrete structures. They also hint at interesting new ways of designing experiments and measurement techniques, which ultimately will contribute to better predict the aging of concrete infrastructure.

REFERENCES

- [1] B. Elsener, C. Andrade, J. Gulikers, R. Polder, M. Raupach, Half-cell potential measurements - Potential mapping on reinforced concrete structures, *Materials and Structures* 36 (September) (2003) 461-471.
- [2] G.P. Gu, J.J. Beaudoin, V.S. Ramachandran, Techniques for corrosion investigation in reinforced concrete, in *Handbook of Analytical Techniques in Concrete Science and Technology*, V.S. Ramachandran & J.J. Beaudoin eds. (2001) 441-504.
- [3] G.P. Gu, J.J. Beaudoin, Obtaining effective half-cell potential measurements in reinforced concrete structures, *Construction Technologies Update* 18 (1998) 1-4.
- [4] C. Andrade, C. Alonso, J. Gulikers, R. Polder, R. Cigna, O. Vennesland, M. Salta, A. Raharinaivo, B. Elsener, Test methods for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method, *Materials and structures* 37 (November) (2004) 623-643.
- [5] A. A. Sagües, S. C. Kranc, On The Determination of Polarization Diagrams of Reinforcing Steel in Concrete, *Corrosion* 48 (8) (1992) 624-633.
- [6] B. Elsener, Macrocell corrosion of steel in concrete - implications for corrosion monitoring, *Cement and Concrete Composites* 24 (2002) 65-72.
- [7] B. Elsener, Corrosion rate of steel in concrete - Measurements beyond the Tafel law, *Corrosion Science* 47 (12) (2005) 3019-3033.
- [8] S. Feliu, J. Gonzalez, M. Escudero, S. J. Feliu, A. C, Possibilities of the guard ring for electrical signal confinement in the polarization measurements of reinforcements, *Corrosion* 46 (12) (1990) 1015-1020.
- [9] S. Feliu, J. Gonzalez, S. F. Jr, M. Andrade, Confinement of the electrical signal for in situ measurement of polarization resistance in reinforced concrete, *ACI Materials Journal* 87 (5) (1990) 457-460.
- [10] K. Videm, R. Myrdal, Electrochemical Behavior of Steel in Concrete and Evaluation of the Corrosion Rate, *Corrosion* 53 (9) (1997) 734-742.
- [11] H. Wojtas, Determination of corrosion rate of reinforcement with a modulated guard ring electrode; analysis of errors due to lateral current distribution, *Corrosion Science* 46 (2004) 1621-1632.
- [12] S. Feliu, J. Gonzalez, J. Miranda, V. Feliu, Possibilities and problems of in situ techniques for measuring steel corrosion rates in large reinforced concrete structures, *Corrosion Science* 47 (1) (2005) 217-238.
- [13] P. V. Nygaard, M. R. Geiker, B. Elsener, Corrosion rate of steel in concrete: evaluation of confinement techniques for on-site corrosion rate measurements, *Materials and Structures* 42 (8) (2009) 1059-1076.
- [14] A. Poursaei, C. Hansson, Galvanostatic pulse technique with the current confinement guard ring: The laboratory and finite element analysis, *Corrosion Science* 50 (10) (2008) 2739-2746.
- [15] C. Andrade, J. Sanchez, On-site corrosion rate measurements: 3D simulation and representative values, *Materials and Corrosion* 63 (12) (2012) 1154-1164.
- [16] S. Laurens, P. Hénocq, N. Rouleau, F. Deby, E. Samson, J. Marchand, B. Bissonnette, Steady-state polarization response of chloride-induced macrocell corrosion systems in steel reinforced concrete – Numerical and experimental investigations, *Cement and Concrete Research* 79 (2016) 272-290.
- [17] M.G. Sohail, S. Laurens, F. Deby, J.P. Balayssac, Significance of macrocell corrosion of reinforcing steel in partially carbonated concrete: numerical and experimental investigation, *Materials and Structures* 48 (1-2) (2015) 217-233.
- [18] A. Clément, S. Laurens, G. Arliguie, F. Deby, Numerical study of the linear polarisation resistance technique applied to reinforced concrete for corrosion assessment, *European Journal of Environmental and Civil Engineering* 16 (3-4) (2012) 491-504.
- [19] G. Song, Theoretical analysis of the measurement of polarisation resistance in reinforced concrete, *Cement and Concrete Composites* 22 (2000) 407-415.

