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HCLKP7 - REYNA GRAHAM

The aim of the paper was to show the important aspect of treating waste additives as the main way to achieve sustainable development in the concrete technology. The author considers the effects of minimizing the use of cement replacing it with waste additives, on the concrete durability. The depth of carbonation is adopted as the possible measure of durability. Results of accelerated and natural tests of carbonation progress for concrete with normal and fluidal fly ash, silica fume and blast furnace slag are shown, influence on carbonation of the additive type, its content in concrete and its role (cement or aggregate substitution) is discussed.

The important impact of early water curing on depth of carbonation is stated also.

Thus the study of the effect of carbonation in the s/s waste is important for assessing the long-term effectiveness of the s/s treatment process. This research investigated the effect of carbonation on the leachability of toxic metals and the compressive strength of cement-solidified and geopolymer-solidified synthetic metal wastes. Synthetic sludges containing 0.1M copper nitrate, 0.1M lead nitrate, 0.1M chromium chloride, 0.1M zinc nitrate, 0.05M potassium dichromate and 0.1M cadmium chloride were mixed with ordinary portland cement (OPC) and fly-ash based polymers."--from Abstract.

This research deals with

the carbonation phenomena in concrete for the first 28 days of the concrete curing period. The reactions known as carbonation are those which take place with the hydrated and un-hydrated components of the cement paste in the concrete mixture and the atmospheric carbon dioxide (CO₂). A literature review of the chemistry of cement and concrete as well as the physical phenomena of carbonation governed by Fick's first law and the influential factors in the carbonation reaction has been summarized. Moreover, information of different studies done at several conditions to measure carbonation rates, have been gathered and compared with the experimental results obtained in this research. Also, information

regarding CO₂ emissions from the calcination reaction in the cement process was brought together in order to find out how much of the CO₂ emitted can be absorbed by concrete the first 28 days of the curing period. In order to study how is the process of concrete carbonation for the period of time specified, concrete specimens right after being poured in cylindrical molds, were exposed to accelerated carbonation conditions during 28 days, with controlled atmosphere of 5% CO₂ vol., 30°C and 65%RH. Products of the carbonation reaction in the concrete were measured versus time, with techniques such as Carbonation depth by phenolphthalein stain and Carbon Dioxide content by Thermo Gravimetric Analyses and Mass Spectrometry. Calculations of carbonation rate with phenolphthalein data and CO₂ absorption rates with TGA-MS data were done with the information collected. When phenolphthalein test and CO₂ content by TGA and TGA-MS techniques were used, the same tendency in the results was found; which coincides at the same time with formulations done by Fick's first law. The higher values of CO₂ content

achieved by the concrete were consistent with the maximum availability of components to react within the concrete matrix. Similar results were found between the data obtained in the literature review, especially when laboratory set-up of accelerated carbonation conditions was simulated, and the measurements obtained in this experiment. Measurements done in here to find out carbonation rate showed that this value was smaller were compared with other studies in which the concrete was at normal atmospheric conditions of exposure. Results have shown that from data obtained by the different techniques used, the percentage of CO₂ absorbed during the first 28 days of the concrete curing period (with the specificities of the concrete used and the calculations done) goes from 0.34% to 1% of that emitted in the calcinations reaction of the cement process.

The market for carbonated beverages has grown dramatically over recent years in most countries, and this growth has required changes in the way factories are run. Like other food products, soft drinks are required to be produced under stringent

hygiene conditions. Filling technology has progressed rapidly to meet the needs of manufacturers and consumers alike. Packaging choices have changed and there have been improvements in closure design. This book provides an overview of carbonated soft drinks production in the early part of the twenty first century, presenting the latest information on carbonation and filling methods. There are also chapters on bottle design, can making, general packaging considerations, production and distribution. A final chapter deals with quality assurance, and environmental and legislative issues. Detailed references provide opportunity for further reading in more specialised areas. The book is aimed at graduates in food science, chemistry, microbiology and engineering who are considering a career in the soft drinks industry, as well as technical staff already employed within the industry and associated suppliers.

