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THE RESPONSE OF PORTLAND CEMENT CONCRETE TO HIGH TEMPERATURES

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ABSTRACT

Concrete made with Portland cement is extensively used in the construction of power plants and industrial facilities. Standards and Codes of Practice place limits on the temperatures that concrete can be exposed to, for both operating and accidental situations. An extensive literature review has been carried out investigating the response of concrete to temperatures beyond the limits placed by codes of practice. Suggested concrete constituents for improved steady state high temperature response and a preliminary test of one such mix design are given.

INTRODUCTION

This paper presents a study on the response of Portland cement concrete (henceforth referred to as 'concrete') to high temperatures. Specific focus is given to the temperature ranges of 200°C to 450°C, for steady state conditions. The Standards and Codes of Practice that regulate the use of concrete in the nuclear industry place limits on the temperatures that structural concrete can be exposed to, in both operational and accidental situations. Examples of these limits from ACI 349 (2001) are 65°C and 176°C respectively. To meet these limits insulation or cooling systems are often employed. The use of concrete that can withstand higher temperatures could reduce the cost and complexity of new reactor designs such as high temperature gas cooled reactors.

This paper considers concrete properties including strength and dimensional stability and attempts to correlate these to changes on a microscopic level, with a view to identifying characteristics that are beneficial to the response of the material at and after heat exposure.

FACTORS AFFECTING THERMAL RESPONSE OF CONCRETE

Concrete is a complex, multiphase material that has a varied response to temperature exposure depending on several factors. These factors can be related to the response of the concrete to heating, the heating environment the concrete is exposed to and the condition of the concrete being tested.

Research into heated concrete can be broadly split into two categories:

- Short term, transient heating environments such as fires or jet blasts.
- Long term, constant temperature heating situations such as experienced in process or heat energy environments.

This paper focusses on long term, steady heat exposure, with a view to identifying constituents that are beneficial to the response of the concrete. It is however important to consider literature from short term exposure tests, noting that this is a large body of literature. The effects of the change in environment do however need to be considered, including that high thermal gradients and pore pressures will cause higher thermal stresses in the material and subsequently increased damage to the material.

Philajavaara (1972) and Naus (2006) have noted that it is difficult to interpret and use the extensive body of literature available on the topic, indicating that often incomplete information is presented on the various factors that affect the response of concrete to temperature. Philajavaara (1972) suggests a set of 18 factors that need to be considered and accounted for in determining the response. This view is supported by Lankard et al. (1971) who suggest a group of seven factors. A combination of these factors is presented in Table 1, noting that virgin concrete is considered here (i.e. environmental effects of aging and chemical exposure are not included). A description of the factors is included.

Table 1: Factors that Affect Concrete Properties

Factor	Description
Concrete constituents and mix design	Type of binder and aggregate and mix proportions have a significant effect on the temperature response.
Heating Environment	
Heating Rate	High thermal gradients and pore pressures can cause significant thermal stresses.
Final Temperature	This determines the amount of thermal expansion in the aggregate and binder and the chemical changes in the binder such as dehydration.
Thermal Cycling	Repeated cycling to temperature has a significant effect on the properties of the material.
Duration of Heating	Whether the temperature exposure is steady state or transient.
Thermal Differences	Differential thermal expansion can significantly increase stresses in a structure.
Stress Conditions	Prestressing or post tensioning of the structure.
The nature of the surrounding media	Determines the moisture state of the concrete.
Changes in the surrounding media	Changes in the surrounding media (including moisture state and steel/concrete bond strength) due to temperature exposure.

This research took a specific focus on temperature exposure for pebble bed high temperature gas cooled reactors**,** McCormick (2011). In both operating and accidental situations the maximum rate of temperature change for these reactors is expected to be in the order of 7°C per hour, with possible operating temperatures of 225°C and accidental temperatures of 450°C to which the concrete may be exposed.