Three Dimensional Electrical Imaging of Moisture Ingress in Mortar

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ABSTRACT

The durability performance of cement-based materials is directly related to the rate of moisture ingress in them. Moisture ingress in cement-based materials can be assessed using electrically-based methods. Traditionally, the electrically-based assessment of the moisture transport in cement-based materials has relied on two or four-point measurements, enabling one-dimensional (1D) moisture flow monitoring. However, moisture ingress in cement-based materials is most often three-dimensional (3D). The objective of this paper is to investigate the feasibility of 3D electrical imaging of moisture ingress in mortar using Electrical Impedance Tomography (EIT). The EIT reconstructions are compared with the results of unsaturated moisture transport simulations using 3D Finite Element Method. The results of this study support the feasibility of EIT for 3D imaging of moisture flow in cement-based materials.

Author Keywords: Durability, Electrical Methods, Moisture Transport, Non-Destructive Testing, imaging

INTRODUCTION

The durability of concrete structures is closely linked to the resistance of concrete to the ingress of moisture and aggressive agents [Pour-Ghaz 2011]. The rate of moisture transport in concrete, therefore, can be viewed as a measure of durability of reinforced concrete structures. To date, several advanced methods of monitoring moisture transport in concrete have been developed, based on, e.g. attenuation of electromagnetic radiation (including X-rays [Pour-Ghaz et al. 2009, Roels et al. 2007, Roels et al. 2006], gamma rays [Nizovstev et al. 2008, Nielson 1972], neutron imaging [Hallaji et al. 2015, Zhang et al. 2011, Zhang et al. 2010, Kanematsu et al. 2009, McCarter et al. 1997, McCarter et al. 1996, McCarter et al. 1996] and nuclear magnetic resonance [Hall et al. 2012, Chen et al. 2003, Gummerson et al.

1979]. While these methods provide high-resolution results, they may be invasive, limited to small geometries and have significant energy requirements; and therefore, their field applications may be limited [Hallaji et al. 2015]. Electrically-based methods, on the other hand, are not invasive, require comparatively lower energy, and are inexpensive [McCarter et al. 2012, Rajabipour et al. 2005]. However, due to the diffusive nature of the electrical measurements, the interpretation of measurements in traditional electrically-based methods (for example based on pair-wise impedance measurements using electrical impedance spectroscopy) is not straightforward [Hallaji et al. 2015, Hallaji 2015].

Electrical Impedance Tomography (EIT) can be used to overcome the difficulties of the traditional methods, and have been utilized to monitor unsaturated moisture flow in porous media [Cosentini et al. 2012, Comina et al. 2011, Comina et al. 2010, Stacey et al. 2006, Borsic et al. 2005, Buettner et al. 1996, Buettner et al. 1996, Daily et al. 1992]. Recently, Du Plooy et al. [Du Plooy et al. 2015] used EIT to monitor one-dimensional water ingress in concrete slabs. Hallaji et al. [Hallaji et al. 2015] performed simultaneous EIT and neutron radiography imaging on cement paste specimens with one-dimensional (1D) and two-dimensional (2D) water source and showed good agreement between EIT reconstructions and neutron radiographic images.

In this paper, the researchers investigate whether EIT can be used to monitor 3D moisture ingress in cement-based specimens containing fine aggregate. The EIT reconstructions are qualitatively compared with results of moisture flow simulations. While qualitative, this comparison provides insight to the feasibility of EIT for 3D monitoring of moisture ingress. There are two reasons that the authors compare EIT reconstructions with moisture flow simulations and the qualitative nature of this comparison: (1) due to the size of the three-dimensional specimen used, X-ray or neutron tomography was not feasible, and (2) As will be described later in this paper, the difference imaging scheme used was qualitative in nature

and comparison with other methods, including experimental methods, will always be qualitative.

In the following sections of this paper, experimental methods are discussed, which highlights materials and sample preparation. Then a brief background on difference imaging scheme in EIT and numerical simulation of unsaturated moisture transport are provided. Finally, in the results section, the EIT reconstructions are compared with results of numerical simulations.

RESEARCH SIGNIFICANCE

This study examines the feasibility of EIT as a non-invasive and nondestructive imaging method to monitor 3D moisture flow in cementitious material containing fine aggregates. Unlike methods based on the attenuation of electromagnetic waves (e.g., X-ray, gamma rays, neutron imaging, and nuclear magnetic resonance), EIT is non-invasive, requires comparatively less energy, can be applied to large specimens, and is inexpensive. This research shows that EIT can be used to nondestructively monitor moisture flow in cement-based materials, potentially contributing to establishing this method for laboratory and field applications.

