

# **Durability of Concrete Vaults for Radioactive Waste Disposal**

**by G.S. Duffó, E.A. Arva, S.B. Farina, C.M. Giordano,  
and C.J. Lafont**

**Synopsis:** The development of a program for the design and construction of a facility for the final disposal of intermediate-level radioactive wastes in the Argentine Republic is responsibility of the Atomic Energy Commission (CNEA). The proposed model is the near-surface monolithic repository similar to that in operation in El Cabril, Spain. The design of this type of repository is based on the use of multiple, independent, and redundant barriers. Since the vault and cover are made of reinforced concrete and they are major components of the engineered barriers, the durability of these concrete structures is an important aspect for the facilities' integrity. This work presents a laboratory and field investigation performed during the last 6 years on reinforced concrete specimens made with high-performance concrete, in order to predict the service life of the intermediate-level radioactive waste disposal vaults from data obtained from electrochemical techniques. On the other hand, the development of corrosion sensors that allow on-line measurements of reinforcing steel corrosion potential and corrosion current density, incoming oxygen flow that reaches the metal surface, concrete electrical resistivity, chloride concentration, and internal concrete temperature is shown. These sensors, properly embedded in a prototype of the vault, allow the monitoring of the corrosion process of the reinforcing steel embedded in the structure. All the information obtained from the sensors is being used for the final design of the container to achieve a service life greater than the foreseen durability for this type of facilities (more than 300 years).

**Keywords:** concrete vaults; corrosion; embedded sensors; intermediate-level radioactive waste; reference electrodes

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### INTRODUCTION

Since its creation in 1950, the Argentine Atomic Energy Commission (CNEA) has been working on the development of nuclear energy applications for peaceful purposes. This work includes research and development of basic and nuclear technology areas, the operation of important facilities in charge of the production of radioisotopes for medical and industrial applications and the performance of tasks in connection with the nuclear fuel cycle, mining and uranium processing activities, manufacturing of fuel elements, production of heavy water, and the operation of two nuclear power plants. As a result of such activities various types of radioactive waste have been, and are being produced. Such radioactive waste is classified according to their radioactivity level, half life and disposal technology.

The National Radioactive Waste Management Programme is in charge of evaluating and developing different alternatives for the final disposal of radioactive waste, taking into account technical, operational and financial factors. In the case of **Intermediate Level and Short Level Radioactive Waste** (IRLW) the proposed model is the near-surface monolithic repository similar to that in operation in El Cabril, Spain. The design of this type of repositories is based on the use of multiple, redundant and independent barriers in which the waste is immobilized in cementitious matrixes and packed in 200 liter drums or in special concrete containers. The model foresees a period of 300 years of institutional post-closure control.

The engineered barriers can be grouped in two major categories: physical barriers to prevent intrusion of water, biota or fauna and the release of radio nuclides to the environment; and chemical barriers to restrict radio nuclides migration by adsorption and ion-exchange once soluble radio nuclides are released from the source. The barriers that will be used in the near surface repository include: waste forms, disposal containers,

backfill and buffer materials, reinforced concrete vaults, cover and geological medium. Since vaults and covers, made with reinforced concrete, are major components of the engineered barriers, the durability of the concrete is an important aspect for the integrity of the facility [1]. Several projects are involved concerning the durability of the facilities, and one of them is related to the concrete to be used in the engineering of the repository, as well as, to the manufacture of the containers (to hold the drums with conditioned waste), which will be disposed into the concrete vaults. For these reasons a research programme on concrete durability was initiated several years ago. The research and development are focused to design a durable concrete and to establish the methodology to determine the longevity of concrete, through the knowledge of its performance in the long term under disposal conditions. Durability prediction requires an accurate description of the physical and chemical environment characteristics. Durability is influenced by the environment to which the concrete is exposed to, by the quality of the constituents and their proportion in the mixture design and by structural designs and construction techniques, among other factors.

Reinforcing steel corrosion is one of the degradation processes that may cause reduction and premature termination of the nuclear waste disposal facilities service life. Extensive research has been published in this field; however, very few of these studies address the specific demands required for this type of application. The present experience with modern reinforced concrete is much shorter than the expected life of the ILRW concrete disposal. This fact requires extrapolation of short term experience to 300 years foreseen life [2].

This work shows laboratory and field investigations performed during the last six years on concrete specimens containing reinforcing steel segments exposed to different aggressive environments, in order to predict the service life of the ILRW concrete vaults from data obtained from electrochemical techniques. The diffusion coefficient of aggressive species, such as chloride ions and carbon dioxide, was also determined. In addition, a full scale (1:1) concrete vault was constructed and instrumented in order to monitor the evolution of the reinforcing steel corrosion rate in time.

Additionally, the development of an integrated sensor system based on the measurements of temperature inside the structure, the corrosion potential of reinforcing steel, the corrosion current density of reinforcing steel, the electrical resistivity of concrete, the availability of oxygen and the chloride ions concentration in concrete is shown. These sensors, properly embedded in a structure that simulates the vaults and containers, allow the monitoring of the corrosion process of the reinforcing steel embedded in the structure. All the information obtained from the sensors will be used for the final design of the container in order to achieve a service life more or equal than the foreseen durability for this type of facilities.

## EXPERIMENTAL TECHNIQUE

The study was performed using concrete specimens, 20 cm high and with a square section of 10 cm per side, containing reinforcing steel segments. Each specimen contained 3 reinforcing steel segments. The reinforcing steel was 8 mm in diameter and presented an exposed area of 30 cm<sup>2</sup>. The chemical composition of the reinforcing bars used in the study was as follows: C, 0.41%; Mn, 0.73%; Cu, 0.27%; Ni, 0.13%; Si, 0.28%; P, <0.01%; S, 0.02%; N, 0.008%, Fe, balance. At the concrete-air interface the reinforcing steel was isolated with epoxy resin in order to avoid crevice corrosion. The reinforcing steel segments were positioned in such a way that a 2 cm concrete cover was achieved. Each specimen contained an activated titanium (Ti/TiO<sub>2</sub>) internal reference electrode (IRE) with a diameter of 3.8 mm and 50 mm long located in its centre.

The concrete used in this study was developed by the Construction Center of the National Institute of Industrial Technology (INTI, Argentina) at the end of the 90's decade. It was selected based on the concrete mechanical properties, water permeability tests and workability. These results have been published elsewhere [1, 3]. The composition of the mixture proportion was as follows: water-cementitious ratio (w/cm), 0.34; cement content (sulphate resistant cement), 410 kg/m<sup>3</sup>; coarse aggregate, with maximum size of 19 mm, 1040 kg/m<sup>3</sup>; fine aggregate, 810 kg/m<sup>3</sup>; superplasticizer, 1-2.5%; entrapped air, 2-3%. Before casting the specimens, concrete was passed through a mesh with a hole-size of 6.35 mm (1/4"). Specimens were cured for 7 days covering the exposed concrete surface with a plastic foil. Compressive strength evaluated after 28 days ranged from 50 and 54 MPa. In the last years, new concretes have been proposed for this application, that include supplementary cementitious materials such as silica fume, fly ash, etc., to decrease permeability and/or crack susceptibility. The behavior of these materials is the objective of present investigations.

A total of 18 specimens for corrosion testing were made. After a conditioning period of 100 days the specimens were exposed to three different conditions: partially immersed in a 3.5 % NaCl aqueous solution; immersed in a 5 % Na<sub>2</sub>SO<sub>4</sub> aqueous solution and exposed to natural carbonation in the laboratory atmosphere (room temperature and 60-70% relative humidity).

The electrochemical parameters normally used to characterize the corrosion behavior of reinforcing steel in concrete were monitored periodically during approximately 2100 days. These parameters included the corrosion potential ( $E_{\text{corr}}$ ), the corrosion current density ( $I_{\text{corr}}$ ) obtained from polarization resistance ( $R_p$ ) measurements and the electrical resistivity of concrete ( $\rho$ ) determined from resistance measurements between two reinforcing steel segments.

The  $E_{\text{corr}}$  values were measured using a high input impedance voltmeter connected to the IRE. These measurements were then corrected against a copper/saturated copper sulphate reference electrode (Cu/SCS). The results were evaluated according ASTM standard C876 [4].  $R_p$  was evaluated as  $\Delta V/\Delta I$  [5] from potential sweep within  $E_{\text{corr}} \pm 0.01$  V at a scan rate of  $10^{-4}$  V.s<sup>-1</sup>. The results were corrected to compensate the IR drop

error.  $R_p$  values were used to calculate the reinforcing steel corrosion current density ( $I_{corr}$ ) according to the Stern-Geary relationship as follows:  $I_{corr}=B/R_p$ , where  $B$  values should take into account whether the steel segments are in the active or passive state [6]. Finally, the concrete electrical resistance ( $R_s$ ) was measured between bars using an earth ohm-meter. These values were used to estimate the electrical resistivity of the concrete as  $\rho=k.R_s$ , where  $R_s$  is the geometric cell constant measured experimentally ( $k=27.5$  cm).

Chloride concentration profiles for cylindrical concrete specimens, 10 cm in diameter and 10 cm height and partially immersed in 3.5% NaCl solution, were obtained after 1750 days exposure. In order to analyze the chloride transport mechanism in concrete, the effective diffusion coefficient ( $D_{ef}$ ) was determined by solving Fick's second law. The carbonation depth was determined using the phenolphthalein test after a 2350 days exposure.

Additionally, several IRE were embedded in a full scale (1:1) concrete vault in order to monitor the corrosion potential of the reinforced bars. The monitoring has been followed up for the last three years, and it will be continued for the next years.

## RESULTS AND DISCUSSION

The measurement of  $E_{corr}$  as a function of the exposure time (up to 2100 days) on specimens exposed to laboratory environment showed values more positive than  $-0.200 V_{Cu/SCS}$  revealing a passive state (Fig. 1). The reinforcing steel corrosion potentials measured on specimens immersed in 3.5% NaCl aqueous solution, immediately after exposure, showed values in the range  $-0.150 V_{Cu/SCS}$  to  $-0.325 V_{Cu/SCS}$ . The  $E_{corr}$  values showed increasing trends after the first 350 days exposure and after 450 days exposure reaches an  $E_{corr}$  value higher than  $-0.200 V_{Cu/SCS}$  (passive state). Finally, the corrosion potential of specimens immersed in 5%  $Na_2SO_4$  aqueous solution showed that the behavior is similar to that observed on specimens immersed in the NaCl solution: the initial corrosion potential ranged between  $-0.150 V_{Cu/SCS}$  and  $-0.300 V_{Cu/SCS}$  and an almost constant value is reached after 550 days exposure. The values of  $E_{corr}$  for the three exposure conditions after 2100 days are:  $0.05 V_{Cu/SCS}$  for laboratory environment;  $-0.140 V_{Cu/SCS}$  when exposed to 3.5% NaCl solution and  $-0.225 V_{Cu/SCS}$  were exposed to 5%  $Na_2SO_4$  solution.

The reinforcing steel corrosion current density ( $I_{corr}$ ) remained almost constant and close to  $10^{-8} A.cm^{-2}$  during the first 2100 days of exposure at each testing condition (Fig. 2). These results are a clear indication that steel presents a passive state although the current density of specimens immersed in aqueous solutions is almost three times higher than that exposed to laboratory environment.

The evolution of the electrical resistivity of concrete ( $\rho$ ) exposed to different conditions showed that, in all conditions, the values measured increase with the exposure time. This is an indication of the continuous concrete curing process which results in a pore size distribution reduction. As could be expected, specimens exposed to the laboratory atmosphere showed the highest  $\rho$  values, reaching almost  $2.5 M\Omega.cm$  after

2100 days of exposure. On the other hand, the electrical resistivity of specimens immersed in NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions were very similar one to each other, showing values between 10 and 20 kΩ.cm after 2100 days of exposure.

After measuring the total chloride concentration profiles obtained from specimens partially immersed in 3.5% NaCl aqueous solution during 1750 days, the following values of the chloride effective diffusion coefficient ( $D_{ef}$ ) and chloride surface concentration values ( $C_s$ ) were obtained:  $2.75 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$  and 2.64 % (cement base), respectively. These values correlate well with those reported by Bamforth [7] for marine structures (extreme conditions). No evidence of carbonation was observed on concrete after an exposure period of 2350 days (6.4 years). The constant  $K$  in the equation  $x = K \cdot t^{0.5}$ ,  $x$  being the carbonation depth and  $t$  the exposure time, is lower than  $0.395 \text{ mm} \cdot \text{years}^{-0.5}$ , taking into account an  $x$  detection limit of 1.0 mm.