CHEMICAL AND PHYSICAL CHANGES TO CONCRETE

The primary strength giving constituent in the binder of concrete is calcium-silicate-hydrate (CSH) gel, with calcium hydroxide ($Ca(OH)_2$) being a bi-product of the hydration reaction, C&CI (2009). The cement phase can have pozzolanic extenders added to it, including fly ash or ground granulated blast furnace slag. These extenders react with the $Ca(OH)_2$ product from the Portland cement to form further CSH gel like phases. Aggregates used in concrete include calcareous (limestone), quartzitic (quartzite) and igneous (granite) rock.

A primary factor that governs the response of the material to temperature is whether moisture is free to escape from the concrete or not. Typical examples of moisture that is unable to escape (henceforth referred to as 'sealed') are the material in the middle of a massive structural element and concrete against a steel liner. A dominant factor in the response of sealed concrete to temperature are hydrothermal reactions between the CSH and $Ca(OH)_2$ phases in the material, creating more crystalline, lime rich phases, Lankard et al. (1971), Kropp et al. (1986). The addition of pozzolans such as fly ash reduce the amount of $Ca(OH)_2$ available for these reactions to take place, and addition in high enough quantities allows the formation of new CSH phases at temperature. At temperatures above 100°C the reaction between unreacted fly ash and $Ca(OH)_2$ is evident for up to 28 days of heating, noting that the most significant strength gains occur over the first 7 days, Seeberger et al. (1981). This demonstrates that the properties of sealed concrete develop over time due to hydrothermal reactions.

The response of concrete where moisture is free to escape (henceforth referred to as 'unsealed') appears to be dominated by dehydration of the CSH phase and differential thermal expansion between the aggregate and binder phase, Bazant and Kaplan (1996). With temperatures of 150°C to 300°C a net thermal expansion is expected in the binder phase of the concrete, while above these temperatures a net thermal shrinkage is expected in the binder due to dehydration with increased thermal expansion in the aggregate. This differential thermal expansion causes microcracking in the interfacial transition zone (ITZ) between the aggregate and binder phases. The ITZ is an area of increased porosity around an aggregate particle. On exposure to temperatures above 100°C, changes to the properties of the concrete are expected during the initial stages of heating and cooling, while the chemical transformations and microcracking take place.

Differential thermal expansion between the binder and aggregate phases has an effect on both sealed and unsealed concretes.

Migration of moisture away from the heat source can be expected, tending sealed concrete towards an unsealed state. This is shown to be gradual, taking in excess of 500 days for a 1.5m thick wall sealed and heated on one side, with evidence of moisture at the sealed face after 50 days of heating at 200°C, Chapman and England (1977). It has been suggested that low moisture contents are required for hydrothermal reactions to occur and that the hydrothermal reactions take place in a comparatively shorter period of time, Kropp et al. (1986).

STRENGTH

There is considerable literature available on the compressive strength of heated concrete, reporting a broad range of values, for example Freskakis (1980). An improvement up to approximately 250°C can be shown, with generally deterioration at higher temperatures. It is worth noting that this body of literature includes results that show significant deterioration of strength, even at temperatures well below 250°C, Freskakis (1980), Lankard et al (1971).

Lankard et al (1971) have shown that in sealed environments chemical changes to the binder phase cause a significant deterioration in the strength of concrete after exposure to 232°C. This is supported by Kropp et al. (1986) who have investigated the phase changes that occur, and associate the strength deterioration with increased porosity and misalignment of the newly formed, more crystalline binder structure. Kropp et al. (1986), supported by Seeberger et al. (1981), have shown that sealed concretes with high pozzolan content (fly ash in excess of 50%) can have a significant increase in strength from 20% to in excess of 50% with exposure to 225°C and that this increase develops over time. This is in agreement with investigations of concretes with various contents of fly ash, as presented by Ghosh and Nasser (1996), Nasser and Lothia (1971) and Nasser and Marzouk (1979). No literature investigating the sealed response of concrete to temperature above 250°C has been identified.

Considering unsealed concrete, the addition of pozzolans at above normal ratios (40% fly ash) can give strengths the same as unheated after short term exposure to 400°C, Poon et al. (2001) and Xu et al. (2001). Similar improvements have been demonstrated over longer periods of exposure, but this improvement is limited, possibly due to the increased shrinkage over conventional Portland cement concrete, Seeberger et al. (1981).