EXPERIMENTAL METHODS

General

In the experimental study, water movement in a cylindrical specimen was monitored (Fig. 1). Water was added to the specimen by water ponding from a small PVC reservoir installed on top of the specimen, resulting in unsymmetric 3D water ingress. The first set of EIT measurements were carried out prior to the addition of water to the specimen (“reference

measurement”). Several EIT measurements were conducted during water ingress at different time intervals.

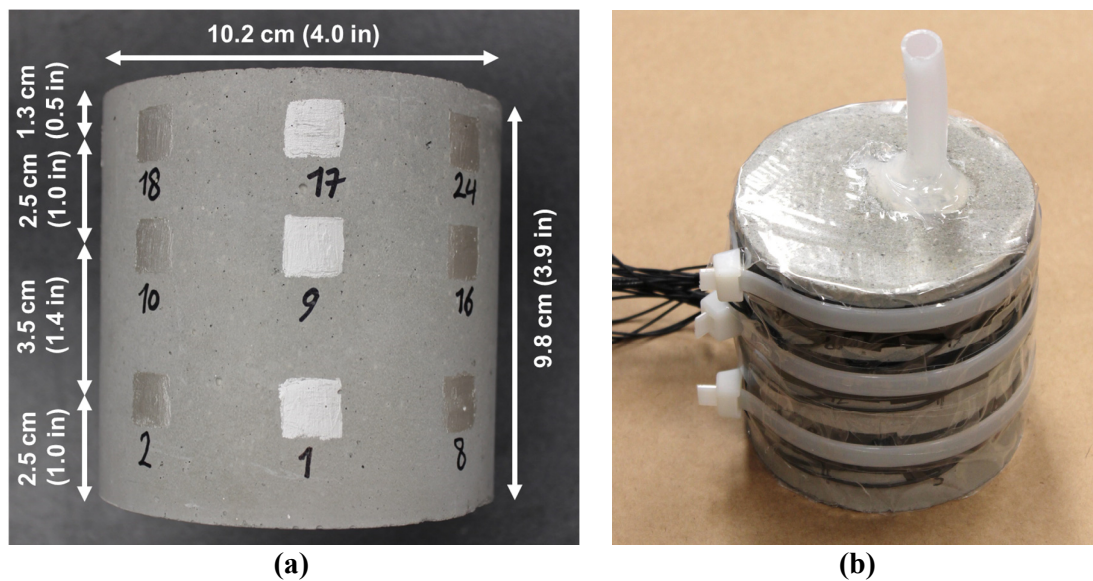


Fig 1 - (a) Side view of the specimen and location of the electrodes, (b) prepared specimen and location of the water reservoir.

Materials and Methods

The specimen used in this work was made of plain mortar. The water-to-cement ratio (w/c) of the mortar mixture was 0.60 and the total aggregate volume fraction was 40%. The high w/c ratio and high cement paste volume fraction was used to accelerate the rate of moisture ingress and reduce the duration of the test. Ordinary Portland cement (OPC, Type I) and fine aggregates consisting of natural river sand were used in the mortar mixture. The mixing was carried out in accordance with ASTM C192-06 and the specimens were cast in two 4.0x8.0 inch (10.20x20.30 cm) cylindrical molds. The specimens were then demolded after 18 hours and cut into 4.0x3.90 in (10.20x9.80 cm) cylinders. The specimens were then moved to an oven at 50°C for 5 hours, and then sealed in two layers of plastic bags and placed inside an environmental chamber at 23°C temperature for 21 days. This process was carried out to achieve relatively uniform moisture content throughout the specimen.

The electrodes used in this work were made of colloidal silver paint which was applied to the surface of the specimen using a regular brush. The colloidal silver paint has very low resistivity and is fast drying. A total of 24 square electrodes (with dimension of 0.5×0.5 in [1.30×1.30 cm]) were placed on the lateral surface of the specimen. The electrodes were arranged in 3 rings of 8 equally-distanced electrodes. Figure 1(a) shows a photograph of the specimen and location of the electrodes. After drying of the silver paint, a stripped 18-gage wire was placed on the surface of the silver paint and a forced contact between the paint and the wires was created by using two pieces of electrical tape and a zip-tie (Fig 1b).

