High Temperature Concrete for Nuclear Reactors

A dissertation submitted for the degree of Master of Science in Engineering

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I declare that:

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- All sources of information used in this report have been clearly referenced according to IEEE convention.
- This report is my own work. I have not and will not allow any other person to use this report, or parts of it and pass it off as their own work.

Darryn McCormick; MCCDAR003

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Date

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Abstract

This dissertation investigates the response of concrete to high temperatures for extended periods, such as those that may be experienced in a normally operating nuclear reactor. Codes of practice, such as the American Concrete Institute's ACI 349, place strict limits to temperature exposure on structural concrete for nuclear reactors.

This project was undertaken for the Pebble Bed Modular Reactor, a generation IV high temperature reactor. Such reactor designs have significantly higher operating temperatures than pressurized water reactors, which would require large and complex cooling systems to keep the supporting structure for the reactor within the limits placed by codes of practice for nuclear reactors. This project investigated the response of concrete to high temperatures with a view to developing a material that was resistent to high temperatures, allowing the reactor cavity structure to be exposed to significantly higher temperatures than those currently allowed by the Codes. The maximum temperature limits investigated were 225°C for operating temperatures for the lifetime of the structure and 450°C for accident situations of approximately 30 days.

An in depth literature study was undertaken, reviewing literature relating to the mechanical, transport and thermal properties of Portland cement concrete. A complex set of parameters were identified that affect the response of a concrete to high temperatures, including material constituents and quantities, temperatures reached, duration at temperature, heating rate, thermal cycling and the ability of moisture to escape from the heated concrete.

It became apparent from literature that a primary concern in designing concrete for high temperature applications was understanding the effect that moisture had on the concrete. This falls into two categories - unsealed and sealed, where unsealed concrete allows moisture to escape from the concrete and sealed concrete prevents moisture from escaping.

Thus, unsealed concretes develop differential thermal expansions and shrinkage between the aggregate and binder paste, leading to the development of microcracking. This has a significant effect above about 250°C as the cement paste begins to shrink significantly due to dehydration of the paste, and the aggregate continues to expand. Sealed concretes also experience dehydration of the chemically bound water in the cement paste, but the main effect temperature has on these concretes is to develop high pore pressures and cause hydrothermal reactions in the cement paste. These reactions result in the

formation of:

1. Hydrogarnets (HG) - $C_3(A,F)SH_4$
2. Hydroxylellestadite (E) - $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$
3. αdicalcium silicate hydrate ($\alpha - C_2SH$) - $C_2SH_{0.3-0.1}$
4. 11Å Tobermorite

Cement pastes that are solely comprised of Portland cement form hydrogarnets, hydroxylesllestadite and αdicalcium silicate hydrate, with the formation of $\alpha - C_2SH$ dominating at 250°C. This phase is crystalline and lime rich, with coarse and poorly interconnected particles. The addition of high quantities of siliceous materials such as fly ash or ground quartz see the formation of hydrogarnets and 11Å tobermorite dominating at high temperatures. These are gel-like phases, and act to either improve the strength retention or even increase strength at temperature. Considering the PBMR reactor cavity structure, sealed concrete is more representative of the material in question.

With the in depth literature study complete a set of concrete constituents were identified that are likely be beneficial at high temperature. These were then applied in a testing program that investigated the strength and several transport properties (oxygen permeability, water sorptivity, chloride conductivity) of two concrete mixes with these suggested constituents.

The results of the testing suggest that the sealed concrete experienced an improvement in strength over the unheated concrete of up to 130% at 225°C, while unsealed concretes showed a much lower strength gain, or even a strength loss. Scanning electron microscope studies confirmed that the improvement in strength in sealed concretes was due to the formation of new gel-like phases in cracks and voids of the concrete. This phase was formed by unreacted fly ash and Portland cement in the concrete, in the presence of the high moisture environment. Sealed concretes exposed to 450°C appeared to be governed by the development of microcracking. A concrete with higher binder content, which would have developed less microcracking, showed a deterioration in strength between 50% and 10%, while a concrete with lower binder content (and subsequently higher aggregate content) showed an improvement of between 30% and 50%. The higher aggregate content lead to greater microcracking in the concrete which exposed unreacted Portland cement and fly ash, which in turn reacted in the high moisture environment to repair the cracks. Although such an improvement in strength is desirable, it was concluded that greater microcracking would not be beneficial in terms of properties such as modulus of elasticity or creep.

At 450°C the unsealed concrete experienced a significant loss in strength that is dominated by the development of microcracking and dehydration of the binder paste.

The transport properties were investigated in an unsealed state, and it was found that temperature generally has a deleterious effect on the transport properties of a concrete. Gas permeability, measured by the OPI test, demonstrated an increase of 2 times for a concrete with a higher binder content, while concrete with a higher aggregate content demonstrated an increase of an order of magnitude. This suggests that concrete with a higher aggregate content experienced greater microcracking at this temperature. Both concretes demonstrated an increase of an order of magnitude from the 225°C results when exposed to 450°C, indicating the development of microcracking.

Interestingly, at 225°C it appears that the porosity of the concrete may experience a significant drop over time, leading to an improvement of properties such as reduced water sorptivity and chloride conductivity. This may be due to the densification of the solid phase of the concrete preventing the ingress of deleterious media. After exposure to 450°C results generally increase with length of exposure, suggesting microcracking is dominating the response.

It was concluded that the mix design that was tested could meet the requirements of the PBMR reactor cavity structure, and that further testing and investigation should be carried out to determine the response of all properties of interest. Of particular interest would be the response of the modulus of elasticity, as literature suggests that such mix designs demonstrate a greater reduction at temperature over concretes without high extender contents.