The effect of the aggregate on the response of the concrete is primarily related to thermal expansion and additional chemical reactions. Lankard et al. (1971) have demonstrated that the use of calcareous aggregates has a deleterious effect on sealed concretes over concrete with gravel aggregate, supported by Kottas et al. (1979). The research of Savva et al. (2005) provides results that demonstrate siliceous aggregates being beneficial over limestone aggregates up to 570°C, where the α to β quartz phase transition causes a significant deterioration of siliceous aggregate concrete strength. Interestingly Abrams (1971) demonstrates that for unsealed concretes there is little difference between calcareous and siliceous aggregates up to the temperature of 570°C.

The heating rate is considered to have a moderate effect on the response of a concrete below 2°C per minute, Khoury (1996). Thermal cycling is expected to have a progressive reduction of properties dependent on number of cycles and the final temperature reached, Bazant and Kaplan (1996).

Considering the tensile and flexural strength of concrete, a similarly broad range of values is reported in literature, Bazant and Kaplan (1996). Generally the trend is deterioration with exposure to temperature and similar causes of deterioration could be expected, such as hydrothermal reactions in sealed concretes.

STRESS – STRAIN CHARACTERISTICS

Similar to tensile strength, deterioration with exposure to temperature is expected for the stress-strain characteristics and subsequently modulus of elasticity. No improvement is expected as can be found with compressive strength after exposure to up to 250°C, and the reduction in modulus can be expected to be of the order of 10% to 65% for exposure to 225°C and 50% to 85% for exposure to 450°C, Freskakis (1980).

The selection of aggregate has a significant effect on the response of the modulus of elasticity to temperature. It has been demonstrated that siliceous aggregates have the least deleterious effect up to 450°C (approximately 85% of cold modulus at 250°C, 75% at 450°C), followed by limestone aggregates (approximately 80% at 250°C, 60% at 450°C), with quartzitic aggregate giving the most deleterious effect (approximately 50% at 250°C, 30% at 450°C), Schneider et al. (1982). Savva et al. (2005) present data supporting siliceous aggregates as having a less deleterious effect than limestone aggregates, although their results indicate a greater deterioration than presented above.

Literature available for sealed concrete demonstrates a significant deterioration over unsealed concrete, Lankard et al (1971), Kottas et al. (1979). It is possible that hydrothermal reactions had a significant effect on these results.

Nasser and Chakraborty (1985) have investigated the effect of extended periods of exposure up to 180 days for both sealed and unsealed concretes. These results demonstrate a gradual deterioration of modulus over time for both sealed and unsealed concretes, with sealed concretes demonstrating a substantially greater reduction in modulus. It should be noted that the same sealed concretes demonstrated a reduction in compressive strength that developed over time, most likely due to developing hydrothermal reactions.

Literature suggests that the addition of high quantities of extenders has a deleterious effect on the thermal stress-strain response of the concrete, demonstrating a marked reduction over concretes with lower quantities of extenders, Ghosh and Nasser (1996), Savva et al. (2005). No investigations have been identified with extended periods of exposure with concretes with high quantities of pozzolanic extenders.

Schneider (1982) has shown that the use of a confining stress has a substantial benefit in retaining the stress-strain characteristics of a concrete. This introduces the added complexity of increased creep of the material on heating, as investigated by Bazant and Kaplan (1996). This is dependent on the temperature of exposure and the movement of moisture.

POROSITY AND PERMEABILITY

Pore size distribution increases with temperature exposure in sealed concretes, apparently related to hydrothermal reactions, Kropp et al. (1986). The addition of pozzolanic extenders appears to reduce the effect of temperature on pore size distribution to similar to that of unheated concrete.

Xu et al. (2001) have shown that lower water:cement ratios significantly reduce porosity, while the addition of fly ash slightly increases the porosity. A stable increase in porosity was demonstrated up to 650°C.