A 2 in (5.1 cm) long PVC pipe with an internal diameter of 0.4 in (0.95 cm) was installed on top of the specimen as a water reservoir using silicon caulk. The water reservoir was positioned 0.5 in (1.30 cm) off-center, from the center of the cylinder, as shown in Fig. 1(b). After placing the water reservoir, the cylinder was wrapped with transparent tape to prevent evaporation of water from the specimen's surface during the experiment.

ELECTRICAL IMPEDENCE TOMOGRAPHY

EIT is an imaging technique in which the spatial distribution of conductivity (σ) (or resistivity) within an object is reconstructed from the boundary potential measurements under the influence of an applied current [Mueller and Siltanen 2012, Brown 2005, Vauhkonen 2004, Vauhkonen 1997]. Broadly, two main imaging schemes exist in EIT: *absolute* and *difference* imaging. In absolute imaging the actual conductivity distribution within the target is reconstructed from a set of measurements by solving the full non-linear estimation problem iteratively. In difference imaging the change in conductivity between two sets of measurements is reconstructed using a global linearization. An extensive discussion of different EIT imaging schemes can be found in [Hallaji 2014, Hallaji et al. 2014, Seppänen et al. 2014, Liu et al. 2014]. In the present paper, difference imaging was used, and therefore, two sets of

measurements were needed. The first set of measurements on the specimen, the reference measurement, was performed before addition of water to the water reservoir, and the subsequent sets of measurements were performed at different intervals after addition of water. The change in conductivity was then estimated between the reference measurements and each subsequent measurement set. A brief explanation of the difference imaging scheme used in this work is given below.

To reconstruct the conductivity distribution from the applied current and measured electrode potentials at the boundaries of a target, a mathematical model that enables estimation of the electrode potentials from the conductivity distribution within the target is required. Such a model is referred to as forward model. To date, Complete Electrode Model (CEM) is the most accurate forward model for EIT [Kaipio and Somersalo 2005, Somersalo et al. 1992, Cheng et al. 1989] and is utilized in this study. The CEM consists of the partial differential equation shown in Eq. 1 and boundary conditions shown in Eqs. 2 to Eq. 4. Eq. 5 ensures the current conservation law is satisfied and Eq. 6 fixes the potential reference level.

$$\nabla \cdot (\sigma \nabla u) = 0, \quad x \in \Omega \quad (1)$$

$$u + \xi_\ell \sigma \frac{\partial u}{\partial \bar{n}} = U_\ell, \quad x \in e_\ell, \ell = 1, \dots, L \quad (2)$$

$$\sigma \frac{\partial u}{\partial \bar{n}} = 0, \quad x \in \partial\Omega \setminus \bigcup_{\ell=1}^L e_\ell \quad (3)$$

$$\int_{e_\ell} \sigma \frac{\partial u}{\partial \bar{n}} dS = I_\ell, \quad \ell = 1, \dots, L \quad (4)$$

$$\sum_{\ell=1}^L I_\ell = 0 \quad (5)$$

$$\sum_{\ell=1}^L U_\ell = 0 \quad (6)$$

where σ is the electrical conductivity, Ω is the target volume, $\partial\Omega$ is the target boundary, u is the electric potential, ξ_ℓ is the contact impedance, $\bar{n}$ is outward unit normal, U_ℓ is the electrode

potential, I_ℓ is the total current through the electrode and e_ℓ is the ℓ th electrode. Boundary conditions in Eqs. 2 and 3 are applied to electrodes, e_ℓ , and the surface between the electrodes respectively. To approximate the solution of the CEM for a target with arbitrary shape, finite element method is used [Vauhkonen 2001, Vauhkonen 1999].

In difference imaging the objective is to trace the change in electrical conductivity ($\delta\sigma$), from a reference conductivity state (σ_o) to the conductivity after the change-of-state (σ). In difference imaging, the non-linear model between the conductivity and the electrode potentials is globally linearized at σ_o by neglecting higher terms in the Taylor polynomial. This leads to an observation model, Eq. 7:

$$\delta V \approx J\delta\sigma + \bar{v} \quad (7)$$

where $\delta V = V(\sigma) - V(\sigma_o)$ is the change in electrode potentials measured between the reference state and after moisture ingress, $\delta\sigma = \sigma - \sigma_o$ is spatial conductivity change, $\bar{v}$ is the difference in observation noise between the two sets of measurements, and J is the Jacobian calculated at an estimated σ_o . The solution of Eq. 7 is represented in Eq. 8 using regularization