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List of Abbreviations

AAR	Alkali Aggregate Reaction
ACI	American Concrete Institute
ASR	Alkali Silica Reaction
ASME	American Society of Mechanical Engineers
ASTM	American Society for the Testing of Materials
CAC	Calcium Alumina Cement
CH	Calcium Hydroxide ($Ca(OH)_2$)
CSF	Condensed Silica Fume
CSH	Calcium Silicate Hydrate
DI	Durability Index
FA	Fly Ash
GGBS	Ground Granulated Blast Furnace Slag
HAC	High Alumina Cement
HTR	High Temperature Reactor
ITZ	Interfacial Transition Zone
LOCA	Loss Of Coolant Accident
OPI	Oxygen Permeability Index
PBMR	Pebble Bed Modular Reactor
PWR	Pressurized Water Reactor
RT	Room Temperature
S	Sealed
SEM	Scanning Electron Microscope
UCT	University of Cape Town
US	Unsealed

Chapter 1

Introduction

This dissertation is concerned with investigating and developing concrete that is able to withstand high temperatures for application in nuclear reactors. This project was undertaken for the Pebble Bed Modular Reactor (PBMR), a generation IV high temperature gas cooled reactor (HTR) that was investigated by PBMR (Pty) Ltd in South Africa. HTR's have been researched over several decades because of the potential of significantly higher operating temperatures of the reactor. The PBMR could give an expected outlet temperature of more than 900°C against 330°C for current light water reactors, allowing the possibility of higher electricity generation efficiencies, the production of hydrogen and co-generation for chemical and process industries [1, 2].

The PBMR design has several key distinguishing features, where probably the most important is the aspect of inherent safety. This concept implies that the reactor has many passively safe systems that reduce the risk associated with accident scenarios and radiation exposure. The most significant aspect is that the reactor has a negative temperature coefficient of reactivity, namely that as the temperature of the reactor rises the fission reaction slows, effectively moderating the temperatures reached in an accident scenario [2]. The concept of inherent safety also applies to the structure surrounding the reactor, with the effect of the very high operating and accident temperatures on the structure requiring consideration.

The use of structural concrete in nuclear reactors has strict limits placed on temperature exposure. An example of these limits are those set by the American Concrete Institute of 65°C with hot spots of 93°C for operating temperatures and 176°C with local hot spots due to steam of 343°C for accident temperatures in ACI code 349 [3]. However, the Code has provisions allowing for the design of structures to operate at higher temperatures if adequate evidence of sustained strength is provided.

There have been many years of research carried out in this topic, with research into the fire related response of concrete beginning at least as early as 1904 [4]. One of the first references available where concrete was considered for high temperature structures was the patent by Platzmann in 1925 for the manufacture of a refractory concrete based upon Portland cement, chamotte and either trass or reactive silica [5, 6]. The body of literature steadily grew up to about 1960, from which it expanded significantly as interest in nuclear reactors gained momentum with consequent interest in high temperature structures [7]. Since then many directions of research in the topic have been appropriately answered, a good example being the thermal properties of concrete, however, a definitive answer to the response of Portland cement concrete to high temperatures still remains incomplete.

1.1 The Pebble Bed Modular Reactor and High Temperature Concrete

High temperature reactors operate at temperatures significantly higher than conventional pressurized water reactors (PWR). When one considers the temperature limits placed on the surrounding concrete structures it becomes apparent that large cooling systems or bodies of insulation would be needed to keep the concrete within the limits imposed by current Codes. Another alternative would be to develop a material that has a predictable and resistant response to temperature. This is the reasoning behind this project.

Generally, a nuclear reactor pressure vessel needs to be supported by a structure made of concrete. This concrete also serves as a radiation shield between the reactor and the containment structure. In the case of the PBMR this involves a concrete cylinder, with an air gap between the reactor and the cylinder, called a reactor cavity. Figure 1.1 gives a section view of the HTR-Modul reactor cavity, upon which the PBMR is based [8]. In the case of a loss of coolant accident (LOCA), the temperature rise in the air gap is intended to cause natural convection, drawing heat away from the area. In previous HTR designs a reactor cavity cooling system (RCCS) was implemented in this air gap to reduce the temperatures the concrete is exposed to [9].

PBMR (Pty) Ltd commissioned the University of Cape Town (UCT) to research a concrete that met several requirements as outlined in a scope of research document [10] with the key requirements outlined below.

1. A concrete is required that can withstand operating temperatures of 225°C, and accident temperatures of 450°C for a period of 30 days, while maintaining sufficient compressive strength (that is, remaining above the room temperature (20°C) compressive strength of 40 MPa) and modulus of elasticity to be able to remain structurally stable throughout.

2. Permeability shall be such that a leakage rate (of gas) of less than 5% volume/day at a design pressure of 150 kPa(g) (times 1.15 for testing, i.e. 172.5 kPa(g)) is obtained.

3. The concrete shall be sulphate and chloride resistant with a low heat of hydration (large pours are required).

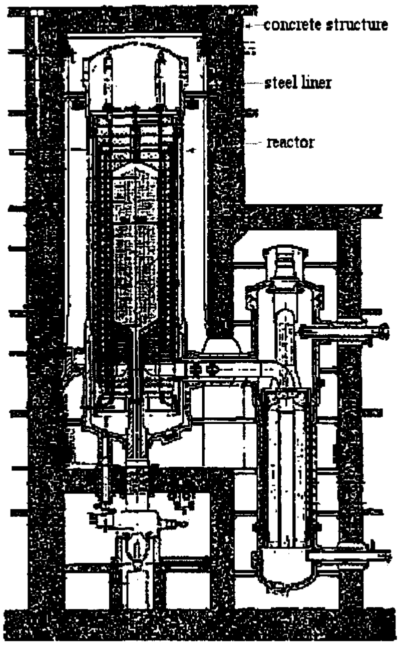


Figure 1.1: Section view of the HTR-Modul [8]

4. A design life of 40 years for operation and a further 40 years for storage of waste is required in a coastal environment.

The approach of developing a material that itself is resistant to temperature supports the theory of inherent safety behind the PBMR, as opposed to having active cooling systems that would increase both the complexity and risk of system failure in the case of an accident. This could also reduce the overall cost of the reactor.

1.2 Objectives

The primary objective of this project was to research a concrete that is able withstand significantly higher sustained temperatures than those that are currently stipulated in Codes such as ACI 349 [3]. This primary objective was broken down into two secondary objectives, namely:

1. To develop a comprehensive understanding of the response of Portland cement concrete to high temperatures.

2. To utilize this understanding to present and test a suggested concrete mix design that allows the design of nuclear structures according to the criteria outlined above.