Permeability is related to the transport of media through the concrete. Water permeability has an increase of two orders of magnitude above 100°C, Bazant and Thonguthai (1978). Chloride transport with varying levels of fly ash replacement have been investigated by Xu et al (2001), demonstrating that the use of extenders and low water:cement ratios provide the beneficial effect of inhibiting the transport of chlorides.

SUGGESTED CONCRETE CONSTITUENTS

Within the body of literature there is a broad range of constituents that have been tested with varied results. The following conclusions may be drawn:

- Conventional Portland cement is an adequate binder for the temperatures of interest. The main factors causing deterioration of the binder phase with temperature exposure are dehydration of the paste with associated thermal expansion and shrinkage, and hydrothermal reactions in sealed concretes.
- Pozzolanic extenders such as fly ash have a beneficial effect on the compressive strength of both sealed and unsealed concrete. This is particularly in high replacement quantities (50% or more). Literature does however suggest that high quantities of extenders significantly reduce the modulus of elasticity of heated concrete.
- The selection of aggregate is significant in sealed environments, where limestone has a deleterious effect related to hydrothermal reactions. Quartzitic aggregate concretes have demonstrated a marked reduction of modulus of elasticity on heating. Siliceous aggregates have been demonstrated to provide the best response over compressive strength and modulus of elasticity.
- Water:cement ratios have an impact on permeability and porosity, where lower water contents reduce the porosity and chloride permeability of the material.

Three mix designs identified with the above principles are given in Nasser and Chakraborty (1985), Nasser and Lothia (1971) and Xu et al. (2001). A summary of these consituents is:

- Water:binder ratio – 0.27 to 0.4
- Extender replacement ratio – 30% to 60% (fly ash)
- Cement content – 117kg to 325kg
- Siliceous or quartzitic aggregates.

The range of reported properties for these concretes was:

- Unheated strengths of between 54 MPa and 80 MPa
- 200°C to 250°C:
    - Sealed
        - strengths of 105% to 125%
        - Modulus of elasticity of 50% after 90 days of heating
    - Unsealed
        - Strengths of 80% to 125%
        - 300% increase in chloride diffusivity
- 400°C to 450°C:
    - No information is available for sealed concretes
    - Unsealed
        - Strengths of 80% to 104%
        - 600% increase in chloride diffusivity

Using the constituent quantities presented above as a basis for a mix design, tests were carried out to assess the suitability of such a concrete for temperature exposure.

TESTING

Testing was carried out on concrete specimens manufactured using the above mix design principles. Each specimen was a cylinder 30mm in diameter and 60mm in length, with a 6mm coarse granite coarse aggregate and quartzitic fine aggregate. A water:binder ratio of 0.3 was used, with 55% fly ash replacement. Specimens were cured for either 70 or 90 days.

Specific challenges were encountered during the testing, including concerns with curing and difficulties with sealing the concrete, which raise concerns about the validity of the data. For this reason incomplete information is presented on the testing, and it is simply used to be illustrative of the mechanisms that are taking place.

The heating rate was low at 10°C/hour to be representative of pebble bed high temperature gas reactors. The testing schedule included temperature exposure to 225°C and 450°C for between 1 and 14 days and up to 3 thermal cycles. All samples were tested cold.

The compressive strengths that are presented here are of concrete exposed to 225°C for 5 days (including the rise to temperature) and 450°C directly afterwards for a further 4 days, McCormick (2011). This was carried out for both sealed and unsealed concretes.