Figure 3 shows the evolution of the corrosion potential as a function of time, for corrosion probes embedded in the full scale (1:1) container. It can be shown that, up to now, reinforcing steel remains passive, with corrosion potential values higher than the potential limit for passivity breakdown ( $-0.2 \text{ V}_{\text{Cu/SCS}}$ ).

According to the threshold values of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  for the passive to active transition for steel corrosion in concrete ( $E_{\text{corr}} < -0.35 \text{ V}_{\text{Cu/SCS}}$  and  $I_{\text{corr}} > 0.1 \mu\text{A} \cdot \text{cm}^{-2}$ ), the results obtained in laboratory and in field show that, in all cases, the steel reinforcement remains in the passive state. The service criterion proposed by Andrade and Alonso [2] for reinforced concrete in ILRW facilities assumes that the durability of these structures ends once the reinforcing steel corrosion has been initiated. According to Tuuti's service life model [8], no propagation period must be considered. In order to fulfill this criterion, the concrete must be designed to completely avoid corrosion during the period of almost 300 years. Two consequences of this statement are: ILRW facilities must not be located in places where chlorides, sulphates or the carbonation front could reach the reinforcing steel during the service life of the structure and, all other degradation processes, which might affect cover integrity and impermeability (leaching, sulphate attack, freezing and thawing, etc), have to be avoided as part of the design phase.

It is worth mentioning that the site for the near surface disposal facility in the Argentine Republic has not yet been determined. The location considered should be compatible with long-term concrete performance. That is to say, the site should be at a considerable distance from chloride containing environments (e.g. marine environments) and located in an area with no abnormal content of carbon dioxide and other acid contaminants. Then, the next most important cause of reinforced corrosion is the carbonation during the period in which the vaults are kept in contact with air [9]. Taking into account the diffusion rate of CO<sub>2</sub> in concrete, after 300 years, the carbonation depth would be less than 7 mm, that is to say, much less than the concrete cover thickness. Then, it is expected that the concrete under study fulfills the requirements for the foreseen life-time. Besides, in the present work, the influence of both chloride and sulphate ions on the corrosion behavior of reinforcing steel was studied taking into account the remote possibility of accidental contaminations. Finally, it is important to point out that after the selection of the site for the near surface disposal facility, new tests

will be carried out to evaluate the service life of the concrete and its behavior in the environment of the repository.

## DEVELOPMENT OF EMBEDDED SENSORS

The electrodes proposed as reference electrodes to be embedded in concrete for a long time were made from metal-metal oxide (MMO) activated titanium rod (ATR) stock 3-mm dia. commercially produced for permanent impressed-current anodes in cathodic protection of reinforcing steel in concrete. The surface of the ATR was covered with a precious mixed-metal oxide applied using a proprietary process. Energy-dispersive x-ray spectroscopy (EDS) of the ATR coating identified Ir and Ta as the main metallic species. The electrodes were prepared by cutting the rod in 5-cm segments, drilling a 1-mm dia. hole 6 mm in depth at one end, and crimping the stripped end of an insulated braided Cu cable in the hole. The crimped and opposite ends of the bar were covered by epoxy resin. A complete electrochemical study of this ATR electrode was performed in order to determine its ability to be used as reference electrode [10].

The specific chloride electrodes were made with a 50 mm long silver wires (99.99% pure), 2 mm in diameter, soldered onto a low noise screened cable. A 1 cm heat shrink tubing was cut and fitted over the connection between the silver wire and the cable. The silver wire was then subject to an anodic treatment to produce a stable film of AgCl. The specific chloride electrode so manufactured above was tested in KCl solutions with concentrations ranging from  $10^{-5}$  to 1 M in order to determine the calibration curve. The results shows a quite good linear fit between the electrode potential and the logarithm of chloride concentration with an slope close to that predicted by the Nerst equation ( $-0.063 \pm 0.003$ ).

The oxygen availability is obtained by recording the current density measured after 300 s when a 6 mm dia 316L stainless steel rod is polarized at  $-0.950 \text{ V}_{(\text{ATR electrode})}$  using a similar stainless steel rod as a counter electrode. The current density (I) is then converted into oxygen flux by using the Faraday's Law.

The concrete electrical resistivity is measured by applying a sinusoidal signal ( $\Delta V = 10 \text{ mV}$ ,  $\nu = 1 \text{ kHz}$ ) between two identical 316L stainless steel rods (6 mm dia.), and computing the value of the resistance ( $\Omega$ ). The cell constant is obtained by measuring, with this technique, the resistance of a series of solutions of known resistivity (KCl solutions with concentrations ranging from  $1 \times 10^{-5}$  to 1M).

The corrosion potential ( $E_{\text{corr}}$ ) is measured on a 5 mm dia. black steel rod, while the corrosion rate is obtained by cathodically polarizing this rod at a preselected current density ( $I_{\text{appl}}$ ) and measuring the potential of the rod (E) after a certain period of time. The polarization resistance ( $R_p$ ) is obtained as:

$$R_p = -\frac{E - E_{\text{corr}}}{I} - R_s$$

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where  $R_s$  is the solution resistance measured as mentioned above. The corrosion rate was calculated by applying the equation  $I_{\text{corr}}=R_p/B$ , where  $B$  is a constant, which in the present case has been given a value of 0.026 V [11].

The temperature is measured with a conventional platinum resistance thermometer (Pt 100 type) protected from the environment using 316L stainless steel as sheath material.

All the above mentioned electrodes and the thermometer were embedded in a special epoxy resin, resistant to the alkaline environment, and the exposed part of the electrodes (and thermometer) were then covered with a repair mortar and then attached to the reinforcing steel cage (in the case of a new structure) or embedded inside an existing structure.

The sensor is connected via an 8-pin connector to a control case, and this case is connected via USB port with a notebook which has a software named HormiCor 400, developed specifically for this purpose, that makes possible to programme the sequence of measurements and generates a system of alarms when the recorded value exceeds a previously determined value. As regards the measurement methods, temperature, corrosion potentials—of the probe and the reinforcing steel cage—and the potential of the specific chloride electrode are simple recordings of the response generated by the sensor. For the measurement of the concrete electrical resistivity, corrosion current density and oxygen flux, it is necessary to generate a signal disturbing the sensor and the response to this induced disturbance is recorded and used to compute the desired parameters.

Up to now, this system has been embedded in a simulated wall of a concrete vault for intermediate-level radioactive waste disposal and in the spillway of a dam in the south of the Argentine Republic. The results obtained so far are promising and allow the follow up of the state of the structures from the reinforcing steel corrosion point of view.

### CONCLUSIONS

- a) The concrete made of sulphate resistant cement provides a passive status of corrosion to reinforcing steel characterized by corrosion rates lower than  $0.1 \mu\text{A}\cdot\text{cm}^{-2}$  ( $\approx 1 \mu\text{m}\cdot\text{year}^{-1}$ ), assuming low levels of chloride and sulphate ions.
- b) The values of the chloride effective diffusion coefficient ( $D_{\text{ef}}$ ) and the chloride surface concentration when reinforced concrete is exposed to extreme conditions (in contact with sea water), are low enough and the carbonation ratio is also adequate to comply with the foreseen specifications.
- c) To guarantee a 300 years service life, the reinforcing steel corrosion rate on intermediate level radioactive waste disposal containers, must be lower than  $0.01 \mu\text{A}\cdot\text{cm}^{-2}$  ( $\approx 0.1 \mu\text{m}\cdot\text{year}^{-1}$ ). The measured data show that this durability criterion is fulfilled.

- d) The electric resistivity of concrete has a tendency to increase with time, which reflects the continuous curing process showed by concrete at an early stage.
- e) In order to fully evaluate the behavior of concrete durability from the reinforcing steel corrosion point of view, after the selection of the site for the near surface disposal facility is made, the medium and long term evolution of the electrochemical parameters under study will be followed up.
- f) Durable, embeddable and inexpensive sensors for monitoring the corrosion process of new and existing reinforced concrete structures were developed.
- g) The sensors provide *on-line* information of the corrosion potential and the corrosion rate of the reinforcing steel, the concrete electrical resistivity, the oxygen availability, the chloride content and the temperature inside the structure. Besides, the software generates a system of alarms that allows the specialist to make a decision concerning what mitigation strategies to apply.
- h) Results from sensors installed over the past months are promising because they show changes as the concrete cures and dries out in new structures.

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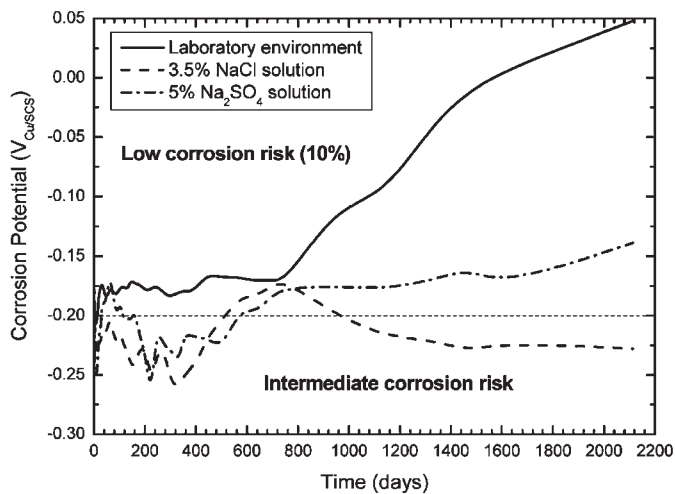


Fig. 1–Evolution of the corrosion potential as a function of time for steel bars embedded in concrete and exposed to different environments.

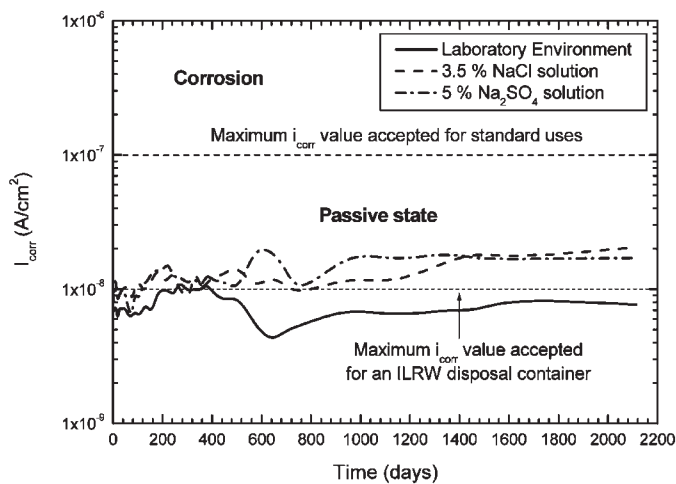


Fig. 2–Evolution of the corrosion current density as a function of time for reinforcing steel embedded in concrete and exposed to different environments.

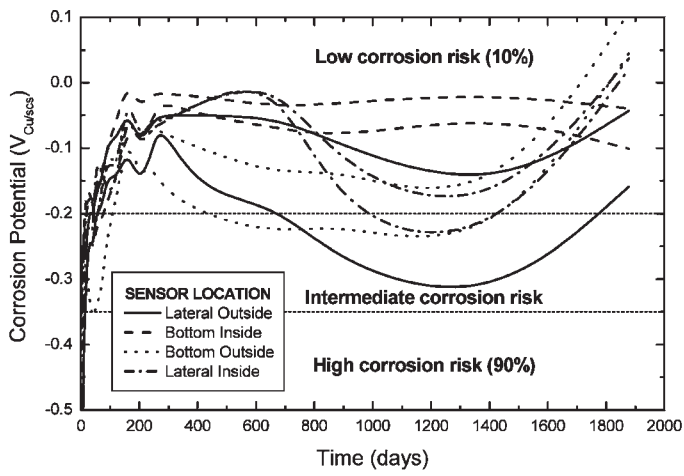


Fig. 3–Evolution of the corrosion potential of corrosion probes located inside the intermediate-level radioactive waste concrete vault.



Fig. 4–Sensor (embbeded in mortar) and adquisiton data system for measurements on concrete structures.