This Digest discusses the carbonation of normal dense concrete which results from the reaction of atmospheric carbon dioxide gas with hydrated cement compounds. It re-

lates particularly to the assessment of the risk of corrosion to embedded steel. The Digest describes the carbonation process and how the depth of carbonation can be measured.

To reduce the carbon footprint of ordinary Portland cement (OPC)-based concrete, a novel technique, pre-carbonation process, has been developed to produce CaCO_3 nanoparticles in fresh concrete. In this technique, gaseous CO_2 is first absorbed into a slurry of calcium-rich minerals which is then blended with other ingredients to produce mortar/concrete. The objective of this work is to obtain an in-depth understanding of the underlying scientific mechanisms associated with the enhancement of strength and durability of the concrete induced by the new method. A comprehensive research plan has been carried out to study the carbonated slaked lime slurry and the effect of carbonated slaked lime slurry on the performance of OPC-based concrete, and to evaluate the potentials of the pre-carbonation method. Experimental studies show that carbonating the calcium-rich mineral slurry with CO_2 can produce CaCO_3 nanoparticles and $\text{Ca}(\text{HCO}_3)_2$

in the slurry, and these carbonation products were dictated by four parameters of the pre-carbonation method: the duration and temperature of the carbonation, the concentration of the calcium source slurry, and the stirring method of the calcium source slurry during the carbonation. The mechanical properties and durability of the mortar/concrete made with the carbonated slurry were significantly improved, which can be attributed to major mechanisms induced by the pre-carbonation method: promoted hydration of the cement and denser microstructure of the mortar/concrete. Calorimetry testing showed that the hydration of OPC was greatly improved by the pre-carbonation because of the extra heterogeneous nucleation sites provided by the CaCO_3 nanoparticles. XRD and TGA results revealed that more ettringite was produced in the mortar/concrete with pre-carbonated slaked lime slurry. The overall volume of the hydration products of the cement was increased by the pre-carbonation, leading to denser microstructure of the mortar/concrete. It has been found that the pre-carbonation can be used to the OPC--

supplementary cementitious materials (SCMs) blended cement mortar/concrete, as evidenced by the improved mechanical properties achieved by these mortars produced by using the pre-carbonation method. A preliminary study was also conducted to examine whether other calcium-rich minerals, such as Class C fly ash and limestone, can be used as calcium source in the pre-carbonation method.

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"Carbonation curing of precast concrete has shown enhanced durability performance and carbon storage capacity. However, carbonation curing may reduce the pH of concrete. Furthermore, the progressive weathering carbonation in service may aggravate the problem, leading to the corrosion of steel in concrete. This thesis is to investigate the effect of early carbonation curing on concrete resistance to weathering carbonation. The concrete cubes were prepared with two water-to-cement (w/c) ratio: 0.65 and 0.40. The samples were initially in-mold cured, off-mold fan dried, then carbonated with pure CO₂ gas at 5 bars for 2 and 12 hours respectively, and finally subsequent by hydrated. To evaluate the degree of weathering car-

bonation, carbonation depth, carbonation coefficient, pH distribution, carbon content, and X-ray diffraction analysis were performed. It was found that the volume of permeable voids was lower in carbonated samples than in hydration reference, which was indirectly proved to be beneficial to decrease the permeability and porosity of concrete by carbonation curing. For concretes with w/c = 0.65, the carbonation depth, pH value and carbon content analysis were found to be more affected by weathering carbonation in 12-hour carbonated concrete than in 2-hour carbonated and hydrated concretes. Early carbonation curing even helped to reduce the carbonation coefficient in weathering carbonation. For concretes with w/c = 0.40, the carbonation depth, carbonation coefficient, pH value and carbon content of different carbonated and hydrated concretes were comparable during weathering carbonation. Therefore, the early carbonation curing was not more detrimental to precast reinforced concrete in this mix design over weathering carbonation." --