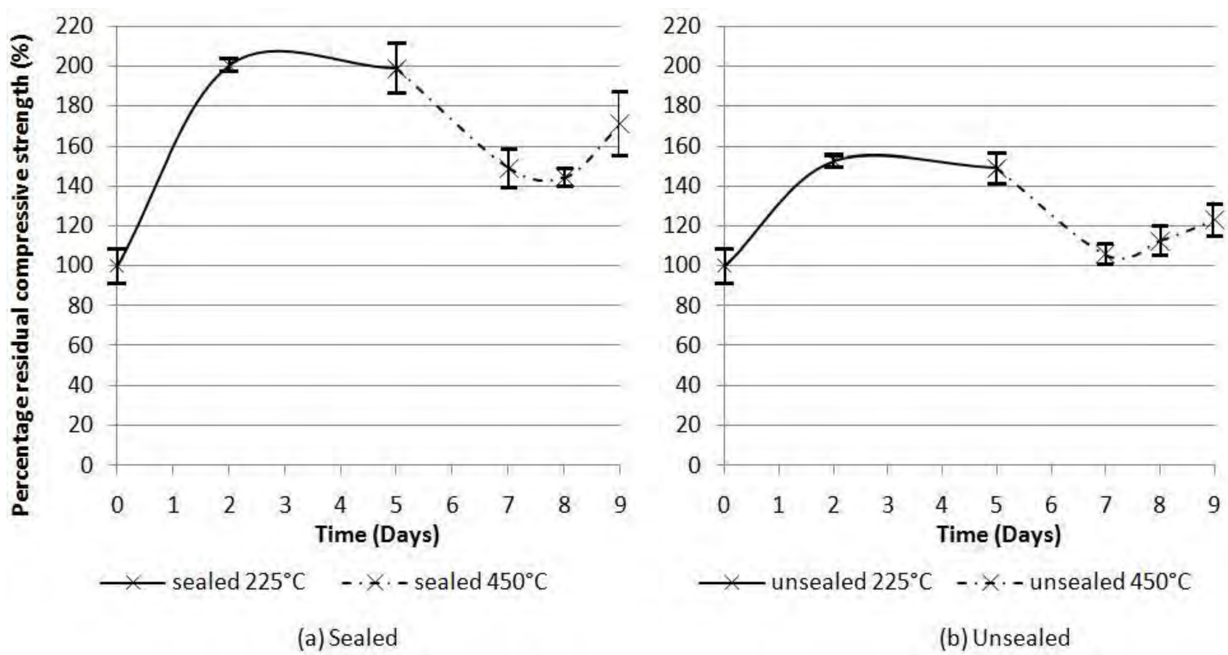

Figure 1: Residual Compressive Strengths of Concrete After Thermal Exposure (a) Sealed and (b) Unsealed, McCormick (2011)

Scanning electron microscope investigations of the concrete were carried out to identify any changes in the microstructure of the material as shown in Figure 2, Figure 3 and Figure 4.

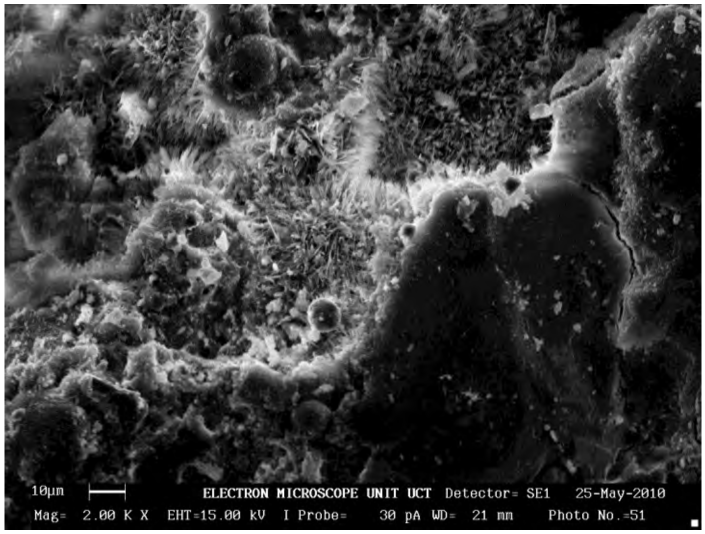

Figure 2: Evidence of CSH formation after exposure to 225°C for 7 days in a sealed environment