1.3 Scope and Limitations

This dissertation primarily focuses on developing an understanding of the response of concrete to high temperatures. This is carried out through an intensive literature study. A testing series has been carried out to verify the concepts gained from literature, and to develop a suggested mix design for further testing.

As will be described in Chapter 3, concrete has a complex response to high temperature exposure, with a significant difference between the response to different environments (for example operating power plants or a fire situation). As such, and due to the broad range of literature available for concrete exposed to high temperatures specific focus has been given to literature relating to the heating environment of the PBMR. This is a considerable volume of literature that provides relevant insights in the topic.

The testing phase of the project considered some concepts developed from the literature review. This phase was not a comprehensive characterization of the material, rather a testing and validation of concepts gained from literature, with a view to demonstrating the direction for more intensive testing to take place.

It should be noted that some properties were given a cursory consideration in this project, such as radiation shielding and creep. This allowed a more focused and comprehensive study of properties, such as strength, that were requested be investigated. Such properties would require consideration in the complete characterization of the material.

1.4 Organization of this Dissertation

This dissertation begins with a review of the basic concepts of concrete at room temperature. This is followed by an in-depth study of available literature on the topic, including:

- A review of the relevant factors that affect the response of a concrete to high temperatures.
- An assessment of the PBMR environment to assist in identifying the relevant literature.
- A review of Portland cement concrete response to the temperatures of interest according to mechanical, transport and thermal properties.
- A brief review of the response of steel reinforcement to high temperatures (to assess the interaction between concrete and steel at high temperatures).

Various concepts and trends were developed from the literature review. The testing methodology used to validate the concepts gained from literature is discussed in Chapter 4, followed by the results of the testing in Chapter 5. The dissertation is concluded with a discussion, conclusions and recommendations. Appendix A contains the results of the testing while Appendix B contains the designs of testing apparatus used in the project.

Chapter 2

Basic Concepts of Concrete

In this Chapter the concepts of Portland cement and concrete are dealt with. This is to enable the reader to understand the response that the constituents of a concrete, and the greater concrete material, has to high temperatures. For further reading on this topic the reader is referred to Neville [11] or Fulton's Concrete Technology [12].

Concrete is a complex, multi-phase material that consists of a binder (generally Portland cement) and stone (commonly called aggregate). Each of these phases has different properties and functions in the concrete material, while the two phases interact to effectively form a third phase around each piece of aggregate called an interfacial transition zone (ITZ). One needs to understand the different functions of these phases, their respective properties and the way the phases interact.

2.1 The Binder Phase

The binder phase is the matrix that bonds aggregate particles to form a composite that is rigid and strong [12]. The binder may also be referred to as cement, glue or adhesive.

2.1.1 Portland Cement

The primary component of the binder phase for concrete is generally Portland cement. Portland cement is used because it is relatively cheap, sets at normal temperatures and pressures and can be made to be strong and durable [12]. It is worth noting that the concrete industry is the biggest consumer of raw materials worldwide, using 11.4 billion tonnes annually [13]. Portland cement is a fine powder that hydrates and forms a solid phase when mixed with water. Its constituents are presented in Table 2.1.

When Portland cement is mixed with water it undergoes a hydration reaction forming the following products [12]:

1. $2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$

Table 2.1: Compound composition of South African Portland cements [12]

Compound	Formula	Abbreviation	% by mass in cement
Tricalcium silicate	$3CaO.SiO_2$	C_3S	35 – 55%
Dicalcium silicate	$2CaO.SiO_2$	C_2S	20 – 40%
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	5 – 12%
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	5 – 10%
Magnesia	MgO	M	0.3 – 4.0%
Gypsum	Raw material	-	4 – 7%
Free lime	CaO	-	0.5 – 2.5%

2. $2C_2S + 4H \rightarrow C_3S_2H_3 + CH$
3. $C_3A + CH + 12H \rightarrow C_4AH_{13}$
4. $C_4AF + 4CH + 22H \rightarrow C_4AH_{13} + C_4FH_{13}$

The calcium hydroxide, $Ca(OH)_2$ (abbreviated CH), reactions 3 and 4 are provided for by 1 and 2. Equation 3 has intermediate reactions that are not shown.

$C_3S_2H_3$, calcium silicate hydrate (abbreviated CSH), also commonly called CSH gel, solidifies as plates and needles, forming a porous medium that provides the most significant contribution to the strength of the cement.

Calcium hydroxide is another primary product of the cement hydration and solidifies in the form of large crystals; however it has a small contribution to the strength development of the cement paste. Any excess water in the cement is generally a saturated solution of calcium hydroxide as it is soluble.

For an average composition of Portland cement, 1 kg of cement will produce approximately 615g of CSH gel and 255g of CH [12].

2.1.2 Cement Extenders

The building of structures with Portland cement usually includes the use of extenders. Extenders are materials that are added to cement that have beneficial effects either in property development and/or cost basis. There are three extenders that are generally used [12]:

- Fly ash (FA)
- Condensed silica fume (CSF)
- Ground granulated blast furnace slag (GGBS)

Fly ash is a residue from flue gasses from furnaces fired with coal. When used as an extender fly ash is normally in the range of 0% - 30% by weight of binder content. Its use offers several advantageous properties in concretes:

- Development of CSH gel through a pozzolanic reaction.
- Reduction of early age hydration temperatures due to the slow evolution of the pozzolanic reaction.
- Improved durability of concretes with increased resistance to sulphates, carbonation, aggressive environments and alkali-aggregate reaction.

Condensed silica fume is a fine powder resulting from the production of silicon or silicon bearing metal alloys carried by flue gases from the burning area of a furnace by exhaust gases. Condensed silica fume is used generally in the range of 0% – 10% by weight of cementitious materials. It offers the following beneficial properties in concretes:

- Development of CSH gel through a pozzolanic reaction.
- Fine filler effect significantly reducing the size of the interfacial transition zone.
- Increased rate of strength development.
- Improved durability with increased resistance from sulphates, carbonation, aggressive environments and alkali-aggregate reaction.