# Effect of Coarse Aggregate Shape and Texture on Self-Compactability

by J.M. Tobes, L. Anahí, G. Giaccio, and R. Zerbino

**Synopsis:** The shape and texture of coarse aggregate affect the properties of fresh and hardened concrete. However, there is limited information about the effects of aggregate characteristics on self-compactability, which can be relevant in countries like Argentina, where a large variety of aggregates is available even in the same region. This paper analyzes the effect of shape and texture of coarse aggregate on self-compacting concrete (SCC) properties. Three different types of coarse aggregate were selected: granitic crushed stone, quartzitic crushed stone, and a siliceous river gravel. The granitic crushed stone presents irregular shape, rough texture, and low absorption. The quartzitic crushed stone also has irregular shape and rough texture, but it has high water absorption. Finally, the natural siliceous river gravel is composed by strong particles with smooth surface and low porosity. SCC was prepared using each type of coarse aggregate with 19 mm maximum size and similar particle size distribution. Slump-flow, V-funnel, and J-Ring tests were carried out. Effects of the changing volume of batched and mixing energy were also studied. The homogeneity of the coarse aggregate distribution was evaluated along vertical cuts on 1 m in height tubes and along a U-tube with 1.80 m height, measuring the ultrasonic pulse velocity and the unit weight in different sections. In addition, the compressive strength and modulus of elasticity were determined. From the results, was concluded that, as expected, the shape and texture of coarse aggregate modify the flowability, but also the mixing energy can strongly affect the plastic viscosity of SCC.

**Keywords:** coarse aggregate type; mortar flowability; self-compacting concrete; shape; texture

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### INTRODUCTION

During the past few years a large amount of experimental research and applications has been performed on self-compacting concrete (SCC). This fact reflects the impact of this material on the construction industry. Filling ability, passing ability and resistance to segregation have been accepted as the main requirements for self-compactability<sup>1, 2</sup>. Typical values of engineering tests such as slump-flow or V-funnel time have been recommended for different SCC classes<sup>3</sup>.

Many researchers have studied methods and models to design SCC. Some of them are based on previous tests on paste or mortar, in order to optimize powder combination and superplasticizer compatibility and to select the necessary volume of paste for the selected fine aggregate<sup>4, 5, 6</sup>.

Xie Y., Li Y., and Long G., studied the effect of the coarse aggregate volume ( $V_g$ ) and mortar volume ( $V_m$ ) ratio in fresh and hardened properties of self-compacting concrete. They found that to obtain the best workability, including flowability, passing ability and stability there is an optimum  $V_g/V_m$  ratio. The compressive strength and the flexural strength decrease when the coarse aggregate volume is increased, but there is an optimum volume for the modulus of elasticity<sup>7</sup>.

McBride J. and Mukai D. J. analyzed the effect of coarse aggregate in filling and passing capability. Concretes were made according to different mixture design philosophies employing for all experiences a crushed stone with a very angular shape, three aggregate gradations and two maximum sizes (13 and 19 mm). Slump-flow, horizontal flow box and a specially designed passing ability test were performed while stereology was used to determine the aggregate spacing. The results show that both, mixtures with lowest

aggregate content and with lowest maximum size, achieve the highest slump-flow. Horizontal flow box tests show that concrete with the lowest aggregate content had the highest filling percentage. On the other side, for mixture with similar coarse aggregate content, when using more sand and less cement, filling ability decreases<sup>8</sup>.

Saak et. al. have proposed a methodology to design self-compacting concrete considering the yield stress and viscosity of cement paste, defining a self-flow zone, where aggregate segregation is avoided<sup>9</sup>. Bui et. al., have expanded this model including the effect of aggregate interaction. In this new model, the fine-coarse aggregate ratio, the aggregate shape and the particle size distribution are considered by means of the void content and the average diameter of aggregate particles. The study determined a minimum paste flow and a minimum apparent viscosity and an optimum flow-viscosity ratio to get enough deformability and filling capability avoiding segregation. This is related to the average aggregate diameter of particles ( $D_{av}$ ) and the aggregate average spacing ( $D_{ss}$ ). However, the surface characteristics of the aggregate were not considered in this model<sup>4</sup>.

As in normal vibrated concrete, the shape and texture of coarse aggregate modify the properties of fresh and hardened SCC. However, there is limited information comparing the effects of coarse aggregate characteristics on self-compactability, which can be relevant in countries like Argentina, where a large variety of aggregates is available even in the same region. This paper analyzes the effect of shape and texture of coarse aggregate in SCC.

## EXPERIMENTAL RESEARCH

With the aim of discussing the effect of coarse aggregate on SCC, there were selected three types of coarse aggregate usually employed at the Buenos Aires Province, Argentina, that show significant differences in their shape and texture. Concretes were proportioned keeping constant the volumes of all component materials and changing only the type of coarse aggregate.

The differences in density, absorption, shape and texture of the used aggregates, probably implies changes in volumes and properties of the mortar to achieve the self-compacting properties. The self-compacting properties were measured through known engineering tests. In addition the segregation resistance in the hardened concrete was analyzed.

### Materials

All concretes were prepared with portland cement (incorporating 19% of calcareous filler, Blaine surface area 337 m<sup>2</sup>/kg, density 3.11) and additional calcareous filler (density 2.8) as powder materials. A polycarboxilate superplasticizer (density 1.09, solid content 18%) was used. A combination of natural siliceous sands was employed as fine aggregate (modulus of fineness 2.38, particles smaller than 0.75 mm 0.4% and voids content 30%).

Three different types of coarse aggregates (maximum size 19 mm) were selected: granitic crushed stone (GCS), quartzitic crushed stone (QCS) and siliceous river gravel (RG). The

granitic crushed stone presents irregular shape, rough texture and low absorption. The quartzitic crushed stone also has irregular shape and rough texture, but it has high water absorption. Finally, the natural siliceous river gravel is composed by strong particles with smooth surface and low porosity. Properties of the aggregates are detailed in Table 1. It can be seen that the GCS and the QCS have similar void content, and that it is higher than in the RG. QCS has the highest absorption, and the GCS the highest density, while fineness modulus are all similar. The particle size distribution of each aggregate is given in Fig. 1.

### Experimental details

Mixture proportions were selected following a proceeding based on slump-flow and V-funnel tests on mortars to make self-compacting concrete. Mortars tests allow to verify the compatibility of the cement – filler – superplasticizer system and to obtain the volume of paste and the superplasticizer dosage required to achieve the self-compacting properties for the selected fine aggregate. The loss of the flowability along time can be also evaluated<sup>5</sup>. The w/c was fixed at 0.50. The selected mortar had a slump-flow of 280 mm and V-funnel time of 4 seconds, with 0.25% (solid percentage respect to the cement mass) superplasticizer quantity. Losses in slump-flow and V-funnel time measured 45 minutes later indicate differences smaller than 10%. The paste volume was equal to 57% that corresponds to a filler / cement ratio of 0.90.

Concretes were prepared using the same mixture proportions only changing the coarse aggregate weight to obtain the same volume in all cases (31 % of total concrete volume). The coarse aggregate was used in saturated dry surface condition in order to avoid water absorption. Firstly batches of 40 L were made; in a second step with the aim of analyzing the effect of the mixing energy, concretes were repeated changing the mixer and the volume of the batch (100 L). Mixtures were named C1 or C2 in accordance to the volume of the concrete trial.

The mixture proportions are given in Table 2. Concretes were identified in accordance with the used coarse aggregate as C-GCS, C- QCS, and C-RG. Initially in 40 L batches the superplasticizer dosage was kept constant; after that 0.9 kg/m<sup>3</sup> of additional superplasticizer was used in C- GCSb, to obtain the same slump-flow as C-QCS and C-RG. It must be noted that it was not necessary to correct the mortar previously selected, keeping the water/cement ratio (0.50), the relative volume of paste (0.57 of the total mortar) and the superplasticizer dosage (solid content = 0.25% of the cement mass).

Table 3 summarizes the main properties of the combination of coarse and fine aggregate, including the average aggregate diameter of particles ( $D_{av}$ ) and the aggregate average spacing ( $D_{ss}$ )<sup>4</sup>. The average aggregate diameter is similar for all aggregates being a little difference in the average aggregate spacing. The  $D_{ss}$  is influenced not only by the  $D_{av}$  but also by the voids content of the combination of aggregate and the volume of paste.

Slump-flow, V-funnel and J-ring were measured as well as the air content in the fresh state. Water temperature was  $20 \pm 1$  °C, and the room temperature was 23 °C.

In order to measure the mechanical properties 100 x 200 mm cylinders were cast and these were cured in moist room until the age of testing, to measure the compressive strength, the modulus of elasticity, and the splitting-tensile strength.

To evaluate the effect of the different coarse aggregates on the homogeneity of concretes (segregation resistance) tubes of different height and shape were cast. With the small batches (C1) tubes 1 m height and 10 cm diameter were filled, and after 7 days they were sawn alongside to survey coarse aggregate distribution. In the case of 100 L batches (C2), tubes with U shape (U-tube) of 1.80 m height, 0.70 m base and 0.10 m diameter were cast; after 28 days they were sawn in transversal direction obtaining specimens 0.40 m length for the determination of the ultrasonic pulse velocity (UPV) and the unit weight (UW).

The groups of specimens corresponding to the upper zone of the tube (entrance and exit), lower zone of the tube (entrance and exit) and middle zone (base of the tube) were compared (Fig. 2).

## RESULTS AND DISCUSSION

Table 4 shows the results of slump-flow (spread diameter  $D_f$  and  $T_{50}$  time), V-funnel flow time ( $T_v$ ), J-Ring (spread diameter  $D_j$ ) and air content.

In the case of 40 l trials, when the same dosage of superplasticizer was used, the slump-flow varies from 655 to 710 mm, except the C1-GCSa which achieved 605 mm. The highest slump-flow was obtained using the river gravel, possibly due to its rounded and smooth particles<sup>7</sup>. On the other hand, in the case of 100 l trials, slump-flow was the same in all cases studied (680 – 700 mm). According to ASTM C1611<sup>10</sup> the Visual Stability Index Values (VSI) for all concretes were equal to 0, which corresponds to a highly stable concrete with no evidence of segregation or bleeding. The concretes prepared with GCS needed more superplasticizer to obtain the same slump-flow than the other mixtures.

The V-funnel times varied from 7 to 14 s for C1 mixtures. The highest  $T_v$  was obtained with the QCS and the lowest with the RG. C1-QCS had also the highest  $t_{50}$  value, so this mixture seems to have a higher plastic viscosity than the others. However, for the C2 concrete, no differences in both the  $T_v$  and the  $t_{50}$  value were found.

The J-Ring test determines the passing ability of SCC. The difference between the slump-flow and J-Ring spread diameters can be used as an indication of the passing ability. A difference smaller than 25 mm indicates good passing ability while a difference greater than 50 mm means noticeable to extreme blocking<sup>11</sup>. From the results, it can be noted that all concretes presented an acceptable performance, except the C1-GCSa.

Table 5 shows the results of hardened concrete. C-QSC achieves the highest compressive strength, but had the lowest modulus of elasticity. The lowest value of splitting tensile

strength corresponds to C-RG and there were no differences between both the C-GSC and C-QSC.

Figure 3 shows the fractured surfaces obtained from the splitting tests. In the case of the QSC it can be observed a plane surface, where all aggregate particles have been fractured. On the contrary, a tortuous broken surface with most aggregate particles debonded was seen in concrete with RG. This difference can be justified considering the high strength of gravel particles added to the weaker interfaces produced by a rounded shape and smooth texture. GSC presents both fractured and debonded particles.

Differences in compressive strength, modulus of elasticity and tensile strength are related to the changes in the interface bond strength and the stiffness of the coarse aggregates. The effect of coarse aggregate on the properties of hardened concrete agrees with the results obtained on normal and high strength concrete<sup>12</sup>.

Regarding the stability and segregation resistance of SCC, all C1 mixtures show a homogeneous distribution of coarse aggregate particles along the height of 1 m tubes. As it was indicated in the case of C2 mixtures 1.80 m height U-tubes were filled. Figure 4 shows the variation of ultrasonic pulse velocity (UPV) and the unit weight (UW) measured on different sections of the U-tubes. As it can be seen, no significant differences (smaller than 3%) between the sections considered were found. As expected the UPV varies with the type of coarse aggregate; mean values of 4.56, 4.54 and 4.27 km/s were obtained on C-GSC, C-RG and C-QSC respectively. The very small variation reflects the excellent filling ability of these SCC.