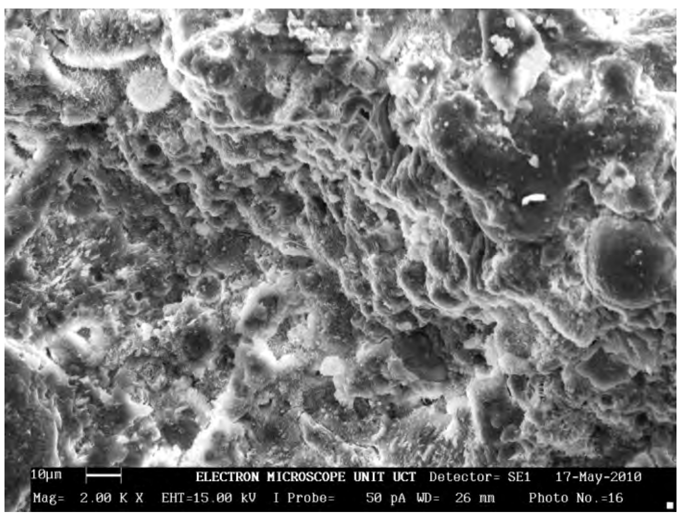

Figure 3: Sealed concrete after 225°C exposure for 7 days

It is evident from the scanning electron microscope images that there is new formation of CSH phases in the concrete in a sealed environment, particularly around unreacted fly ash particles. It is also evident that the concrete is dense with little cracking after exposure to 225°C.

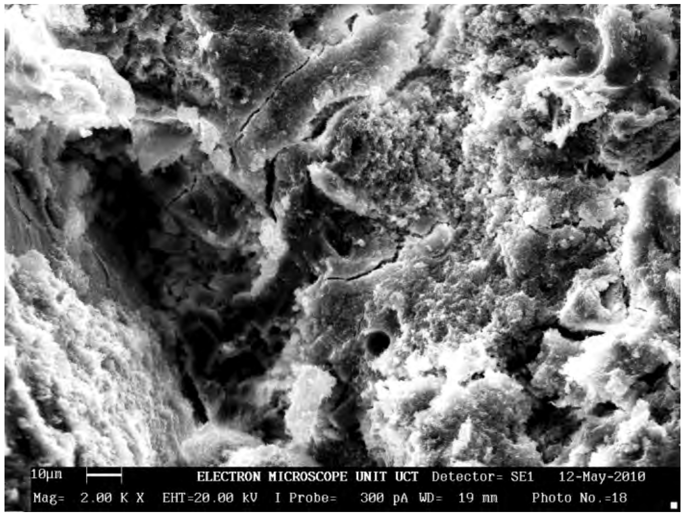

Figure 4: Unsealed concrete after exposure to 450°C

After exposure to 450°C in an unsealed environment extensive microcracking is evident, with a substantial increase in the porosity of the material. This supports the reduction in strength over 225°C.

CONCLUSION

There is an extensive body of literature available on the topic of heated concrete. There are also several literature reviews compiling this information together. This paper attempts to use this information to identify concrete constituents that are particularly beneficial for long term, operational heated environments as can be expected in structural concrete for nuclear reactors.

It has been demonstrated that, at least for compressive strength, Portland cement is a suitable binder with high contents of replacement with a pozzolanic binder such as fly ash, in the region of 50% to 60% replacement. The use of siliceous aggregates is also ideal and calcareous aggregates should be avoided for sealed environments.

It is evident that hydrothermal reactions have a significant effect on the response of concrete in a sealed environment, forming phases that are weaker, lime rich and more crystalline. The addition of pozzolanic extenders reduces the $Ca(OH)_2$ content in the concrete and the extenders react at temperature to form CSH phases similar to those produced by Portland cement. This can cause significant improvements in strength of the concrete on exposure to 225°C and strengths similar to the unheated properties after exposure to 450°C. Exposure to 450°C causes microcracking due to differential thermal expansion between the aggregate and binder phases. This affects both sealed and unsealed concretes.

Data available on the modulus of elasticity and the stress strain characteristics of heated concrete demonstrates a reduction in properties without the possible increase as expected with compressive strength. Literature has demonstrated that the application of a confining stress to the concrete substantially improves the retention of stress strain characteristics of the material.

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