$$\delta\sigma_{min} = \underset{\delta\sigma}{\operatorname{argmin}}\{\|\delta V - J\delta\sigma\|_2^2 + A(\delta\sigma)\} \quad (8)$$

where $\delta\sigma_{min}$ is the estimate for the change in the conductivity. The difference imaging approach leads, in principle, to a least square estimation problem where the parameter vector $\delta\sigma_{min}$ is estimated by minimizing $\|\delta V - J\delta\sigma\|_2^2$ with respect to $\delta\sigma$. However, due to the ill-posed nature of the estimation problem, the solution of the least square problem has to be regularized using $A(\delta\sigma)$ [Tikhonov 1977]. Further, $A(\delta\sigma)$ is a side constraint, which regularizes the solution of the minimization problem. The side constraint has an important

role in the solutions of the inverse problem, because it can be constructed so that it favors selected properties – such as spatial smoothness – of the conductivity distribution. For different choices of $A(\delta\sigma)$ [Kaipio and Somersalo 2005].

Due to the global linearization discussed above, the results of difference imaging are qualitative and the estimated conductivity change does not necessarily indicate the actual change in the conductivity of the material. Difference imaging, nevertheless, is very useful and a powerful tool when the objective is to qualitatively trace the change in the electrical conductivity and information about the location of this change in resistivity is of interest (i.e., wetted area due to the water ingress). In this paper, the objective is to monitor 3D moisture transport in unsaturated mortar; difference imaging is well-suited for this application since moisture ingress results in distinct change in the electrical conductivity of the cement-based materials. The EIT measurements in this work were performed using an automatic EIT system developed in Hallaji 2015 and the EIT difference reconstructions, were carried out using MATLAB implementation [Adler 2006, Polydorides et al. 2002].

NUMERICAL SIMULATION OF UNSATURATED MOISTURE TRANSPORT

General

Moisture ingress in this work is simulated by finite element approximation of the governing differential equation for isothermal unsaturated moisture transport where air diffusion and dissolution are neglected [Richards 1931].

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[K(h) \frac{\partial h}{\partial x} \right] + \frac{\partial}{\partial y} \left[K(h) \frac{\partial h}{\partial y} \right] + \frac{\partial}{\partial z} \left[K(h) \frac{\partial h}{\partial z} + 1 \right] \quad (9)$$

where $K = K(h)$ (in/hr [mm/hour]) is the unsaturated hydraulic conductivity, θ is the volumetric moisture content, h (in [mm]) is the pressure head, and x, y, z (in [mm]) are the spatial coordinates.

Material Model

The unsaturated hydraulic conductivity (K) in Eq. 9 is a function of pressure head ($K = K(h)$), and is expressed as a product of the saturated hydraulic conductivity, K_s , and the relative hydraulic conductivity, K_r ($K = K_s K_r$). The saturated hydraulic conductivity ($K_s = 1.6 \times 10^{-4}$ (in/hr [4.0x10⁻³ mm/hr]) value used in this study was taken from [Nokken and Hooten, 2008] using a material porosity of 0.15. In this work, Maulem's model [Maulem 1976] for relate relative hydraulic conductivity is used (Eq.10)

$$K_r = \Theta^I \left[\frac{\int_0^\Theta \frac{1}{h(x)} dx}{\int_0^1 \frac{1}{h(x)} dx} \right]^2 \quad (10)$$

$$\Theta = \frac{\theta - \theta_r}{\theta_s - \theta_r} \quad (11)$$

where $0 \leq \Theta \leq 1.0$ is the effective material saturation, and θ_s and θ_r are saturated moisture content and residual moisture content, respectively. The value of $\theta_s = 0.15$ was experimentally measured in this work from drying a saturated sample and measuring the final moisture loss, and $\theta_r = 0$ is considered from [Pour-Ghaz et al. 2009a, Pour-Ghaz et al. 2009b]. I is an empirical parameter which has been described as accounting for the effect of tortuosity and connectivity of pores [Maulem, 1976], in this study the value of ($I=-9.0$) is taken from [Smyl et al. 2015].