The pozzolanic reaction has a general formula of [12]:

1. $2S + 3CH \rightarrow C_3S_2H_3$

From this equation it becomes apparent that pozzolans consume the calcium hydroxide product of Portland cement. This effectively reduces the amount of calcium hydroxide in the cement paste, as has been shown by Lam [15].

Ground granulated blast furnace slag is a residue of iron production, that has been ground to a powder. Blast furnace slag hydrates in a similar reaction to Portland cement, but requires a high alkali environment to increase the rate of reaction. The reactions are outlined below [12]:

2. $3(C + S) + 3H \rightarrow C_3S_2H_3 + S$
3. $(a \times S) + (b \times CH) + other \rightarrow C_3S_2H_3 + (CA products)$

From these equations it becomes apparent that blast furnace slag consumes calcium hydroxide in its hydration reaction. Blast furnace slag is generally used by replacing up to 50% of Portland cement content, and offers the following benefits:

- Reduced early age hydration temperatures
- Improved durability with increased resistance from sulphates, carbonation, aggressive environments and alkali-aggregate reaction

As will be described in Section 3.2, extenders play a vital role in providing a concrete that is resistant to high temperatures, largely due to the consumption of calcium hydroxide [16, 17].

2.1.3 Alternative Binders

With the project topic in consideration, it becomes necessary to discuss other binders that are commonly used in high temperature environments. A brief discussion is carried out here, describing only a few of the alternatives that are available and those that appeared to be most relevant to the project.

Calcium aluminate cement (CAC), also called high aluminate cement (HAC), is the cement that is most commonly used in refractory contexts due to excellent resistance to high temperatures. This cement has however been banned from structural use by codes of practice in many countries including South Africa. This is because the primary constituents of high alumina cements are calcium aluminates, other than C_3A, that undergo conversion when exposed to moisture and temperature [12].

The hydration products are calcium aluminate hydrates, with the most important being the unstable hexagonal hydrates CAH_{10} and C_2AH_8. These hydrates undergo conversion to the stable cubic hydrate form C_3AH_6 accompanied by a significant volume change. This conversion, irrespective of the age of the concrete, results in a significant increase in porosity, loss of strength and resistance to chemical attack, rendering the cement unsuitable for these environments. The primary use of CAC is as an insulating concrete in dry hot environments, and with special aggregates can withstand temperatures up to 1800 °C [6, 7, 12].

Several other materials have been considered in the past and present, including waterglass [6] and geopolymers [18, 19]. Waterglass is an anhydrous, inorganic binder that hardens in air [6]. It is a silica rich sodium silicate, with the ratio of $SiO_2 : Na_2O$ determining the material properties. The binder itself is unremarkable compared to other binders, however is remarkably stable with temperature exposure aside from dehydration of the silica phase between 100°C and 150°C and a slight exopeak between 600°C and 650°C relating to crystallization.

Geopolymers utilize fly ash or ground granulated blast furnace slag in an inorganic aluminosilicate binder. Geopolymers provide a remarkable response to temperature, with Kong et al. [18] showing an increase in strength of 53% with temperature exposure to 800°C of the binder. Tests on a concrete using basalt aggregate however showed a 65% decrease in strength, largely due to microcracking between the aggregate and paste. The manufacturing of geopolymers is also somewhat complicated when compared to Portland cement concrete, requiring several chemicals and well controlled manufacturing processes.

Another option for a binder for high temperature applications could be a polymer, a suggested example being Scott Bader Crystic Crestapol 1230 [20, 21]. This polymer is believed to be fundamentally stable to temperatures in excess of 400°C, with a stated heat deflection temperature of 243°C[21], and would not face any of the issues surrounding moisture migration or permeability with Portland cement concrete, as will be discussed in Chapter 3. With this in mind a polymeric binder has several clearly useful aspects relating this application.

With these alternative binders in consideration, a decision to focus research on Portland cement was made, due to the following reasons:

1. Literature suggests that Portland cement concrete can be effectively used for operating temperatures of 300°C to 400°C [22].

2. The body of literature relating to Portland cement concrete exposed to high temperatures is extensive.

3. The well developed construction processes and methods for Portland cement concrete.

2.2 The Aggregate Phase

Concrete generally consists of between 70% to 80%, by volume, aggregate and as such has a major role to play in the properties of the material. Aggregate lends dimensional stability to the concrete and has a direct effect on the modulus of elasticity of concrete (as it has a higher modulus of elasticity than the binder phase). In general the goals for a concrete in terms of aggregate are that it is not reactive with the cement paste and has good grading and sizing.

2.2.1 Options for Aggregates

Choice of aggregate for any massive concrete structure is normally limited to that which is locally available, and is usually natural stone. In the case of refractory concretes, a strong case can be made for the use of special aggregates such as chamotte or crushed firebrick [6, 7]. These aggregates generally have a low coefficient of thermal expansion and are stable to very high temperatures, supporting their use in refractory concretes. The selection and choice of an aggregate in this case has to be made on both economic and suitability grounds.

The first point that needs consideration is that the use of special aggregates is generally accompanied by a significant increase in costs. This may be justified if there are no suitable natural aggregates available in the local area, and is a decision that would have to be made in the assessment of the site.

With this in mind, one has to carefully analyze and select aggregates for use in high temperature environments. A specific focus on natural aggregates has been given in this project to illustrate the viability of considering these for the temperature ranges considered. Conventional aggregates broadly fall into four groups (when one considers their viability for concrete at high temperatures):

- Sedimentary carbonate

- Igneous amorphous

- Igneous crystalline

- Quartzitic

These groupings are broadly related to the silica content of the aggregate, with sedimentary carbonate aggregates (for example limestone) having little or no silica content, amorphous igneous aggregates having very small formations of silica crystals, crystalline igneous aggregates having larger silica crystals and quartzitic aggregates having high silica contents in large crystals. Coefficients of thermal expansion for various aggregates at room temperatures were determined by Browne as shown in Table 2.2 which clearly shows the correlation between silica content and expansion properties [23]. In terms of the igneous rocks, basalt falls into the category of amorphous, while granite can vary between amorphous and crystalline.