### CONCLUSIONS

This paper studied the influence of coarse aggregate type on the properties of SCC. Concretes prepared with granitic and quartzitic crushed stones and natural siliceous river gravel were compared. The following conclusions are drawn:

- Based on the slump-flow and V-funnel tests on mortars it was possible to obtain SCC using 20 mm coarse aggregates with marked differences in shape and texture.
- The shape and texture of the coarse aggregate affected the flowability of SCC. Granitic crushed stone required a higher dosage of superplasticizer than the other aggregates to achieve the same slump flow class of SCC. In addition, it was observed that concrete with river gravel showed the lowest values of V-funnel time.
- It was observed an important influence of mixing energy; the main differences seem to be related to the viscosity of concrete. Concretes with similar slump flow showed important reductions in the  $t_{50}$  and V-funnel time when bigger batches were prepared.
- The analysis of sections of SCC tubes showed that all concretes present a homogeneous distribution of coarse aggregate particles along the height, indicating a high stability and segregation resistance.

- The effect of coarse aggregate type on the properties of hardened SCC agrees with the behavior previously observed in normal and high strength concretes.

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Table 1 – Coarse aggregate properties

| Coarse aggregate                           | GCS       | QCS       | RG     |
|--------------------------------------------|-----------|-----------|--------|
| Density                                    | 2.76      | 2.49      | 2.58   |
| Absorption (%)                             | 0.4       | 2.13      | 0.9    |
| Fineness modulus                           | 6.53      | 6.73      | 6.59   |
| Unit weight (kg/m <sup>3</sup> )           | 1440      | 1300      | 1600   |
| Unit weight-compacted (kg/m <sup>3</sup> ) | 1580      | 1430      | 1660   |
| Voids content (%)                          | 48        | 49        | 38     |
| Voids content-compacted (%)                | 43        | 42        | 36     |
| Shape                                      | Irregular | Irregular | Round  |
| Texture                                    | Rough     | Rough     | Smooth |

Table 2 – Concrete mixture proportions

| Concrete                              | C-GCSa | C-GCSb | C-QCS | C-RG |
|---------------------------------------|--------|--------|-------|------|
| Cement (kg/m <sup>3</sup> )           | 332    | 331    | 332   | 332  |
| Filler (kg/m <sup>3</sup> )           | 299    | 298    | 299   | 299  |
| Water (kg/m <sup>3</sup> )            | 166    | 166    | 166   | 166  |
| Sand (kg/m <sup>3</sup> )             | 745    | 744    | 745   | 745  |
| Coarse agg. (kg/m <sup>3</sup> )      | 856    | 856    | 772   | 800  |
| Coarse agg. vol.                      | 31     | 31     | 31    | 31   |
| Superplasticizer (kg/m <sup>3</sup> ) | 4.6    | 5.5    | 4.6   | 4.6  |

Table 3 – Properties of the used combinations of fine and coarse aggregates and estimated aggregate spacing

|                                            | GCS   | QCS   | RG    |
|--------------------------------------------|-------|-------|-------|
| Paste volume (l)                           | 384   | 384   | 384   |
| Vg/Vf                                      | 1.08  | 1.08  | 1.08  |
| Modulus of fineness                        | 4.60  | 4.59  | 4.56  |
| Dav (mm)                                   | 6.4   | 6.7   | 6.5   |
| Unit weight-compacted (kg/m <sup>3</sup> ) | 2095  | 1980  | 2075  |
| Void content-compacted (%)                 | 22.1  | 22.5  | 20.2  |
| Dss (mm)                                   | 0.517 | 0.530 | 0.584 |

Table 4 – Results of fresh concrete

| Concrete         | t50<br>(s) | Df<br>(mm) | Tv<br>(s) | Dj<br>(mm) | Df - Dj<br>(mm) | Air<br>content<br>(%) |
|------------------|------------|------------|-----------|------------|-----------------|-----------------------|
| batches of 40 l  |            |            |           |            |                 |                       |
| C1- GCSa         | 3.1        | 605        | 11.0      | 525        | 80              | -                     |
| C1- GCSb         | 2.3        | 710        | 7.1       | 680        | 30              | 5.7                   |
| C1- QCS          | 3.6        | 655        | 14.2      | 650        | 5               | 4.5                   |
| C1- RG           | 2.3        | 685        | 6.8       | 650        | 35              | 5.0                   |
| batches of 100 l |            |            |           |            |                 |                       |
| C2- GCSb         | 1.4        | 700        | 4.8       | -          | -               | 6.5                   |
| C2- QCS          | 1.5        | 680        | 5.2       | -          | -               | 6.0                   |
| C2- RG           | 1.5        | 680        | 4.6       | -          | -               | 4.5                   |

Table 5 – Results of hardened concrete

| Concrete | Age<br>days | f'c<br>(MPa) | E<br>(GPa) | MR  | ft<br>(MPa) |
|----------|-------------|--------------|------------|-----|-------------|
| C1- GCSb | 7           | 41.6         | 30.1       | -   | 3.7         |
| C1- QCS  |             | 42.7         | 25.4       | -   | 3.6         |
| C1- RG   |             | 37.0         | 32.6       | -   | 3.1         |
| C2- GCSb | 28          | 47.5         | 32.5       | 4.9 | -           |
| C2- QCS  |             | 48.2         | 27.1       | 4.7 | -           |
| C2- RG   |             | 42.4         | 34.9       | 3.6 | -           |

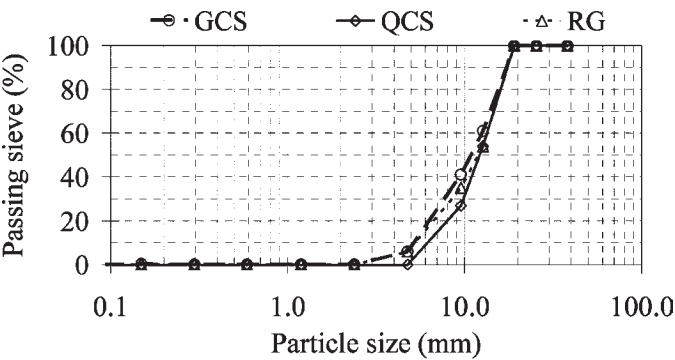


Fig. 1 – Particle size distribution of coarse aggregates.

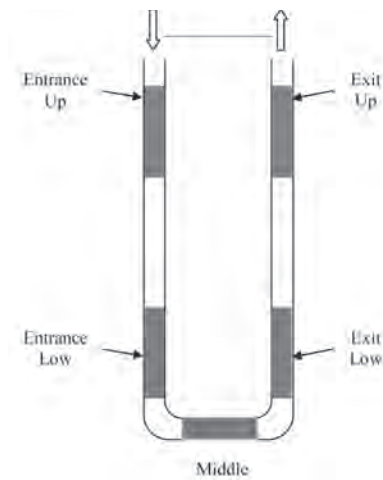


Fig. 2 – U- tube.



Fig. 3 – Fracture surfaces (splitting tests).

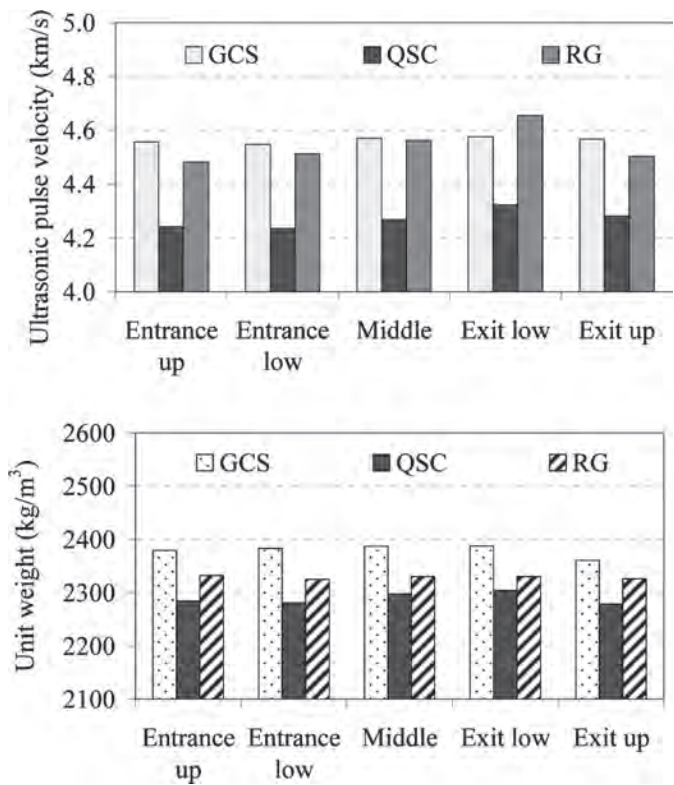


Fig. 4 – Ultrasonic pulse velocity and unit weight measured on different sections of U-tubes filled with SCC.



# **Influence of Curing Conditions on Transport Properties of Blended Cement Concrete**

**by V.L. Taus, Y.A. Villagrán, and A.A. Di Maio**

**Synopsis:** Concrete curing is an essential stage in construction in order to obtain an adequate degree of hydration of cement. Frequently, this step is not carried out correctly, but an adequate structure performance depends to a great extent on curing. Nowadays, blended cement concrete (BCC) is used widely in Argentina, despite the lack of long-standing BCC structures constructed to demonstrate adequate service-life performance. In this paper, the modification of BCC pore structure due to curing treatment is analyzed by evaluation of transport properties in concretes with different w/c and maximum coarse aggregate size. To simulate diverse weather conditions to which the same concrete type may be exposed according to geographical location, different curing conditions were applied during 28 consecutive days. Transport properties evaluated were water permeability under pressure, capillary suction, and chloride ingress rate. Total porosity and 24-h water absorption were also determined. According to the results obtained, a notable influence of curing conditions on the pore structure of BCC was observed, emphasizing the importance of a proper curing on the service life of BCC structures.

**Keywords:** concrete; curing conditions; durability; hydration; porosity; transport mechanisms

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### INTRODUCTION

Concrete curing is essential for the correct development of concrete properties. During curing treatment water loss is prevented and adequate temperature is maintained for the development of hydration products. Frequently, concrete curing is not performed correctly, but a proper structure performance during service life depends to a great extent on this step.

A structure that was properly designed and built with adequate quality materials can be remarkably affected, or it may not reach its planned service life, due to deficiencies in the concrete curing process. A USA report indicates that in 1979 approximately 24% of nonresidential structures lacked the curing process, and only 26% were cured following the specifications (1). For this reason, national and international regulations strictly state the conditions (methodology and duration) under which concrete curing should be performed according to the type of concrete, geographical location and time of the year.

The importance of adequate curing does not only involve attainment of adequate strength but also attaining adequate durability. The different attacks that reinforced concrete structures can suffer are mostly related to the ingress of external substances from the environment by different transport mechanisms. Concrete vulnerability depends on the volume and size of the pores, but more importantly on their connectivity. Thus, by means of an effective curing method, concrete durability can be improved by achieving a degree of hydration that allows capillary disconnection.

Hydration can only take place when vapor pressure in the capillaries is sufficiently high (0.8 of saturation pressure) (2). For a given w/c, after 180 days of moist curing, compressive strength tripled that which was achieved without curing treatment (3). However, if humidity conditions are maintained only during 3 days, at the age of 28 days, 70 to 80% of the compressive strength obtained after 28 days of continuous moist

curing can be reached (4). This is why it is important to provide concrete a minimum period of curing.

Storage in air during early ages allows water loss from concrete, whose magnitude depends on the surface/volume relationship of the structural element, temperature, relative humidity and wind speed.

In Argentina, blended cements with calcareous filler and blast-furnace slag content as high as 35% have been used for the last few years. However, there is a lack of experience about the long term performance of this type of cement.

It is well known that calcareous filler in blended cements increases early hydration and decreases cement paste porosity. Blast-furnace slag produces a similar effect but at more advanced ages, with an additional pozzolanic action. Thus, the simultaneous addition of these two mineral admixtures produces a complementary effect (5). For this reason, it is expected that concrete made with this type of cement would be durable, but there are no service records available of old structures made with this cement. In this aspect blended cement can be especially sensitive to curing conditions. In practice it is important to quantify the effect on transport properties.

Although w/c and curing conditions determines the porosity of concrete, aggregate size can also affect its permeability. The aggregate size and grading affect concrete bleeding and microcracking in the transition zone, and consequently concrete permeability (3).

In this paper, the durability of concretes made with blended cement are studied by analyzing modifications of pore structure produced by the type of curing, by the assessment of transport properties. Four concretes with different w/c and maximum coarse aggregate size were assessed. They were subjected to different types of curing to simulate conditions to which concrete can be subjected depending on environmental conditions and the methodology applied during curing.