To compute the integrals in Eq. 10, the effective saturation must be expressed as a function of pressure head ($\Theta = \Theta(h)$). In this paper, the van Genuchten model [van Genuchten, 1980, van Genuchten and Nielson 1985] is adopted (Eq. 12).

$$\Theta = \frac{1}{[1+(\alpha h)^n]^m}, m = 1 - \frac{1}{n} \quad (12)$$

where α and n are fitting parameters (α , inversely proportional to the mean pore diameter ($\text{in}^{-1} [\text{mm}^{-1}]$) and n (non-dimensional) is the curve shape parameter). Parameters $\alpha = (4.7 \times 10^{-4} \text{ in}^{-1} [1.2 \times 10^{-2} \text{ mm}^{-1}])$ and $n = 2.1$ were obtained from [Smyl et al. 2015] from undamaged mortar. These values are obtained by fitting the model in Eq. 12 to the water retention curve. For cement-based materials, instead of water retention expressed as $\Theta = \Theta(h)$, the sorption isotherm of material is experimentally obtained as $\Theta = \Theta(RH)$ where RH = relative humidity. The sorption isotherm then is converted to the moisture retention curve using Kelvin-Laplace Equation (Eq. 13) [Pour-Ghaz et al. 2009a, Leech et al. 2006]:

$$h = \frac{\rho_w R T}{m_w} \ln(RH) \quad (13)$$

where ρ_w ($\text{lb-in}^{-3} [\text{g/mm}^3]$) is the density of water, R ($\sim 8.314 \text{ lb.in.K}^{-1}\text{mol}^{-1} [8.845 \text{ J.K}^{-1}\text{mol}^{-1}]$) is universal gas constant, T (K) is the temperature, and m_w ($\text{lb/mole} [\text{g/mole}]$) is the molecular weight of water.

Simulation of Moisture Flow

Commercially available Finite Element Software HYDRUS 3D (Sejna et al., 2014) was used for simulating the moisture flow. The specimen used in the EIT experiment was modeled

with exact dimensions in HYDRUS 3D. Zero-flux boundary conditions were considered at all surfaces except the surface from which water penetrated (area of water reservoir) which was modeled as a 0.4 in [9.5 mm] diameter circle with saturated throughout the simulation. Uniform initial moisture content, ($\theta_i = 0.07$) was considered in this study and was taken from experimentally measured specimen initial condition. Although θ_i is generally nonuniform, the assumption of uniformity was necessary as the initial moisture distribution was not known. Finite element modeling consisted of tetrahedral elements with a maximum dimension of 0.4 in [9.5 mm]. The finite element model was solved in terms of moisture content.

RESULTS AND DISCUSSION

Figure 2 illustrates the 3D EIT reconstruction of moisture flow in the specimen after 15, 30, 60, and 120 minutes of adding water to the reservoir. The rectangles shown on the exterior of the specimen are the electrodes in their respective locations. The scale bar on the right side of the reconstructions reports the change in conductivity $\Delta\sigma$ (mS/in [2.54 mS/cm]). Note, however, that $\Delta\sigma$ represents the change in conductivity only qualitatively because of the difference imaging approach. An increase in electrical conductivity at location of the water reservoir is clearly observed, due to the local increase in the moisture content. EIT reconstructions clearly show the water ingresses over time. In addition, the non-uniformity of the moisture flow inside the specimen is detected, which is shown graphically by the color gradient in the reconstructed images.