Table 2.2: Coefficients of thermal expansion for different rocks and concretes at normal temperatures [23]

Rock group	Typical silica content by weight (%)	Coefficient of thermal expansion ($10^{-6}°C^{-1}$)			
		Rock		Concrete	
		Range	Average	Range	Average
Chert	94	7.4 - 13.0	11.8	11.4 - 12.2	13.2
Quartzite	94	7.0 - 13.2	10.3	11.7 - 14.6	12.1
Sandstone	84	4.3 - 12.1	9.3	9.2 - 13.3	11.4
Marble	Negligible	2.2 - 16.0	8.3	4.1 - 17.4	10.7
Siliceous limestone	45	3.6 - 9.7	8.3	8.1 - 11.0	10.7
Granite	66	1.8 - 11.9	6.8	8.1 - 10.3	9.6
Dolerite	50	4.5 - 8.5	6.8	-	9.6
Basalt	51	4.0 - 9.7	6.4	7.9 - 10.4	9.3
Limestone	Negligible	1.8 - 11.7	5.5	4.3 - 10.3	8.6

An interesting aspect to consider is the locality-specific nature of the aggregates. A table representing the room temperature coefficient of thermal expansion of various South African aggregates is given in Table 2.3 [24]. Of these aggregates, only granite and greywacke are readily accessible in the Western Cape region. It is interesting to observe the reasonably high coefficients of thermal expansion in these aggregates, suggesting a higher silica content.

2.2.2 Chemical Reactivity of Aggregate

Ideally an aggregate would be chemically inert, however there are several chemical reactions and constituents found in an aggregate that can cause undesirable reactivity when used in concrete [12]:

1. Water soluble substances – reduce strength and induce efflorescence e.g. common salt

Table 2.3: Values of Coefficient of Thermal Expansion for Commonly Found Aggregate in South Africa [24]

Aggregate Rock Type	Coefficient of thermal expansion (µstrain/°C)
Andesite	7.4
Dolerite	6.0 – 8.1
Dolomite	7.5 – 9.2
Felsite	9.2
Granite	6.4 – 9.7
Greywacke	10.9
Quartzite	9.4 – 12.2
Tillite	6.6

2. Substances soluble in cement paste – e.g. humic acid
3. Substances that destroy hardened cement paste – e.g. sodium sulphate
4. Alkali reaction with constituents in the aggregate e.g. opal
5. Corrosion of reinforcing steel – e.g. salt

Of these reactions, one of the most prevalent is alkali-aggregate reaction (AAR) and alkali-silica reaction (ASR) [12]. This consists of the highly alkaline environment of cement paste (recall that water in cement paste is a saturated solution of calcium hydroxide) reacting with silica in the aggregate, causing an expansion. This expansion causes cracking in the concrete, with a subsequent decrease in engineering properties and exposure of steel reinforcement to the atmosphere. One of the commonly used aggregates in the Western Cape region, greywacke, has a high incidence of ASR with substantial damage to infrastructure in the region.

Another fairly important consideration is the availability of deleterious ores in some aggregates that specifically contain sulphides, e.g. pyrite, zinc blende (sphalerite), lead glance (galena) etc. [12].

2.3 The Concrete Material

Concrete as considered here is a mixture of a Portland cement and extender binder phase and aggregate phase, with the area between the two called the interfacial transition zone. The binder phase, as its name suggests, serves as a matrix that bonds the aggregate together and ultimately forms the solid material. The aggregate phase serves to add mechanical properties to the binder phase, assisting in strength development, dimensional stability and modulus of elasticity. Concretes generally contain between 70% to 80% aggregate and 12% to 25% binder, by weight [7]. Some interesting work, primarily in the field of refractory concretes using high alumina cements, suggests that the use of micro-fillers such as silica fume and zirconia can allow the cement content to be dropped to 3% - 6% for low cement concretes and 1% - 2% for ultra low cement concretes [7].

2.3.1 The Interfacial Transition Zone

The interfacial transition zone (ITZ) requires special consideration because it has a significant effect on the properties of the concrete. The ITZ is generally the weakest area of a concrete and has a significant impact on the modulus of elasticity of the concrete. This area is characterized by a more porous structure with a high content of calcium hydroxide and ettringite crystals, all caused by collection of water around aggregate particles in fresh concrete. When one notes that calcium hydroxide provides limited mechanical properties and the more porous structure suggests less CSH formation around the aggregate, reduced mechanical properties are obvious.

Several factors affect the ITZ [12], as outlined below.

1. Lower water:cement ratios provide denser microstructures in the entire binder phase, including the ITZ.
2. If a concrete has enough water to sustain cementing reactions, the age of the concrete reduces the size of the ITZ.
3. Cementitious extenders containing very fine particles such as silica fume develop a denser ITZ.
4. Ultra fines in aggregate have a 'fine filler' effect of reducing the bleeding of the concrete and densifying the ITZ.
5. Rougher aggregates reduce the size and effect of the zone.
6. Absorbent aggregates improve the interface strength and density.

The high porosity of the area also adversely affects the transport properties of the concrete as will be discussed in Section 2.3.2.6 concerning durability, supported by Figure 2.5 on page 20, which is a useful representation of the impact that the ITZ can have properties.

2.3.2 The Properties of Interest of Concrete at Room Temperatures

To give a comprehensive summary of the properties that a concrete technologist or structural engineer is interested in at room temperatures is beyond the scope of this dissertation. A short description of some of the properties, their generally encountered values and factors surrounding these properties has however been addressed. It should be noted that this project was primarily concerned with high performance concretes (in terms of strength and other properties) and a specific focus is given to these. The consideration of high performance concretes is justified in the context of the minimum specified design strength and the environment of exposure for the concrete. Much of the information for this section has been gathered from Fulton's Concrete Technology [12].

Strength

The compressive strength of a concrete is the commonly used primary determinant for a concrete design. Concretes have strengths that can range from less than 20 MPa to well in excess of 130 MPa for ultra-high strength concretes. Generally the definition between normal and high strength concretes is either 40 MPa or 60 MPa, dependent on whether one is using the American or European design philosophies [12, 14]. This differentiation suggests various characteristics about its constituents [12].