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Bridge Maintenance, Safety, Management, Resilience and Sustainability contains the lectures and papers presented at The Sixth International Conference on Bridge Maintenance, Safety and Management (IABMAS 2012), held in Stresa, Lake Maggiore, Italy, 8-12 July, 2012. This volume consists of a book of extended abstracts (800 pp) and a DVD (4057 pp) co

Carbonation is a naturally-occurring process whereby Ca-containing cement phases lose their hydration water and are converted to carbonate minerals by reaction with atmo-

spheric CO₂. As these secondary minerals develop in the microstructure of hydrated cement, porosity, pore-size distribution and permeability are decreased. These are all considered desirable properties in a wasteform. The objective of this study was to examine the effect of carbonation and different pozzolans on the leach performance and mechanical strength of ordinary Portland cement (OPC) wasteforms. Two methods of accelerated cement carbonation were used: 1. A vacuum carbonation method, where wasteforms are placed in an evacuated, sealed cell and subjected to small additions of CO₂ over several days at near vacuum conditions; and 2. A one-step carbonation method, where CO₂ gas is added to the wasteform paste as it is being mixed. Thirteen elemental constituents of interest to the safety assessments of long-term management of Ontario Power Generation's radioactive waste (Cl, N, S, Se, ¹³⁷Cs, Th, Pb, Co, Ni, Cu, Sr, Ba and Cs) were stabilised/solidified via cement mix water. Wasteforms were produced with only OPC, OPC and fly ash, or OPC and silica fume. Most wasteforms were carbonated using

one of the carbonation methods. Some wasteforms were not carbonated and served as controls. Wasteforms were subjected to either standard leach tests or compressive strength tests. The extent of carbonation was found to be about 20% for vacuum carbonation method, substantially higher than that for one-step treatment (up to about 10%). For vacuum carbonated wasteforms, carbonation occurred at the outer selvages of the wasteforms, whereas one-step treatment resulted in homogenous carbonation. Generally, compared to uncarbonated OPC wasteforms, vacuum carbonation increased leaching of elements that are anionic in cementitious conditions (Cl, N, S, Se, ¹³⁷Cs, Th), decreased leaching of large metal cations (Sr, Ba, Cs, Pb) and had negligible effect on the leaching of the elements that form hydroxyl complexes (Co, Ni, Cu). ¹³⁷Cs was the only anionic element whose leachability was reduced by vacuum carbonation, as it may be precipitated in the form CO₃²⁻ in the large quantity of secondary carbonate minerals produced during the vacuum carbonation process. One-step carbonation did not result in sub-

stantial reductions in leachability, compared to uncarbonated OPC wasteforms. However, it had an interesting inverse effect on large metal cation leachability from fly ash- and silica fume-containing wasteforms. A model is presented that proposes that porewater pH changes can have an effect on waste element leachability because 1) the C-S-H Ca/Si ratio is dependent on the equilibrating porewater pH and 2) the degree of ion sorption on C-S-H is dependent on the C-S-H Ca/Si ratio. This model should be tested experimentally as it has important implications on wasteform design. Because of this inverse behaviour, overall neither pozzolan outperformed the other with respect to leachability. Generally, for uncarbonated wasteforms, OPC retained the elements more effectively than OPC with pozzolans. For pozzolans, the leachability of these elements from OPC with fly ash was lower than that of OPC with silica fume. Leaching of Cs was anomalously low from uncarbonated OPC wasteforms, but follow-up experimentation did not corroborate this anomaly. Further testing of these wasteforms to determine how the minera-

logical fate of Cs can differ between wasteforms is recommended. All wasteforms tested were of acceptable strength (