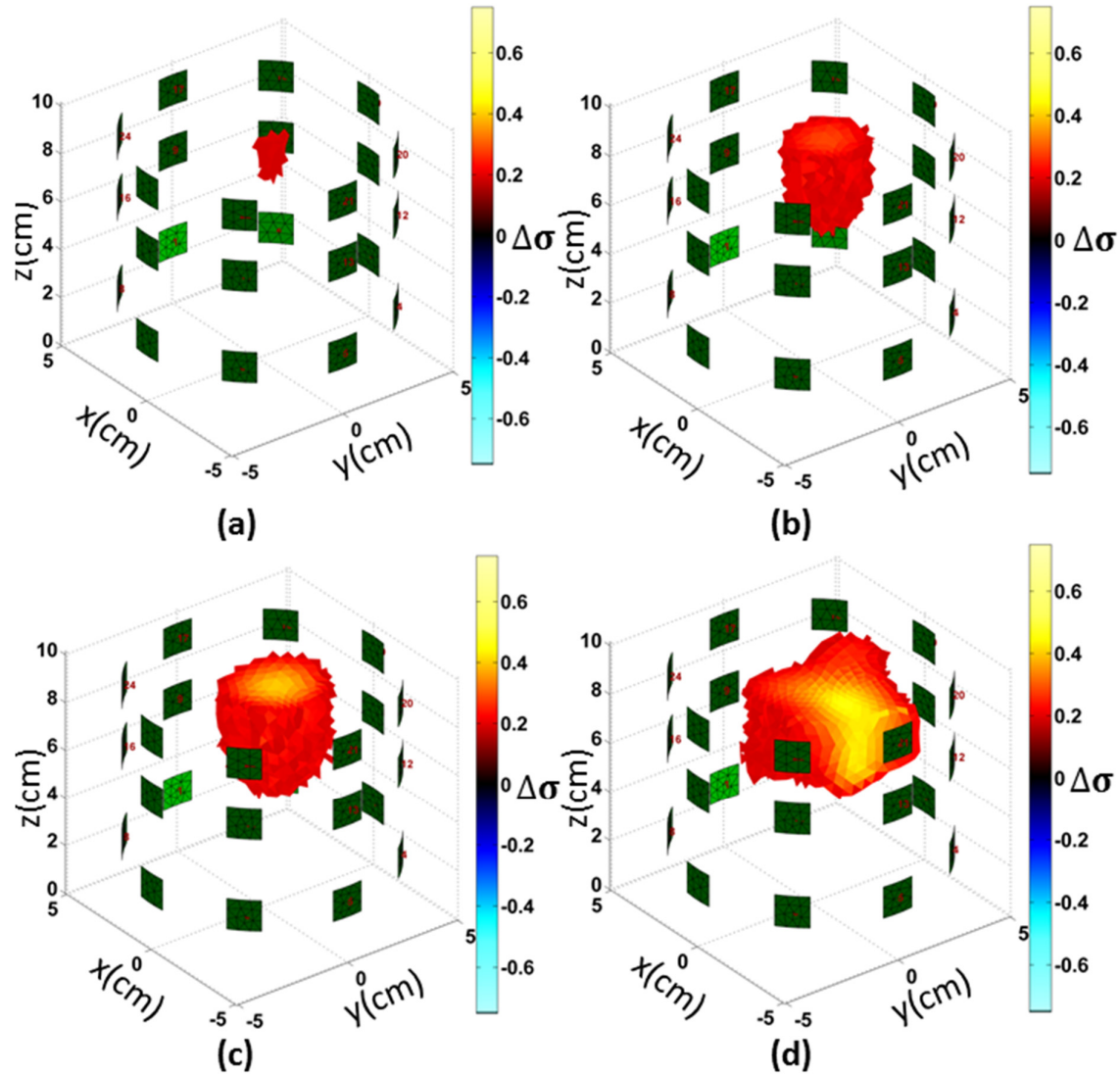


Figure 2- 3D EIT reconstruction of moisture flow in the specimen: (a) 15 minutes, (b) 30 minutes, (c) 1 hour, (d) 2 hours; * $\Delta\sigma = \Delta\sigma(\text{mS/cm})$, 1 in = 2.54 cm

To qualitatively corroborate the EIT reconstructions, Fig. 3 shows a comparison between results of the EIT and the simulation of the unsaturated moisture transport. To make the comparison between results of EIT and moisture flow simulations easier, a vertical slice was taken through the specimen. This slice passes through the center of the water reservoir and the specimen extending to the opposite sides of the specimen. The EIT reconstructions and results

of moisture flow simulations are illustrated in the left column and right column of Fig. 3, respectively. It should be noted that the EIT images show the change in electrical conductivity of the specimen while the moisture flow simulation images show the specimen's volumetric water content. The change in the electrical conductivity with the water content is not linear, and therefore, only a qualitative comparison is possible.