- Probably the most important aspect is the use of very low water:cement ratios, well below the 0.4 ratio that defines the boundary for complete hydration of the cement paste. Water:cement ratios of 0.3 and lower are not uncommon.
- Extensive use of admixtures (chemical additives that improve properties of the concrete e.g. super plasticizers improve workability) and extenders.
- Aggregates that require special attention in terms of grading, quality and water content.

Strength development for concrete is generally considered to be complete after 28 days, with any strength gain after this continuing at a very low rate. Interestingly the addition of extenders such as fly ash and ground granulated blast furnace slag slow the strength development considerably, with these concretes effectively achieving complete cure after 90 days.

Tensile strength of concrete is considerably lower than its compressive strength, with no specific relationship between the two. It is however generally an order of magnitude lower than the compressive strength.

Modulus of Elasticity (E)

The modulus of elasticity (E) is the ratio between uni-axial stress and un-axial strain. Considering that the stress-strain relationship for concrete is non linear up to failure, the modulus is calculated for the first 30% to 40% of the failure stress [12]. Generally modulus values can range from between 20 GPa and 50 GPa, and the property develops most significantly over the first 7 days of cure. Several relationships exist that relate compressive strength to the modulus of the concrete.

There are several factors that affect the modulus independently of temperature [12, 14], namely:

- Concrete constituents and quantities, where generally higher contents of the stiffer phase (normally the aggregate) result in higher modulus.
- Water:cement ratio, which generally determines the porosity of a cement paste, which implies that lower ratios tend towards higher modulus values.
- Age of the concrete causes a rapid increase in the first few months, and continual increase up to approximately 3 years.
- Aggregate type and grading, as shown by Kaplan [25], has a significant effect on a concrete's stiffness, with the modulus of the aggregate being particularly notable in this respect.
- Moisture content during testing has an effect on the modulus of a concrete, with high water saturation levels giving a lower value.

Considering high strength concretes, the modulus is more dependent on the type of coarse aggregate used than the compressive strength of the concrete. Similarly there is a significant increase in the rate of modulus development, with most of the property developing within the first 24 hours of cure.

Modulus of elasticity can be tested according to two methods, namely static and dynamic. Static tests consists of loading a concrete sample to about one third of the failure strength several times, and accurately measuring load and deformation. Dynamic tests involve applying very small and rapid loadings to the concrete, often by means of resonance. These tests give different results, with the dynamic E generally being higher than the static E, largely relating to the non-linearity of the concrete stress-strain relationship.

Poisson's Ratio

Poisson's ratio is the ratio of lateral strain to axial strain with a uni-axial loading. As with modulus of elasticity the Poisson's ratio can be tested either statically or dynamically and generally the static Poisson's ratio falls between 0.2 and 0.1 while the dynamic ratio falls between 0.18 and 0.3. The static value is strongly affected by the type and quantity of aggregate, with higher aggregate contents significantly decreasing the ratio. The dynamic value decreases with increasing age of the concrete, increasing aggregate content and lower water:cement ratios [12].

Creep

Creep is the time-dependent change in strain of a solid body under constant or controlled stress, or alternatively the reduction of stress under constant or controlled strain. Creep occurs with any loading in concrete, although the mechanism driving creep changes above 40%-50% of failure loading, with microcracking playing a significant role above these values [12]. Creep can

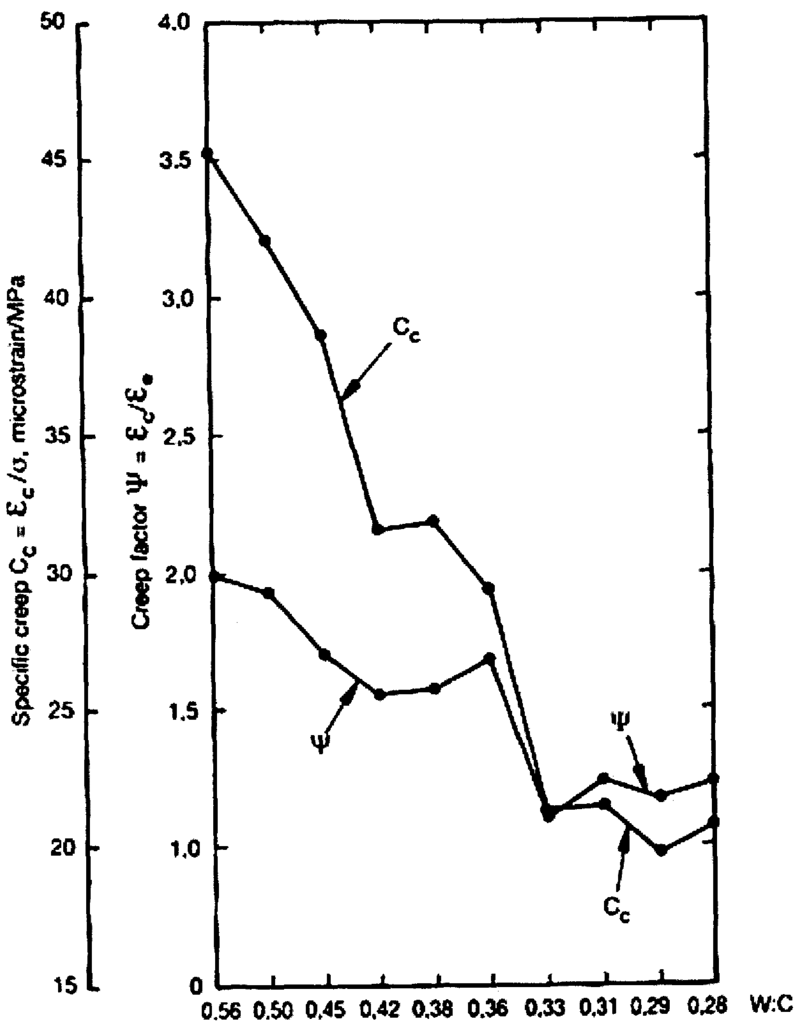


Figure 2.1: Specific creep and creep factor versus water:cement ratio for concretes made with andesite aggregates [26]

be several times larger than the initial deformation caused by loading of the structure. It is also important to note that creep of concrete is affected by intrinsic factors such as concrete design and age, extrinsic factors such as applied stress, relative humidity and curing.