## EXPERIMENTAL

### Materials and methods

Tests were performed on four concretes with different w/c: two with w/c= 0.40 (C-1 and C-3) and two with w/c= 0.60 (C-2 and C-4). All mixtures were made with blended cement, with 18 % calcareous filler and 12 % blast-furnace slag contents. Siliceous river sand was used, and coarse aggregate was a granitic crushed stone (GCS) with maximum size of 19 mm in C-1 and C-2, and 25.4 mm in C-3 and C-4. Table 1 shows physical and chemical characteristics of the cement used. Table 2 shows the mixtures proportions and some properties in the fresh state. All concretes had slumps of  $70 \pm 15$  mm.

**Curing methodology** – For the concrete types evaluated, specimens were maintained in forms for the first 24 h. Then, each series was divided in three groups cured until the age of 28 days according to the following modalities:

**Moist curing (f.g.):** Specimens were cured in fog room ( $T: 20 \pm 2^{\circ}\text{C}$ ,  $\text{RH} > 95\%$ ) on the basis of ASTM C 192 (6).

**Laboratory atmosphere (lab.):** Specimens were stored at laboratory atmosphere ( $T: 20 \pm 2^{\circ}\text{C}$ ,  $\text{RH}: 50\%$ ).

**Outside (out.):** Specimens were placed outside in La Plata city (Province of Buenos Aires, Argentina), in a sector protected from wind, with average temperature, humidity and precipitation during the month of curing at  $11^{\circ}\text{C}$ ,  $80\%$  and  $63\text{ mm}$ , respectively.

After the above mentioned period of curing, different laboratory tests were carried out as described below.

### RESULTS AND DISCUSSION

**Compressive strength** – Compressive strength was determined on cylindrical specimens ( $150\text{ mm} \times 300\text{ mm}$ ) at the age of 28 days according to ASTM C 39 (7). Figure 1 shows compressive strength values, where each value corresponds to the average of 3 determinations. It can be observed that the highest compressive strength levels were obtained from the specimens cured at high relative humidity.

**Absorption and porosity** –. These characteristics were determined following ASTM C 642 (8). Figures 2 and 3 show the average values of absorption and porosity for each type of concrete and curing condition. Each reported value corresponds to the average of 6 determinations on  $100\text{ mm}$  cubic specimens.

The results indicate that the highest absorption and porosity values were for the specimens stored in the laboratory atmosphere due to the lack of humidity required for the hydration products to achieve a proper growth and an adequate capillary disconnection for the w/c used. The lowest values were observed in specimens cured in the fog room, while those placed outside showed almost the same performance. This is because of the high relative humidity present in La Plata city.

As expected, for the same curing process and maximum coarse aggregate size, the greater the w/c the higher the values of the parameters. This fact confirms the direct relationship between the w/c and pore structure. For  $w/c=0.40$ , porosity and absorption increase slightly with increasing size of coarse aggregate. For  $w/c=0.60$ , however, this performance is not confirmed indicating a slight reduction of these parameters with increasing maximum size. It must be pointed out that the difference due to the maximum aggregate size is not significant.

**Water penetration under pressure** – Structures such as water tanks, pipes, dikes and dams have the function of containing liquids. In these cases, the structures are subjected to hydrostatic pressure, and permeability is the property that characterizes the resistance of a porous material to be penetrated by a fluid under pressure. The test method of measuring water penetration under pressure is one of the methodologies used to quantify this property (9).

The technique consists of subjecting the specimen (in the present case: concrete prisms of 200 mm x 200 mm x 100 mm) to a series of steps of variable pressures during a standardized time interval. The interpretation of the test involves measurement of the profile of water penetrated in the specimen (Fig. 4), by splitting the specimens into two halves.

This test allows assessing the quality of the concrete's permeability, which is governed by the pore structure. According to the Argentine regulation (CIRSOC 201:2005) (10), average and maximum penetrations should be lower than 30 mm and 50 mm, respectively, when the concrete structure is subjected to freezing and thawing, chemical aggressiveness or a marine atmosphere. Table 3 shows the average and maximum penetration values of the assessed concretes. Figures 5 and 6 display the profiles of penetration corresponding to the average of 3 specimens.

It is interesting to note that C-1 and C-3 concretes ( $w/c=0.40$ ) cured in the fog room do not exceed the limit values proposed by the CIRSOC 201:2005 Regulation, because they have a sufficiently low  $w/c$  and because the standardized curing provides optimum conditions for the development of hydration products. Under this curing condition only a little difference was observed between concretes with different maximum coarse aggregate size.

On the other hand, specimens stored in the laboratory exceed the limits proposed by CIRSOC. This is a consequence of the lack of humidity, required to reach an adequate growth of the hydration products and to prevent an early microcracking.

For the moist curing condition, concretes C-4 and C-2 ( $w/c=0.60$ ) showed acceptable and fair performance, respectively (see Table 3). Such a high  $w/c$  implies a greater amount of mixing water than necessary to complete the hydration reactions, and the remaining water results in a high number of capillaries which can not be filled with the hydration products. Poor curing conditions magnify these deficiencies. Then, in the case of the specimens placed in the laboratory atmosphere and outdoors, water fully penetrated the thickness of the specimen.

Figures 5 and 6 show that for  $w/c=0.40$ , in the case of specimens stored outdoors, the penetration profiles increase with the maximum coarse aggregate size. The same effect in a minor degree can be observed on the specimens stored in the laboratory. Uncontrolled curing conditions would lead to a higher microcracking at the interfacial zone and consequently to a higher permeability. This fact explains the importance of correct curing treatment regardless of the use of a sufficiently low  $w/c$ .

In the case of concretes with higher w/c, it is not possible to establish a relationship with the maximum size, due to the high porosity of the matrix.

**Capillary absorption** – Most concrete structures are subjected to wetting and drying cycles in which a liquid, generally water, penetrates into the structure. This transport mechanism is induced by surface tension of water acting on concrete capillaries. This phenomenon is called capillary suction and is evaluated by means of the sorptivity test. Parameters obtained from this test are considered to be representative of the connected pore structure of concrete (i.e., effective porosity) and its resistance to the ingress of aggressive agents from the environment.

Sorptivity tests were carried out on 50 mm thick slices cut from cylindrical specimens (100 mm x 200 mm) according to the scheme in Fig. 7, where the test face is shown shaded. The lowest 30 mm thick slice was discarded to avoid testing an altered face due to contact with the mold.

Tests were performed according to IRAM 1871 (11) which is similar to ASTM C 1585 (12). It consists of recording, at fixed time intervals, the mass increment by capillary suction of a specimen with one face in contact with water. The transport mechanism by capillary absorption is measured by the rate and capacity of capillary suction. Absorption rate represents the speed of penetration of the liquid by capillarity and is expressed in  $\text{g}/(\text{m}^2 \cdot \text{s}^{1/2})$  while capacity is expressed in  $\text{g}/\text{m}^2$  and is the amount of water required to produce full capillary saturation of concrete.

Table 4 shows the absorption parameters obtained in the test. Figure 8 displays the amount of water absorption per unit area as a function of the square root of time. Each reported value represents the average of 3 determinations. The results clearly indicate the dependence of capillary suction on the w/c, which is the most important parameter.

In all cases, the parameters of capillary absorption (rate and capacity) were higher in the specimens stored in the laboratory than in the other ones. Therefore, in geographic sites where relative humidity and temperature are approximately 50% and 20°C, respectively, curing treatment is critical.

As expected, the best performance corresponded to concretes cured in the fog room. Those exposed to outdoor atmosphere exhibited an intermediate performance with some tendency towards the concretes cured in the fog room. This can be explained considering that the place where these specimens had been located (atmosphere of La Plata city) showed high levels of relative humidity, approximately 80%.

Regarding the effect of the maximum coarse aggregate size, it seems that for w/c= 0.40, parameters of capillary suction increase with increasing maximum size. On the other hand, a clear tendency is not noticeable for w/c= 0.60. The effect of the coarse aggregate size is concealed by the high porosity of the matrix.

**Chloride ingress** – To determine the influence of curing treatment on chloride ingress, measurements of the chloride profile were made in specimens exposed to a marine atmosphere (Mar del Plata city, Argentina) at the age of 60 days. The specimens (75 x 150 x 250 mm prisms) were placed approximately 15 meters from the marine coastline and at a height of 5 meters from sea level.

Specimens were laterally covered with at least three layers of waterproof chlorinated rubber paint. One of their faces, the molded one, was not painted in order to allow unidirectional chloride ions ingress. After periods of approximately 6, 12 and 18 months, waterproof paint was removed for each evaluation period, and a portion of the specimen was cut transversally in slices (about 5 mm thick) with increasing depths from the exposed surface (Fig. 9). These sections were ground and water soluble chloride contents were determined by colorimetric titration with silver nitrate according to the Mohr method (13). Figure 10 shows contour plots of the evolution in time of water soluble chloride content versus depth for each concrete and curing condition. Chloride contents in Fig. 10 are expressed as % in sample weight.

The results indicate a clear difference between C-1 and C-3 concretes compared to C-2 and C-4 due to the lower w/c of C-1 and C-3. A clear difference due to the curing method was also observed in C-1 and C-3 concretes, while in C-2 and C-4 differences are not clearly evident. This observation suggests that curing becomes more important regarding to resistance to chloride ingress when the w/c is low. The results confirm that a higher level of hydration through an adequate curing cannot compensate for the high capillary porosity in a concrete with high w/c.

In some cases (C-2 lab., C-2 out. and C-4 lab.) a superficial washing effect produced by rainwater is evident in the external zone. The degree of influence of this effect would seem to vary with seasons according to the wind and rain regimes. These measurements, performed every 6 months, showed a variation probably occurring due to a seasonal factor. In C-3 and C-4 concretes, which contained a higher maximum size of aggregate, the rate of ingress is slightly higher than in C-1 and C-2 concretes. These results are in accordance with the previously presented, which can also be explained as a consequence of the effect of maximum aggregate size on the quality of the interfacial zone.

## CONCLUSIONS

The results obtained from the different parameters to assess transport mechanisms, such as capillary suction, permeability by means of water penetration technique and chloride ingress rate, indicate that the performance of concretes made with blended cement (BCC) is affected by curing conditions.

The most unfavorable conditions were for specimens placed for 28 days in an atmosphere of 20°C and 50% relative humidity, because this lower relative humidity limits the degree of hydration compared with what would be reached in optimal

conditions of humidity. This performance was observed for concretes with  $w/c = 0.60$  and for those with  $w/c = 0.40$ , with higher  $w/c$  being the most sensitive. The results confirm that a low  $w/c$  is a necessary condition but it is not sufficient to achieve an adequate pore system, thus pointing out the importance of a good curing process. This latter fact is of special interest in those geographical locations where low relative humidity makes curing a critical step.

In aggressive environments, BCC structures would not have a long term performance without an adequate curing treatment, even with  $w/c = 0.40$ . Transport parameters required by Argentinean Regulation (CIRSOC 201) for concrete in aggressive environment were fulfilled by BCC with  $w/c = 0.40$  only when it was cured in fog room.

The best performance was observed in the blended cement concretes cured for 28 days at 20°C and relative humidity higher than 95%. A similar performance was observed for those concretes stored outdoors located in an urban-industrial atmosphere (La Plata city, Buenos Aires province, Argentina) at a site protected from wind with average temperature, humidity and precipitation during the month of curing of 11 °C, 80% and 63 mm, respectively.

As regards the influence of maximum coarse aggregate size, BCC with low  $w/c$  cured in fog room do not show appreciable differentiation of the assessed parameters due to the maximum aggregate size. However, when curing conditions were far from ideal, an increase in the parameters of transport was observed as the maximum size of the coarse aggregate increased, however, the difference was not remarkable. For a high  $w/c$ , the high porosity of the matrix and the low quality of the interfacial zone dominates, and the influence of the maximum aggregate size cannot be distinguished clearly. A higher level of hydration with an adequate curing treatment cannot compensate for the high capillary porosity in a concrete with high  $w/c$ .