Environmental impact on concrete parts of buildings results in a variety of unwanted chemical and chemically-induced mechanical changes. The bulk of these changes leads to damaging and destabilization of the concrete itself or of the reinforcement embedded in the concrete. One important destabilization factor is the drop in pH near the steel bars induced by carbonation of the alkaline constituents. This is caused by atmospheric carbon dioxide diffusing in the dry parts and reacting in the wet parts of the concrete pores. The phenomenon is considered as one of the major processes inducing corrosion in concrete. A particular feature of carbonation is the formation of macroscopic sharp reaction interfaces or thin reaction layers that progress into the unsaturated concrete-based materials. The deeper cause for the formation of these patterns is not quite clear, although the major chemical and physical reasons seem to be known. The main objective of this work is to understand the

movement of internal reaction layers in order to be able to predict the carbonation penetration. We describe several relevant settings of the carbonation process by means of moving-reaction interface formulations. Non-local dynamic laws are used to model the advancement of the internal layers, which separate different modeling zones. We derive them via first principles for simple geometries using the physics and chemistry of the problem. The moving-boundary methodology essentially relies on these laws, which are usually descriptions of the velocity of the reaction front position. Specifically, the accuracy of the prediction is based on these supplementary relations and on a proper definition of the reaction front position. We investigate the competition between the non-linear carbonation kinetics effects, molecular diffusion and dissolution-precipitation mechanisms, which take place in the unsaturated concrete fabrics. Mathematically, the proposed models form coupled systems of semi-linear partial differential equations in two-phase moving domains. Non-linear transmission conditions of Rankine-Hugoniot type

are imposed across the inner boundary that separates the carbonated regions from the uncarbonated ones. The movement of these regions is determined via non-local dynamics laws. Local and global existence, uniqueness and stability of the weak solution with respect to the initial data and parameters are shown. Useful upper and lower bounds, for instance on the velocity of the reaction front and on the time to complete the carbonation of a given part of a concrete sample, are obtained. Monitoring of such processes enables conclusions about the behavior of the moving-reaction front and can lead to a better prediction of penetration depths and of the corrosion initiation time. The moving-boundary methodology is illustrated numerically using experimental data extracted from the literature. The theoretical predictions compare well to the data from accelerated and outdoor tests. In particular, the agreement between the experimentally observed motion trajectory of the reaction front (i.e. penetration depth vs. time curves) and that computed via the proposed models is reasonable.

Developing economically feasible strategies for long-term storage of carbon dioxide has become over the past few years a major stake in response to the concerns over global warming. Carbon capture and storage (CCS) is widely believed to be one of the possible scenarios aimed in challenging the global warming phenomenon by targeting the atmospheric CO₂ content. Mineral carbonation - in the platform of CCS - is anticipated to be a premium option for permanent carbon capture and storage owing to the known reactivity of alkaline materials such as magnesium silicates and brucite with carbon dioxide to form stable and environmentally benign carbonates. Passive mineral carbonation of ultramafic mine waste and tailing minerals could be considered as an economically attractive option owing to the availability of large amounts of magnesium-rich mining wastes, which are regarded to be virtually free, typically fine grained and highly reactive. Moreover, the energy input of nature is employed in passive mineral carbonation which is likewise free. In this way, CO₂ is mainly dissolved in water resulting from rain and snow season. Metal ions

such as Mg²⁺ and Ca⁺ are also leached into the water allowing the formation of metal bicarbonate and consequently formation of metal carbonates. Laboratory experimental works were done in order to identify the dynamics of passive mineral carbonation under environmental conditions prevailing the Quebec region, Canada. A differential diffusion carbonation cell was developed to monitor the kinetics of mineral carbonation under ambient conditions. The kinetic measurements revealed the complex role of water both as reacting medium and moiety in the carbonation pathway. Time-dependent X-ray powder diffraction analysis and scanning electron microscopy reveal formation of transitional, metastable porous, flaky magnesium carbonates which subsequently evolved into less porous nesquehonite layers, which are shown to be responsible for surface passivation despite availability of unreacted brucite. However, surface abrasion was shown to liberate previously carbonated NIMT particles resulting in further carbonation on freshly exposed surfaces. Temperature dependent carbonation tests were performed in the ranges of