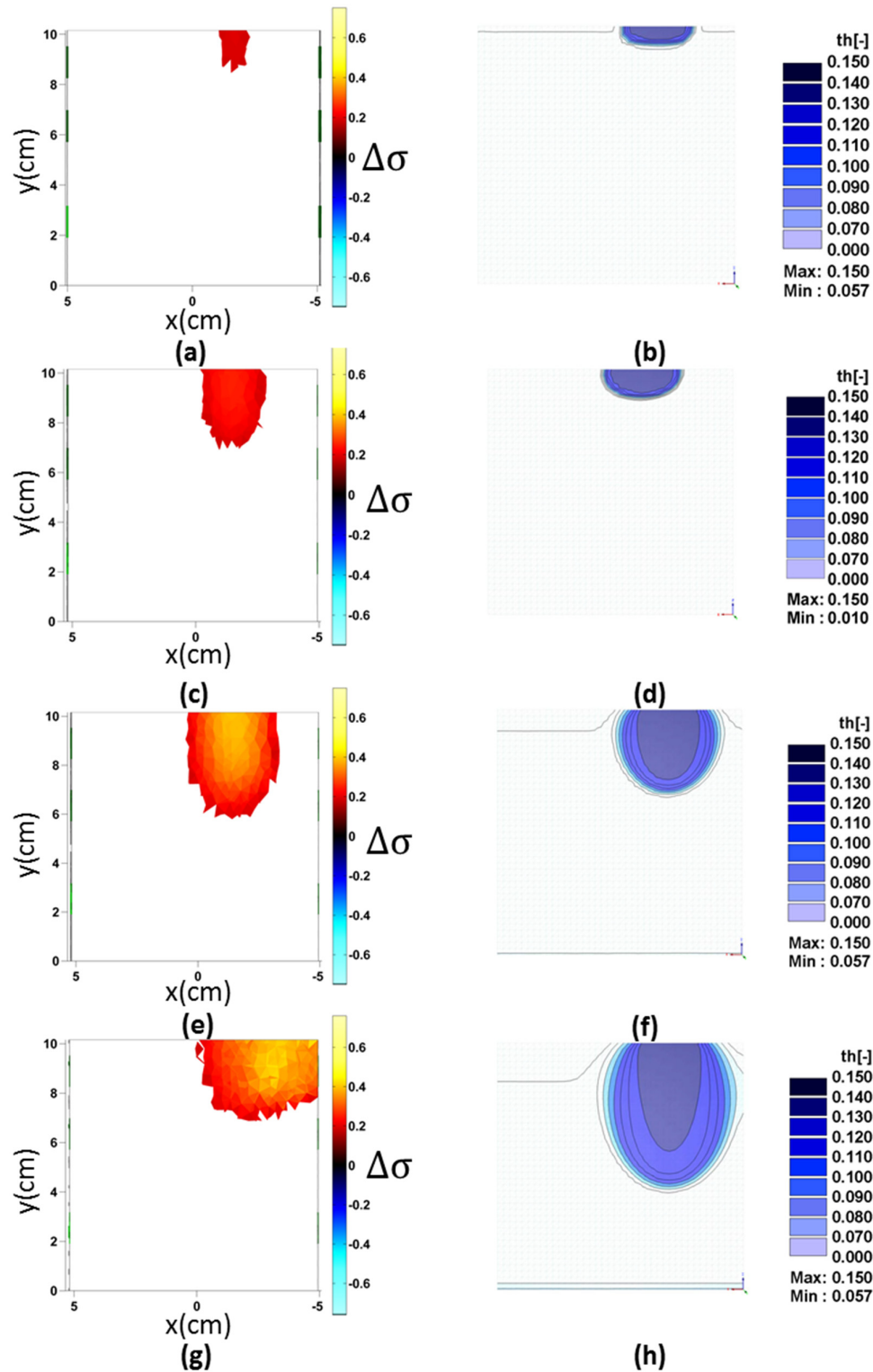


Figure 3- 2D slices of EIT reconstructions (a) 15 minutes, (c) 30 minutes, (e) 1 hour, (g) 2 hours; Results of numerical simulation of moisture flow (b) 15 minutes, (d) 30 minutes, (f) 1 hour, (h) 2 hours * $\Delta\sigma = \Delta\sigma(\text{mS/cm})$, 1 in = 2.54 cm

2D slice comparisons of unsaturated moisture flow and 2D slices of 3D EIT reconstructions compare reasonably at all stages of moisture ingress. Variable moisture content, shown in the moisture flow simulations, is apparent all EIT reconstructions.

CONCLUSION

In this paper the authors studied the feasibility of using electrical impedance tomography (EIT) as a non-destructive test method for monitoring 3D moisture ingress in cement-based materials. A cylindrical specimen made of mortar was tested and water was added to it through a small reservoir on top of the specimen. To corroborate the EIT reconstructions, the numerical simulation of the unsaturated moisture flow using finite element method was used. A qualitative comparison was made between corresponding results of EIT and unsaturated moisture flow simulations. Results of this study suggest that EIT may provide a suitable non-destructive method to monitor 3D unsaturated moisture flow in cement-based specimens.