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Table 1 – Physico-chemical analysis of the blended cement.

|                                                      |       |
|------------------------------------------------------|-------|
| Specific surface (Blaine) (m <sup>2</sup> /kg)       | 438   |
| Density (g/cm <sup>3</sup> )                         | 3,03  |
| Loss on ignition (%)                                 | 3.0   |
| Insoluble residue (%)                                | 2.7   |
| Sulfur trioxide (SO <sub>3</sub> ) (%)               | 1.87  |
| Magnesium oxide (MgO) (%)                            | 0.95  |
| Silicon dioxide (SiO <sub>2</sub> ) (%)              | 19.0  |
| Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> ) (%)   | 3.88  |
| Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> ) (%) | 7.37  |
| Calcium oxide (CaO) (%)                              | 60.95 |
| Chloride (Cl <sup>-</sup> ) (%)                      | 0.011 |

Table 2 – Mixture proportions (kg/m<sup>3</sup>).

| Concretes                        |           | C-1   | C-2  | C-3     | C-4  |
|----------------------------------|-----------|-------|------|---------|------|
| w/c                              |           | 0.40  | 0.60 | 0.40    | 0.60 |
| Maximum aggregate size           |           | 19 mm |      | 25.4 mm |      |
| Materials                        |           |       |      |         |      |
| Water                            |           | 168   | 168  | 168     | 168  |
| Blended Cement                   |           | 425   | 280  | 425     | 280  |
| Fine aggregate                   |           | 790   | 920  | 800     | 920  |
| Coarse aggregate                 | GCS 6-20  | 1000  | 1000 | -       | -    |
|                                  | GCS 10-30 | -     | -    | 1000    | 1000 |
| Air content (%)                  |           | 2.3   | 3.0  | 2.6     | 3.3  |
| Unit weight (kg/m <sup>3</sup> ) |           | 2444  | 2394 | 2430    | 2352 |

Table 3 – Average and maximum water penetrations depths.

| Concrete | Curing     | Average penetration depth (mm) | Maximum penetration depth (mm) |
|----------|------------|--------------------------------|--------------------------------|
| C-1      | Fog room   | 10                             | 16                             |
|          | Laboratory | 52                             | 54                             |
|          | Outside    | 16                             | 21                             |
| C-2      | Fog room   | 34                             | 38                             |
|          | Laboratory | >100                           | >100                           |
|          | Outside    | >100                           | >100                           |
| C-3      | Fog room   | 9                              | 13                             |
|          | Laboratory | 56                             | 62                             |
|          | Outside    | 36                             | 41                             |
| C-4      | Fog room   | 29                             | 32                             |
|          | Laboratory | >100                           | >100                           |
|          | Outside    | >100                           | >100                           |

Table 4 –Capillary suction parameters.

| Concrete | Curing     | Absorption rate<br>(g/(m <sup>2</sup> *s <sup>1/2</sup> )) | Capacity (g/m <sup>2</sup> ) |
|----------|------------|------------------------------------------------------------|------------------------------|
| C-1      | Fog room   | 2.8                                                        | 2602                         |
|          | Laboratory | 9.0                                                        | 4051                         |
|          | Outside    | 3.6                                                        | 3098                         |
| C-2      | Fog room   | 9.5                                                        | 4540                         |
|          | Laboratory | 29.0                                                       | 5460                         |
|          | Outside    | 23.1                                                       | 4718                         |
| C-3      | Fog room   | 4.7                                                        | 3360                         |
|          | Laboratory | 18.2                                                       | 4159                         |
|          | Outside    | 9.8                                                        | 3561                         |
| C-4      | Fog room   | 15.4                                                       | 4138                         |
|          | Laboratory | 25.1                                                       | 4436                         |
|          | Outside    | 19.7                                                       | 4492                         |

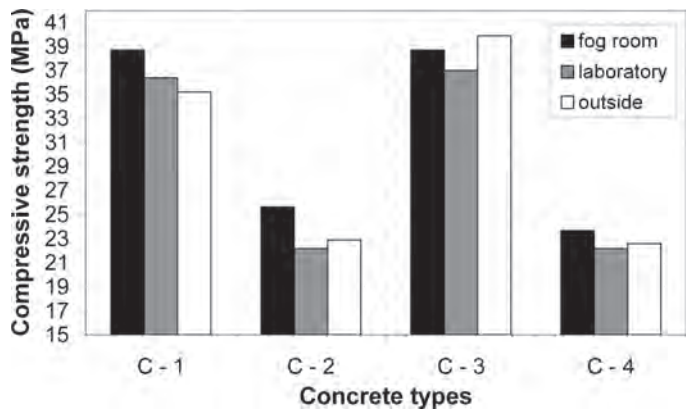


Fig. 1 – Compressive strength.

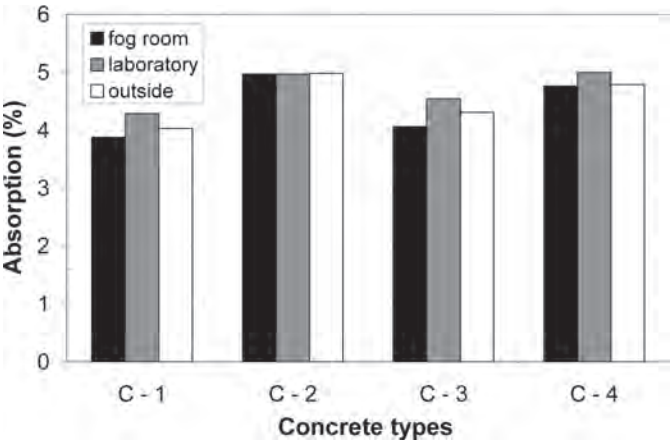


Fig. 2 – Absorption after 24-h immersion.

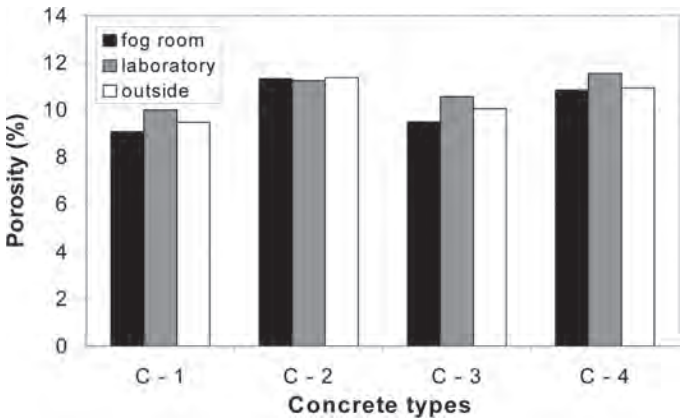


Fig. 3 – Volume of permeable voids.



Fig. 4 – Water penetration profile on both halves of one of the assessed specimens.

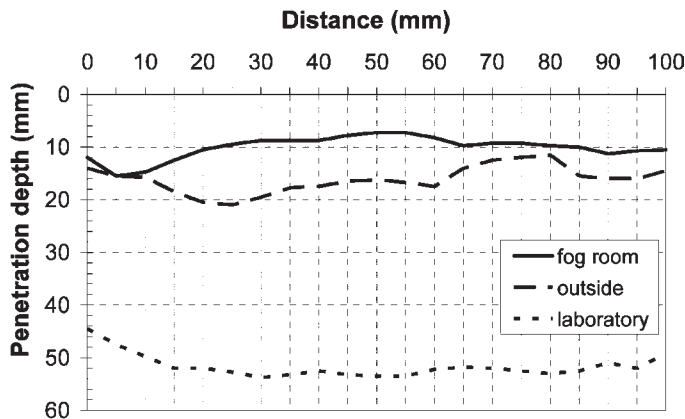


Fig. 5 – Water penetration profiles of C-1 concrete types.

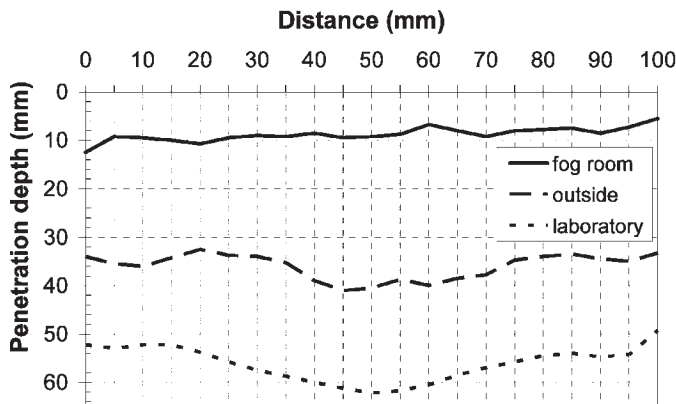


Fig. 6 – Water penetration profiles of C-3 concrete types.

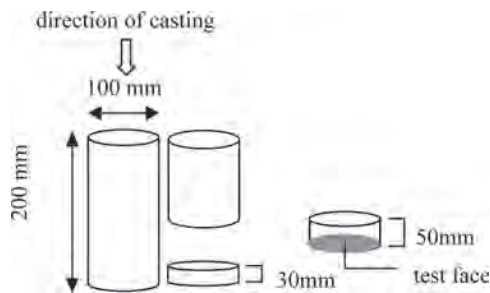


Fig. 7 – Scheme and location of the test specimen for capillary absorption testing.

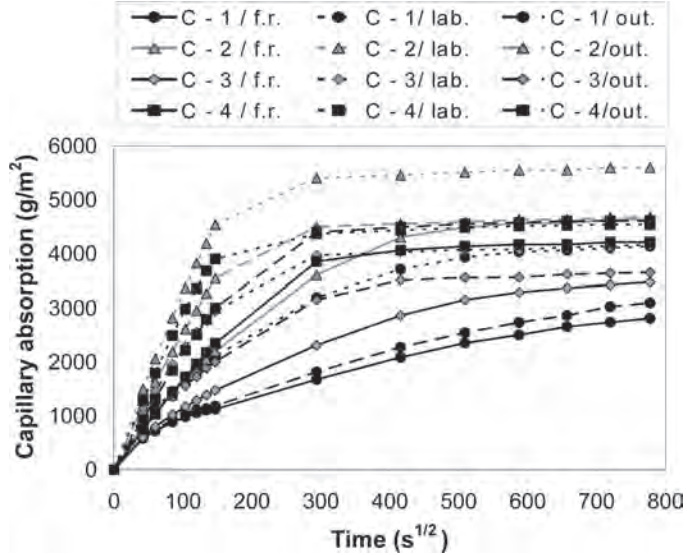


Fig. 8 – Capillary absorption of different concrete types as a function of time.

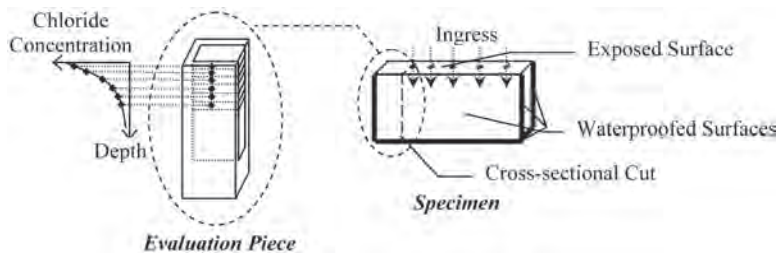


Fig. 9 – Scheme for obtaining samples for chloride content determination.

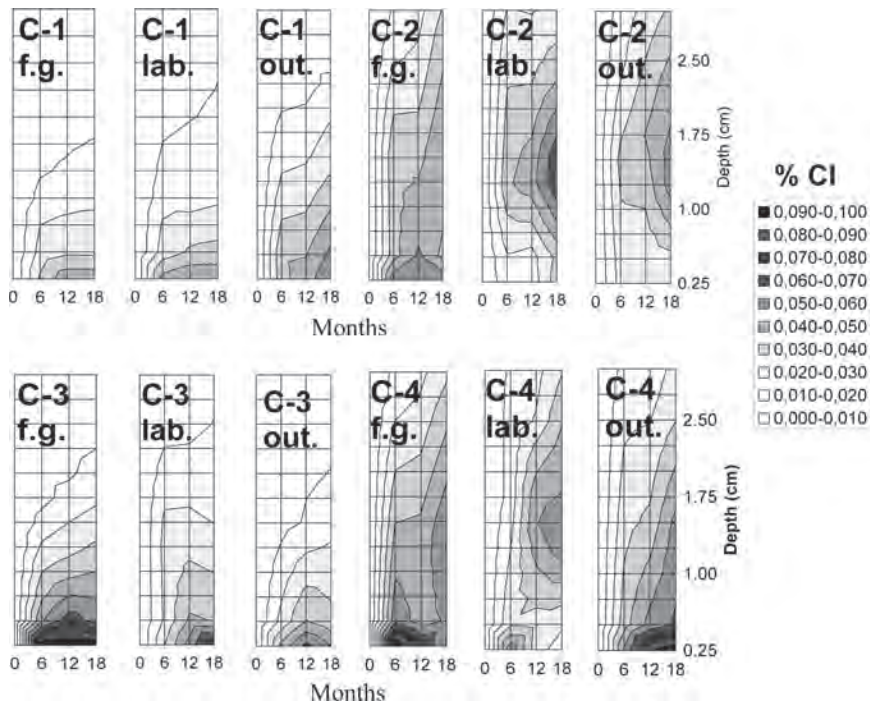


Fig. 10 – Ingress profiles of water-soluble chlorides.