hot (35 ± 1 °C), laboratory (23 ± 2 °C), low (5 ± 1 °C), and freezing (-5 ± 2 °C) to mimic different seasonal conditions. Temperature had a notable effect on the carbonation kinetics and lowering temperature caused a reaction slowdown despite carbonation is thermodynamically defined as an exothermic reaction. Moreover, it was observed that drying and freeze/thaw cycles were at the origin of a thermomechanical "peel-off" effect which inflicted micro-fractures to the carbonate product layers enabling water and gas to engulf beneath and react with freshly unearthed Mg donor sites. FTIR spectroscopy analysis revealed that hydrated magnesium carbonates such as nesquehonite are being formed parallel to brucite dissolution during mineral carbonation of brucite-rich nickel mining tailings. However, it was observed that nesquehonite is not the ultimate hydrated magnesium carbonate product. Long-term monitoring over 2 years of an already carbonated material revealed that the initial nesquehonite has evolved into dypingite and hydromagnesite depending on age, wetting/drying history and the depth where initial carbo-

nate has been formed. Nonetheless, nesquehonite could maintain its stability over prolonged times if not being subjected to wet/ humid environmental conditions.

The study of carbonation perception is limited, even though carbonated beverages are very popular. A series of experiments were conducted to determine the sensory properties of carbonation itself and its interaction with other sensory modalities. First, the power functions of carbonation in carbonated spring water were developed by a trained panel using two assessing conditions, swallowing and expectoration. Five carbonation levels, 1.2, 2.0, 2.5, 3.0, and 3.9 volumes CO₂, were employed. The size of the exponents, 2.79 (swallowing) and 2.65 (expectoration), suggested a sharp increase of perceived carbonation magnitude with increasing concentration. There was no significant difference between exponents resulting from the two assessing conditions. Second, the effects of temperature on carbonation perception in carbonated spring water were determined by use of both a trained panel and a naive panel. Two carbonation levels, 2.4 and 3.0 volumes, and four

temperature levels, 3°, 10°, 16° and 22°C, were employed. Carbonation intensity was perceived to be higher at lower temperatures than at higher temperatures. This effect held true for both trained and naive panels. The temperature effect on carbonation perception, however, was carbonation level dependent. Differences were more evident at the higher carbonation level. Thirdly, the mutual effects of carbonation and tastants (sweetener and acidulant) were determined by a trained panel. How CO₂ affects sweetness and how sweetener level affects carbonation perception were measured in both sucrose and aspartame sweetened systems. How CO₂ level affects sourness and how acid level affects carbonation perception were measured in both citric acid and phosphoric acid acidulated systems. The effects were measured at concentrations of 2-16% (w/v) for sucrose, 0.015-0.12% (w/v) for aspartame, 0.02-0.29% (w/v) for citric acid, and 0.015-0.06% (v/v) for phosphoric acid. Higher carbonation reduced sweetness ratings in aspartame-sweetened samples but had no effect on sweetness in sucrose-sweetened samples.

Only the highest concentration of sucrose (16% w/v) reduced carbonation perception. Carbonation enhanced sourness ratings at the lower acid levels and had no effect at higher acid levels for both acid systems. No effect of acid level on carbonation perception was found.

Elevated levels of carbon dioxide in the atmosphere have created numerous environmental and socio-economic problems, including climate change. The scientific community is experimenting with various emission reduction and carbon capture and storage strategies. Mineral sequestration of carbon with alkaline industrial residues is one such emerging emission reduction technology which is being researched for its ability to be integrated into industrial plants, where both carbon dioxide (CO₂) and alkaline solid residues are generated on site. This concept can be applied to the coal-fired power generation industry, which produces enormous quantities of coal fly ash as a solid by-product along with massive emissions of gaseous CO₂ with the flue gas stream. Therefore, the mineral trapping of CO₂ with coal fly ash can help to sustain coal-based