Considering high strength concretes it is important to note that lower water:cement ratios result in lower creep [12]. This is effectively demonstrated by Figure 2.1 [26]. Note that this figure refers to specific creep with units of µstrain/MPa. This Figure also effectively shows that creep below a water:cement ratio of 0.33 is effectively constant.

One of the primary factors that affects the creep of high strength concretes is the age of loading. This is appropriately represented by Figure 2.2 [27]. From this Figure it becomes apparent that creep can be considerably reduced

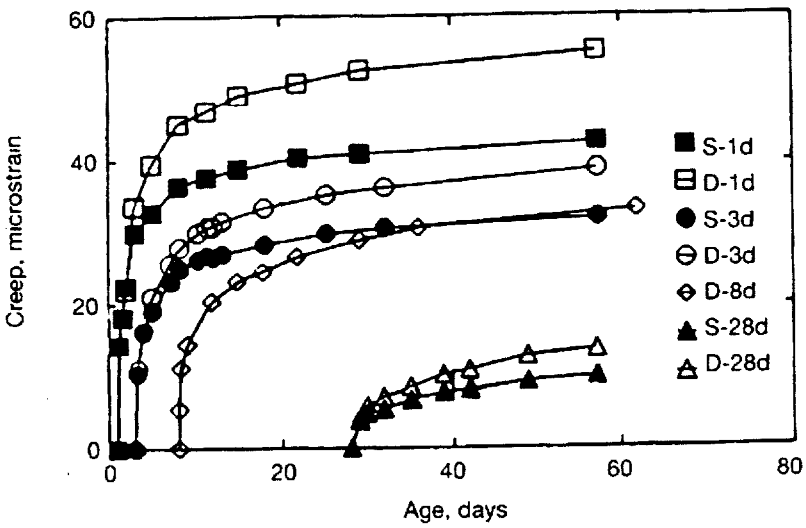


Figure 2.2: Creep of 100 MPa mix loaded at different ages under sealed (S) and unsealed (D) conditions [27]

by extending the duration of unloaded cure that the concrete undergoes.

Shrinkage

Shrinkage in concrete consists of three different concepts.

1. Drying shrinkage consists of the evaporation of excess water from the hardened concrete.

2. Autogeneous shrinkage consists of the shrinkage associated with the consumption of water by the cement paste during hydration and as such happens mostly in the first few days of cure.

3. Carbonation shrinkage consists of the reaction between carbon dioxide in the atmosphere and the hardened cement paste products.

Generally shrinkage, if not managed properly, can cause cracking of the concrete, and is an accepted aspect of design. However the cracking can be significant enough to affect the durability and aesthetics of the concrete. Shrinkage can also affect the deflections of flexural members.

In terms of differentiating the type of shrinkage, normal strength concretes undergo drying shrinkage most significantly, due to the higher water content of the concrete. High strength concretes undergo autogeneous shrinkage of the same order as drying shrinkage. This has considerable implications in terms of cracking when one considers the low tensile strength development of the concrete at this stage. All concretes suffer from carbonation shrinkage over time that may eventually exceed the drying shrinkage of the concrete [12].

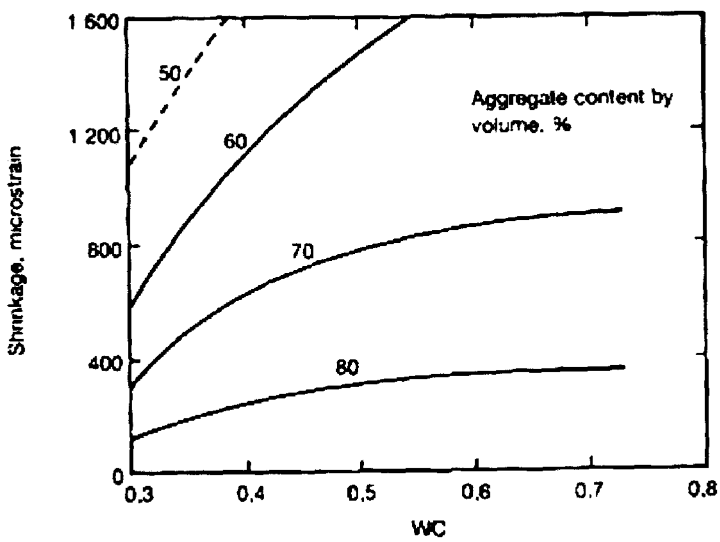


Figure 2.3: Influence of w:c ratio and aggregate content on shrinkage [28]

Due to the multitude of factors affecting the shrinkage of concrete, it becomes difficult to define commonly accepted shrinkage values. Figure 2.3 adequately suggests some of the relationships that can be expected, namely that reduced water content and increased aggregate content decreases the shrinkage of the concrete [28].

Durability

Durability of a concrete is concerned with designing or managing the concrete system to be resilient to the given exposure environment in terms of chemical and physical attack. The concept of durability is related to the transport, mechanical and chemical properties of the concrete. An excellent summary of the different aspects affecting durability is given in Figure 2.4 [12].

Broadly speaking, the transport properties are related to permeation, absorption and diffusion of deleterious chemicals. The transport properties do not themselves damage the concrete, but allow the transport of deleterious chemicals into the concrete that can cause damage to either the concrete or steel reinforcement. Examples of these include acid attack, soft water attack and sulphate attack. The ability for transport to occur in a concrete is fundamentally related to the interfacial transition zone (ITZ), with higher interconnectedness of the ITZ facilitating more transport through concrete, as shown in Figure 2.5 [30].