# Hardening Retarders for Massive Concrete

**by H. Justnes, F. Wuyts, and D. Van Gemert**

**Synopsis:** The heat of hydration in massive concrete structures can raise the temperature to a level where thermal cracks can pose a problem. Hardening retarders are admixtures that lower the rate of hydration, distribute the heat release over time, and lower maximum temperature in concrete. Such admixtures will inherently lead to lower early strength, but should lead to comparable 28-day strength to reference concrete.

Relative large amounts of urea works, in particular when the additional retardation of setting (not hardening) is counteracted by the set accelerator calcium nitrate. However, these dosages are high, and urea will also slowly decompose to ammonia that may limit the urea application to outdoor use, if any.

The latest potential admixtures are combinations of minor amounts of strong setting retarders like organic acids (0.1-0.3 %) with the setting accelerator calcium nitrate (1-3%), where a true synergy between the two leads to hardening retardation.

**Keywords:** admixtures; hardening retarder; heat of hydration; set accelerator; set retarder

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### INTRODUCTION

The heat of hydration in massive concrete structures can raise the temperature to a level where thermal cracks and even delayed ettringite formation can pose a problem. The effect may be even more problematic in hot climates. Elaborate measures to counteract this effect are installed cooling pipes, ice and even liquid nitrogen to cool the concrete. Other countermeasures are replacement of cement by large quantities of mineral additives like fly ash or blast furnace slag with low heat of reaction. Many countries (like Norway) has no access to fly ash or slag other than through import and the logistics and economy of transport of such large amounts of minerals can limit the viability. Thus, there has been a search for admixtures that can lower the rate of cement hydration and thereby distribute the heat release over time with resulting lower maximum temperature, so called “hardening retarders” to differentiate them from “setting retarders”, which just displace the hydration curve in time. Such admixtures would of course lead to lower early strength as a penalty (must be sufficient for demolding), but should lead to comparable 28 days strength to reference concrete without admixture.

Mwaluwinga et al. [1] studied urea as concrete admixture. They used rather large amounts of urea (16 - 48% of cement weight) keeping the cement amount constant and replacing water. This resulted in improved flow and reduction of initial fresh concrete temperature as well as maximum curing temperature under semi-adiabatic conditions, the latter being a sign of “hardening retardation”. On the other hand, the setting time was also delayed. The present study tested urea as “hardening retarder” in much smaller amounts (5-10% of cement weight) as an additive keeping water and cement constant as well as combining it with the set accelerator calcium nitrate trying to counteract the set retardation effect [2, 3]. In addition, the combination of calcium nitrate with strong retarders like citric acid was tested since results obtained by De Weerd and Reyniers [4] indicated such combinations could possibly work as “hardening retarders”.

## EXPERIMENTAL

### Materials

The cement tested was of Type CEM I 52.5 R-LA according to the European standard EN 196-1 [5] and produced by Norcem, Brevik, Norway. The chemical and mineralogical compositions are given in Table 1. The Blaine fineness was  $366 \text{ m}^2/\text{kg}$ .

The urea,  $\text{CO}(\text{NH}_2)_2$ , and calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , was of industrial quality produced by Yara International, Porsgrunn, Norway.

Citric acid,  $\text{C}_6\text{H}_8\text{O}_7$  or  $\text{C}(\text{OH})(\text{COOH})(\text{CH}_2\text{COOH})_2$ , and tartaric acid,  $\text{C}_4\text{H}_6\text{O}_6$  or  $\text{C}_2\text{H}_2(\text{OH})_2(\text{COOH})_2$ , used were chemicals of laboratory grade.

Water for paste experiments were distilled, while ion exchanged tap water was used for the concrete mixtures.

Natural sand and crushed granite gravel from Norstone, Årdal, Norway, were fractioned and composed to comply with the grading requirements in EN 480-1 [6].

### Measurements

The isothermal heat of hydration versus time curves for pastes were measured by accurately weighing 6 to 7 grams of cement paste into a glass ampoule after which the ampoule was sealed and loaded into the isothermal TAM Air calorimeter set to 20, 30, 40 or  $50^\circ\text{C}$ . Only a few examples of the large experimental matrix are shown here. Since the pastes were made outside the calorimeter, sometimes there is an artificial, immediate peak (positive or negative) due to temperature differences. The admixtures were always added as dissolved in parts of the water with the retarder first followed by the set accelerator calcium nitrate.

The admixtures were screened by pouring paste into 100·100·200 Styrofoam boxes with 20 mm wall thickness and recording the temperature evolution in this semi-adiabatic set-up. The most promising admixtures were then tested for concrete.

All concrete mixes were mixed in an Eirich 50 litres forced action mixer, using the procedure described in EN 480-1 [6]. Measurements of slump, spread, apparent density and air content were performed according to methods given in the Norwegian Standards NS 3662 (ISO 4109) [7], NS 3664 (ISO 9812) [8], NS 3660 (ISO 6276) [9] and NS 3659 (ISO 4848) [10], respectively.

The temperature developments in 15 litres of concrete in Styrofoam boxes (100 mm wall) were measured for up to 120 hours. Based on the recorded temperature curve, the mix composition and the thermal properties of the container, the adiabatic temperature and heat development as well as the isothermal heat release could be calculated. The measurements and calculation principle are mainly in accordance with NS 3657 “Concrete testing – Determination of heat release”. The isothermal heat and adiabatic temperature rise are both given at 300 hours maturity. The setting time was determined as the time elapsed from water addition until the accumulated heat was  $12 \text{ kJ/kg}$  cement more than accumulated heat at the end of dormant period.

Compressive strengths were determined after 1, 3, 7, 28, 90 days and up to 1 year of storage at  $+20^\circ\text{C}$  in air of 100 % relative humidity usually as a mean of three 100 mm cubes from steel moulds per mix and testing age. Demolding and testing were performed according to the specifications given in Norwegian Standards NS 3669 and NS 3668 (ISO 4012), respectively. For some of the mixtures, the compressive strength of 100 mm cubes from Styrofoam moulds (20 mm wall thickness) packed in 15 litre boxes with 100

mm Styrofoam walls to compare the effect of temperature evolution (logged) with that of the steel moulds at 20°C.

## RESULTS AND DISCUSSION

### Isothermal calorimetry of cement paste

The synergy of citric acid (CA) and calcium nitrate (CN) is clearly seen from the rate of hydration heat in Fig. 1 and from the cumulative heat of hydration curves in Fig. 2. CA is basically a setting retarder relative to the reference, although the heat of hydration is slightly reduced. CN is clearly a setting accelerator. Together they behave as a hardening retarder lowering the rate of hydration heat and distributing it over a longer time. After 48 h at 20°C the cumulative hydration heat is 62, 61, 51 and 41 mJ/g cement for reference paste, paste with CN, CA and CA+CN, respectively. The rate of hydration heat and cumulative hydration heat for the same mixtures at 40°C shown in Figs. 3 and 4, respectively, shows that the function as hardening retarder is reduced at higher temperature. After 48 h at 40°C the cumulative hydration heat is 77, 75, 76 and 77 mJ/g cement for reference paste, paste with CN, CA and CA+CN, respectively. This indicates that the admixture combination may not function in the practical semi-adiabatic case of massive concrete. This question was further examined in the semi-adiabatic paste and concrete tests.

A synergy effect is also found between tartaric acid (TA) and CN as can be seen by comparing the rate of hydration curves in Fig. 5 for 0.2% TA and TA + various dosages of CN with those of CN only and reference paste in Fig. 1. From Fig. 5 it can be seen that the ratio between TA and CN is important (as it also is for CA and CN, but not shown here). The optimum ratio between the two may not have been found in this study and the examples are merely showing a potential application.

Increasing dosages of urea (U) to the cement paste leads to decreasing rate of hydration heat as shown in Fig. 6. The combination of U with CN gives in this case an additive effect by accelerating the setting and not affecting the hardening.

### Semi-adiabatic studies of cement paste

The temperature evolution in 2 litre paste in Styrofoam boxes are shown in Fig. 7 for different dosages of citric acid (CA) with calcium nitrate (CN) and in Fig. 8 for different dosages of urea (U) with CN. The approximate setting time, time to maximum temperature and maximum temperature are extracted from these curves and listed in Table 2. The reference paste without admixtures reaches a peak temperature of 96°C, while a combination of 0.15% CA and 1.5% CN lowers this to 78°C (18°C lower). As comparison, 5% U with 1% CN lowers maximum temperature to 82°C, but with a much higher total admixture dosage. On the other hand, CA based admixtures delayed the setting time much more than U based admixtures. Increased U dosages lower maximum temperature further, to a level of 64°C (32°C lower than reference) with the combination of 10% U and 2% CN.

### Semi-adiabatic studies of concrete

Based on the promising semi-adiabatic studies on cement paste, it was decided to do some on concrete and also to compare the compressive strength development with the temperature evolution. The temperature evolution was monitored in 15 litre of concrete in Styrofoam boxes with 100 mm wall thickness to simulate massive concrete. Concrete

strength was measured both on 100 mm cubes stored in steel moulds at 20°C ( $\approx$  isothermal conditions) and in Styrofoam moulds (20 mm wall) where several were packed in a bigger Styrofoam box (100 mm wall) to obtain a semi-adiabatic case. The temperature was logged in one of the latter cubes as well.

The proportions and fresh properties are given in Tables 3 and 4, respectively, for concretes ( $w/c = 0.42$ ) without admixtures (reference with only superplasticizer), with 0.15% citric acid (CA) + 1.5% calcium nitrate (CN), 0.2% tartaric acid (TA) + 2.5% CN and 7.5% urea (U) + 1.5% CN. The temperature profiles of the concretes in 2 and 15 litre Styrofoam boxes are plotted in Figs. 9 and 10, respectively. The temperature level is much higher in the 15 litre concrete probably due to a concrete volume versus insulation thickness effect. Note that the cement content in the concrete is much higher than would have been used for concrete designed for a massive structure, but this was done to bring up the temperature to a level that would be comparable to a massive structure considering the heat loss through the insulation in the experimental set-up. Thus, the ultimate test should be done on larger concrete blocks (several cubic metres) before trials in real structures. The temperature reduction by the admixtures is greater in the 2 litre boxes and the hydration heat is distributed over a longer time with maximum temperatures being 41°C at 15 h, 29°C at 36 h, 25°C at 87 h and 33°C at 14 h for reference, 0.15% CA + 1.5% CN, 0.2% TA + 2.5% CN and 7.5% U + 1.5% CN, respectively. The corresponding results for the 15 litre boxes were 57°C at 24 h, 56°C at 39 h, 52°C at 64 h and 52°C at 29 h. The compressive strengths of these concrete mixtures stored in steel moulds at 20°C are given in Table 5, while the strengths after storage in Styrofoam moulds with heat evolution as in Fig. 9 are listed in Table 6. The results in Table 5 shows that both reference and concrete with U/CN admixture reaches demoulding strength ( $\approx 10$  MPa) at 1 day, concrete with CA/CN admixtures at 3 days (probably at 2 days due to strength level), and concrete with TA/CN admixture later than 3 days. The 28 days strengths were on the other hand  $\approx 12$  MPa higher than the 74 MPa strength of the reference for the concretes with CA/CN and TA/CN admixtures, while the concrete with U/CN admixture was  $\approx 14$  MPa lower than the reference when stored in steel moulds. Regarding the concrete in Styrofoam moulds (Table 6), the reference concrete and concrete with U/CN admixture reached demoulding strength at 1 day, the concrete with CA/CN admixture at 2 days, and the concrete with TA/CN admixture at  $\approx 3$  days. Again the concretes with CA/CN and TA/CN admixtures had higher strengths ( $\approx 10$  MPa), and the concrete with U/CN admixture lower strength ( $\approx 9$  MPa), than the reference concrete with 78 MPa strength at 28 days.