power generation, while bringing added advantages to fly ash disposal due to the favourable chemical changes which occur in fly ash during the above carbonation process. However, mineral carbonation to date remains an immature technology due to its main drawbacks related to kinetics and extensive research is necessary to find acceleration to accelerate mineral sequestration. The main aim of the present thesis is to investigate the effect of operational parameters on the accelerated carbonation of coal combustion fly ash and to study the effect of carbonation on the final disposal of fly ash, especially in relation to agricultural soil amendment. The research work is based on experimental studies conducted in the laboratory and in a greenhouse facility. The accelerated carbonation tests for fly ash were conducted in a newly-developed reactor facility in the Deep Earth Energy Research Laboratory in the Civil Engineering Department at the Clayton campus of Monash University. The main component of this facility is a continuously stirred cylindrical tank equipped with adjustable temperature and pressure mechanisms and

monitoring and data acquisition systems. The fly ash materials were collected from the collection ponds of three major power plants located in the Latrobe Valley in Victoria, Australia. The carbonation reactions were designed to test the effect of reaction temperature (in the range of 20 °C to 80 °C), initial CO₂ pressure inside the reactor (in the range of 1 MPa to 10 MPa), water-to-solid ratio or solid dosage (in the range of 0.1 to 1) and the supercritical phase of CO₂. In addition, the effect of fly ash particle size was tested with five different particle size categories varying from

"Early carbonation curing of precast concrete products has shown better durability performance and excellent carbon storage capacity. In this work, the effect of early age carbonation curing on microstructure of cement paste as the CO₂-reactant in concrete was explored for Ordinary Portland Cement (OPC) paste to understand the mechanism. Following concrete-making procedure, OPC pastes were prepared with a water-to-cement ratio (W/C) of 0.36. The pastes were initially air-cured, then carbonated at 0.15 MPa, and finally hydrated under

sealed conditions after partially compensating for water loss by water spraying. Two carbonation durations (2 hours and 24 hours) were used for studying the microstructure. Analyses included X-ray Diffraction (XRD), Thermo-Gravimetric Analysis (TGA) coupled with Mass Spectroscopy (MS), Nuclear Magnetic Resonance (NMR) ²⁹Si, and Scanning Electron Microscopy (SEM). Results indicate that the evolution of carbonation can be distinguished into two steps. The first step occurs in first two hours when the pH is still high and entails the precipitation of near-amorphous to poorly crystalline calcium carbonate (CaCO₃) from a supersaturated solution. The CaCO₃ crystals serve as reinforcement for the calcium-silicate-hydrate (CSH), very similar in structure to CSH obtained from hydration. The carbon uptake was rapid and dominant in this period. The second step occurs when the pH starts to decrease due to prolonged carbonation. The ratio of HCO₃⁻/CO₃²⁻ in the pore solution is increased, and CaCO₃ crystals are allowed to grow inside the pores. The continued carbonation reduces the C/S ratio of CSH and transforms it into a struc-

ture having longer chains without cross-linking. This leads to a higher strength gain despite the low CO₂ uptake experienced in this period. The results suggest a diffusion-controlled kinetic model for carbonation. The pH value of the pore solution is maintained above the corrosion threshold even after 24-hour carbonation."

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The high contribution of CO₂ emissions associated with pavements has driven research to assess the life cycle of concrete versus asphalt structures and to develop a strategy to reduce the carbon footprint. The life cycle of pavement has been

studied with respect to CO₂ emissions in the use phase of concrete as well as after the concrete is demolished. However, only a few have considered the effects of CO₂ uptake in the carbonation process during the use phase, and even fewer have studied the effects of carbonation after demolition. This work fills the gap between estimates of carbonation in a life cycle assessment for pavements by considering the effects of the storage method on the uptake of CO₂ after the concrete demolished. It is observed that how the concrete is stored after demolition can have an influence on the CO₂ uptake of the structure.

There is also an increase in the amount of the CO₂ emitted during the calcination process that is taken back up by the concrete structure during the carbonation process to a level of 6 - 30% from previously predicted values of 5-10% which assume no carbonation after demolition. The incorporation of carbonation after demolition into a comparative life cycle assessment between asphalt and concrete pavement is used to better predict the pavement material with the lower environmental impact considering variations in the climate zone, traffic level, maintenance schedule, design life and analysis period.