A separate study was performed for reference concrete ( $w/c = 0.43$ ) without admixture, 10% U as hardening retarder and 10% U / 2% CN as a combination of hardening retarder and set accelerator (counteracting set retardation effect of U) with proportions as given in Table 7. The fresh properties in Table 8 show that the additions of U and U/CN had significantly improved the consistency of concrete. Based on experience, the obtained effect corresponds to  $\approx 10$  litres extra water per cubic meter of concrete. Thus, the admixtures reduced the water demand with  $\approx 5$  %. This implies that concrete with consistency and  $w/c$  similar to the reference concrete could have been produced by  $\approx 5$  % less cement, and thereby reduced the maximum temperature further. The addition of 10% U has a significant effect on the released heat as seen from Table 9. The isothermal heat release is reduced by 7.9%. The corresponding reduction in adiabatic temperature rise is

4.7°C. In addition, an instant temperature depression (during the mixing process) of 3.4°C is observed. Hence, the total reduction of the maximum adiabatic temperature is 8.1°C. The time of setting (equivalent at 20°C) is doubled, from 5 hours to 10 hours. The combination of 10% U with 2% CN gave an even more pronounced reduction of the heat development (11.8%). The corresponding reduction in adiabatic temperature rise is 8.5°C. The instant temperature depression during mixing is 2.6°C. Hence, the total reduction of the maximum adiabatic temperature obtained from the combined addition is 11.1°C. Furthermore, the combination with 2% CN reduced the setting retardation of the U with almost 3 hours. The strength results in Table 10 show that the 10% U addition reduced the compressive strength at all ages up to 1 year. The strength reduction is somewhat smaller at 90 days and 1 year ( $\approx 12$  MPa) than it is at earlier ages (14 - 15 MPa). However, the 2% CN combination compensated these strength reductions significantly, especially at later ages. The observed strength reductions seem to express not only retardation of the strength development rate, but also permanent reductions of strength as seen by the 1 year results. The permanent strength reduction may be due to a kind of desiccation at earlier time than usual caused by the high concentration of urea in the pore water or associated with the reaction of urea with calcium hydroxide to calcium carbonate and ammonia gas (dissolved in pore water);



If part of the urea is considered as solid when the amount of pore water is reduced by hydration (urea solubility 1,080 g/litre), the reaction will lead to a loss of solids (increase in porosity) since ammonia is a gas. The latter also poses a potential problem of using urea as hardening retarder since ammonia has a pungent smell even at low concentration. At least, the use would have been limited to outdoor structures.

## CONCLUSIONS

Combinations of the set retarders citric and tartaric acid with the set accelerator calcium nitrate have been shown to act as hardening retarders of cement hydration as a synergy. Urea has also been shown to have a potential as hardening retarder, in particular in combination with calcium nitrate to counteract unwanted set retardation.

The potential use of hardening retarders is to lower maximum temperature in massive structures, but by doing so the early strength will necessarily be lower than for reference concrete. However, all insulated concretes with admixtures reached demoulding strength at 3 days at the latest. Citric and tartaric acid based admixtures gave significantly higher 28 days strength than reference, while urea based admixtures gave somewhat permanently lower strength.

Urea as hardening retarder may be limited to outdoor structures due to its slow decomposition to pungent ammonia gas.

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**Table 1** -- Cement compositions

| Cement <sup>1</sup>            | CEM I 52.5 R-LA          |                         |
|--------------------------------|--------------------------|-------------------------|
| <u>Chemical Analyses</u>       |                          |                         |
| CaO                            | 63.71                    |                         |
| SiO <sub>2</sub>               | 20.92                    |                         |
| Al <sub>2</sub> O <sub>3</sub> | 4.21                     |                         |
| Fe <sub>2</sub> O <sub>3</sub> | 3.49                     |                         |
| SO <sub>3</sub>                | 2.67                     |                         |
| MgO                            | 1.87                     |                         |
| Free CaO                       | 0.84                     |                         |
| K <sub>2</sub> O               | 0.46                     |                         |
| Na <sub>2</sub> O              | 0.19                     |                         |
| Equiv. Na <sub>2</sub> O       | 0.49                     |                         |
| Cr <sup>6+</sup> (ppm)         | 0.30                     |                         |
| Carbon                         | 0.17                     |                         |
| Chloride                       | 0.02                     |                         |
| LOI                            | 1.72                     |                         |
| <u>Minerals by</u>             | <u>Bogue<sup>2</sup></u> | <u>QXRD<sup>3</sup></u> |
| Alite                          | 50.4                     | 65.0                    |
| Belite                         | 22.0                     | 12.9                    |
| Aluminate                      | 5.3                      | 0.4/1.7 <sup>4</sup>    |
| Ferrite                        | 10.6                     | 9.6                     |
| Anhydrite                      | 5.8                      | 0.4                     |
| Hemihydrate                    |                          | 1.5                     |
| Gypsum                         |                          | 1.4                     |
| Calcite                        |                          | 4.0                     |
| Periclase                      |                          | 0.3                     |
| Lime                           |                          | 0.6                     |

<sup>1</sup>Notation according to European Standard EN 196-1<sup>2</sup>Bogue calculations taking into account SO<sub>3</sub> as anhydrite and CaCO<sub>3</sub> from QXRD<sup>3</sup>QXRD = quantitative Rietveld analyses of X-ray powder diffractograms<sup>4</sup>Divided between cubic/orthorhombic crystal modifications of aluminate**Table 2** -- Approximate setting time (set t), time to maximum temperature (max t) and maximum temperature (max T) for cement paste at semi-adiabatic conditions.

| CA (%) | U (%) | CN (%) | set t (h) | max t (h) | max T (°C) |
|--------|-------|--------|-----------|-----------|------------|
| -      | -     | -      | 3.0       | 8.4       | 96         |
| 0.10   | -     | 1.0    | 9.0       | 16.0      | 84         |
| 0.15   | -     | 1.5    | 15.0      | 24.0      | 78         |
| 0.20   | -     | 2.0    | 21.0      | 32.0      | 78         |
| -      | 5.0   | 1.0    | 3.5       | 9.9       | 83         |
| -      | 7.5   | 1.5    | 4.0       | 10.7      | 72         |
| -      | 10.0  | 2.0    | 4.5       | 11.9      | 64         |

**Table 3** -- Concrete proportions (kg/m<sup>3</sup>) with different admixture combinations

| Component            | Reference | 0.15% CA<br>1.5% CN | 0.2% TA<br>2.5% CN | 7.5% U<br>1.5% CN |
|----------------------|-----------|---------------------|--------------------|-------------------|
| CEM I 52.5 R-LA      | 425       | 425                 | 425                | 425               |
| 0-8 mm sand          | 858       | 858                 | 858                | 858               |
| 8-11 mm gravel       | 215       | 215                 | 215                | 215               |
| 11-16 mm gravel      | 215       | 215                 | 215                | 215               |
| 16-25 mm gravel      | 362       | 362                 | 362                | 362               |
| Water                | 178       | 178                 | 178                | 178               |
| Glenium SP           | 1.32      | 0.56                | -                  | -                 |
| Calcium nitrate (CN) | -         | 6.4                 | 10.6               | 6.4               |
| Citric acid (CA)     | -         | 0.64                | -                  | -                 |
| Tartaric acid (TA)   | -         | -                   | 0.84               | -                 |
| Urea (U)             | -         | -                   | -                  | 31.8              |

**Table 4** -- Fresh properties for concrete (w/c = 0.42) with different admixture combinations

| Fresh properties             | Reference | 0.15% CA<br>1.5% CN | 0.2% TA<br>2.5% CN | 7.5% U<br>1.5% CN |
|------------------------------|-----------|---------------------|--------------------|-------------------|
| Slump (mm)                   | 190       | 195                 | 195                | 190               |
| Spread (mm)                  | 320       | 322                 | 314                | 282               |
| Density (kg/m <sup>3</sup> ) | 2,400     | 2,410               | -                  | -                 |
| Air (vol%)                   | 2.3       |                     | 1.6                | 1.1               |

**Table 5** -- Compressive strength (MPa) with standard deviation for concrete (w/c = 0.42) with different admixtures measured on 3 parallel 100 mm cubes from steel moulds

| Time (days) | Reference | 0.15% CA<br>1.5% CN | 0.2% TA<br>2.5% CN | 7.5% U<br>1.5% CN |
|-------------|-----------|---------------------|--------------------|-------------------|
| 1           | 26.1±0.8  | 4.0±0.2             | 0.9±0.1            | 12.2±0.2          |
| 3           | 48.1±0.6  | 40.5±0.8            | 3.6±0.1            | 32.6±0.4          |
| 28          | 73.5±1.4  | 85.8±1.0            | 87.2±2.5           | 60.1±0.2          |

**Table 6** -- Compressive strength (MPa) with standard deviation for concrete (w/c = 0.42) with different admixtures measured on 2 parallel 100 mm cubes from Styrofoam moulds

| Time (days) | Reference | 0.15% CA<br>1.5% CN | 0.2% TA<br>2.5% CN | 7.5% U<br>1.5% CN |
|-------------|-----------|---------------------|--------------------|-------------------|
| 1           | 36.3±1.2  | 6.0±0.4             | 0.6±0.0            | 18.5±0.2          |
| 2           | 46.9±0.4  | 35.2±1.4            | 1.3±0.1            | 31.0±0.8          |
| 3           | -         | -                   | 9.1±1.0            | 35.7±0.8          |
| 28          | 70.5±1.3  | 79.5±0.4            | 79.7 <sup>1</sup>  | 59.3 <sup>1</sup> |
| 90          | 77.6±1.1  | 88.2±0.9            | 87.1 <sup>1</sup>  | 68.9 <sup>1</sup> |

<sup>1</sup>Only one cube instead of the usual 2 parallels since 3 day strength was included

**Table 7** -- Proportions of concretes with  $w/c = 0.43$ 

| Addition, % by weight of cement |          | Materials, kg pr m <sup>3</sup> concrete |        |             |
|---------------------------------|----------|------------------------------------------|--------|-------------|
| Urea                            | CN (dry) | Cement                                   | Water* | Aggregate** |
| -                               | -        | 433                                      | 187    | 1775        |
| 10.0                            | -        | 426                                      | 183    | 1743        |
| 10.0                            | 2.0      | 421                                      | 181    | 1723        |

Remarks: \*Water absorbed in aggregate is excluded  
 \*\*Absorbed water (0.7% by weight) is included

**Table 8** -- Fresh properties of fresh concrete with  $w/c = 0.43$ 

| Addition, % by weight of cement |          | Consistency, mm |        | Apparent density, kg/m <sup>3</sup> | Air content, vol% |
|---------------------------------|----------|-----------------|--------|-------------------------------------|-------------------|
|                                 |          | Slump           | Spread |                                     |                   |
| Urea                            | CN (dry) |                 |        |                                     |                   |
| -                               | -        | 130             | 450    | 2395                                | 1.7               |
| 10.0                            | -        | 200             | 550    | 2395                                | 0.8               |
| 10.0                            | 2.0      | 210             | 560    | 2375                                | 0.7               |

**Table 9** -- Results and calculations from concrete temperature evolution

| Addition, % by weight of cement |          | Time of setting, hours:min |             | Instant temperature depression, °C | Isothermal heat release, kJ/kg binder | Adiabatic temperature rise, °C |
|---------------------------------|----------|----------------------------|-------------|------------------------------------|---------------------------------------|--------------------------------|
|                                 |          | measured                   | equiv. 20°C |                                    |                                       |                                |
| Urea                            | CN (dry) |                            |             |                                    |                                       |                                |
| -                               | -        | 4:30                       | 5:00        | -                                  | 330                                   | 54.5                           |
| 10.0                            | -        | 9:30                       | 10:00       | 3.4                                | 304                                   | 49.8                           |
| 10.0                            | 2.0      | 6:50                       | 7:15        | 2.6                                | 291                                   | 46.0                           |

**Table 10** -- Compressive strength of concrete with  $w/c = 0.43$ 

| Addition, % of cement weight |          | Compressive strength, MPa at age |        |        |         |         |        |
|------------------------------|----------|----------------------------------|--------|--------|---------|---------|--------|
|                              |          | 1 day                            | 3 days | 7 days | 28 days | 90 days | 1 year |
| Urea                         | CN (dry) |                                  |        |        |         |         |        |
| -                            | -        | 21.2                             | 40.0   | 50.0   | 62.8    | 68.8    | 79.0   |
| 10.0                         | -        | 6.0                              | 25.7   | 36.0   | 47.7    | 56.6    | 66.6   |
| 10.0                         | 2.0      | 9.7                              | 25.6   | 38.4   | 55.6    | 65.2    | 71.5   |