Two factors that require special mention are carbonation and chloride diffusion of concrete, as both will likely be highly prevalent for the concrete under consideration. Both of these cause corrosion of the steel reinforcement once they have transported through concrete to the reinforcement. This corrosion of

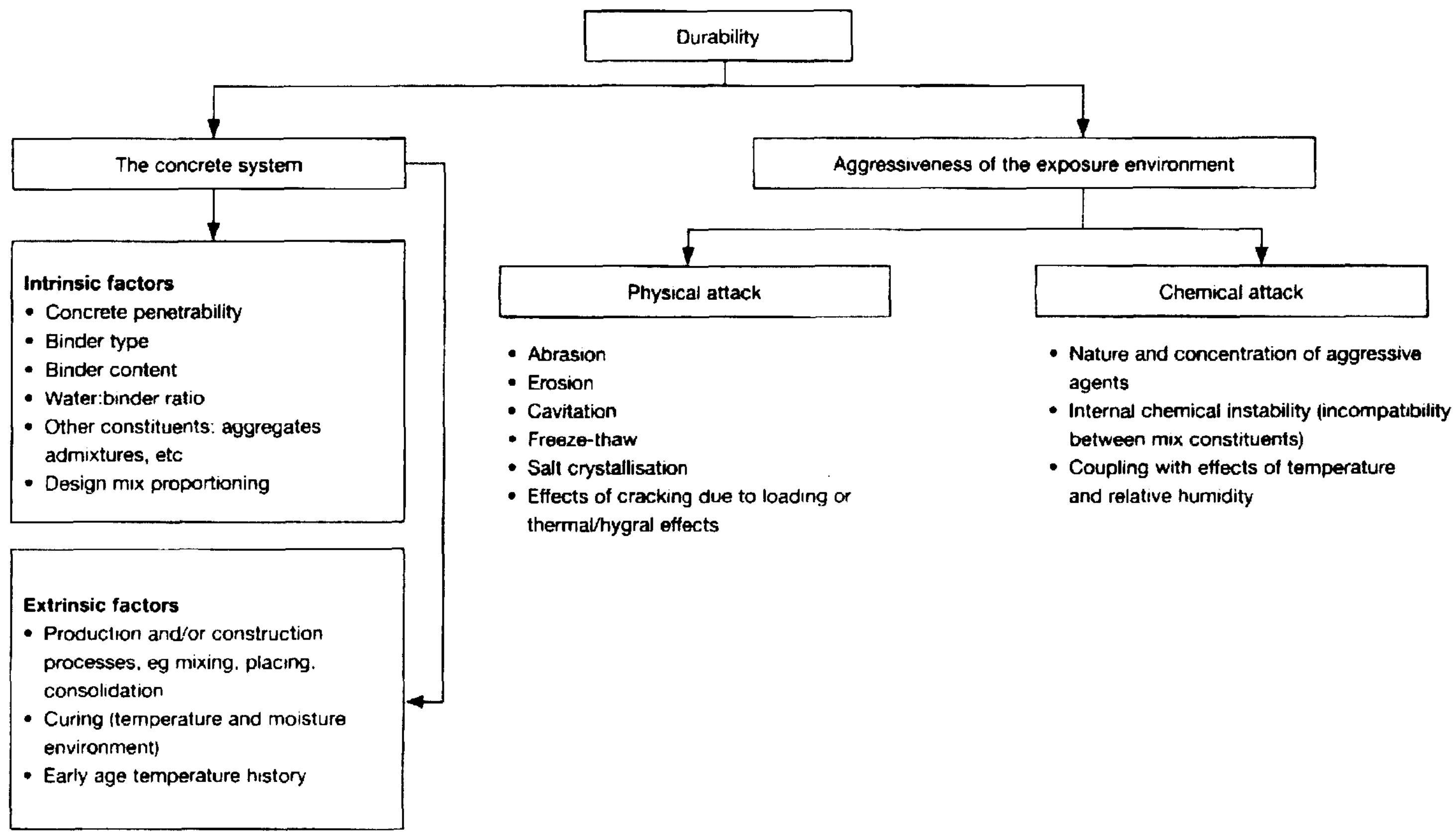


Figure 2.4: Concrete and environment: factors influencing the durability of concrete [12]

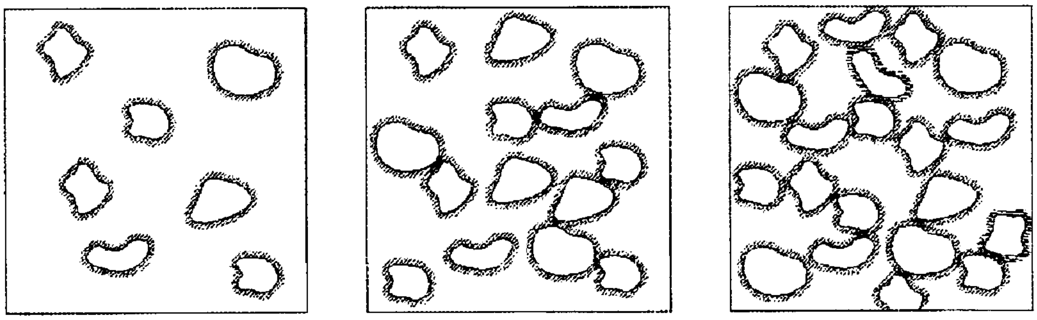


Figure 2.5: Schematic of penetrability and percolation related to ITZ [30]

reinforcement leads to cracking and spalling of concrete due to the expansion of the corrosion products, facilitating further, accelerated corrosion.

Another aspect worth special mention is the attack of concrete by sulphates. This is generally a reaction between calcium hydroxide and the sulphate ion forming gypsum, which is accompanied by a small increase in volume. The products of the first reaction then undergo a second reaction to form ettringite, with a large increase in volume, causing cracking.

Much work has been done on understanding the mechanisms of concrete deterioration and developing approaches to managing the durability of a structure. One of the primary developments in this field is the South African Durability Index [29], which serves to enable the design of a concrete according to service lifetime criteria. This index is supported by three tests:

- Oxygen permeability
- Water sorptivity
- Chloride ion diffusion

These tests enable prediction of the various aspects of concrete durability and the application of a statistically determined lifetime. An interesting insight provided by these tests and others like them suggests that the use of extenders affords a significantly more durable concrete as shown in Figure 2.6 [31].

One factor that is particularly relevant for for this thesis is the effect of nuclear radiation on the properties of the concrete. The use of concrete for nuclear radiation shielding is extensive, as the material has good properties in this regard. The high energy particles released from nuclear reactors require the concrete to be able to absorb and dissipate a large, penetrating energy flux. This can provide two situations of interest [12]:

- Neutrons are absorbed in the concrete, resulting in the production of heat. This can cause localized hot spots in the concrete.

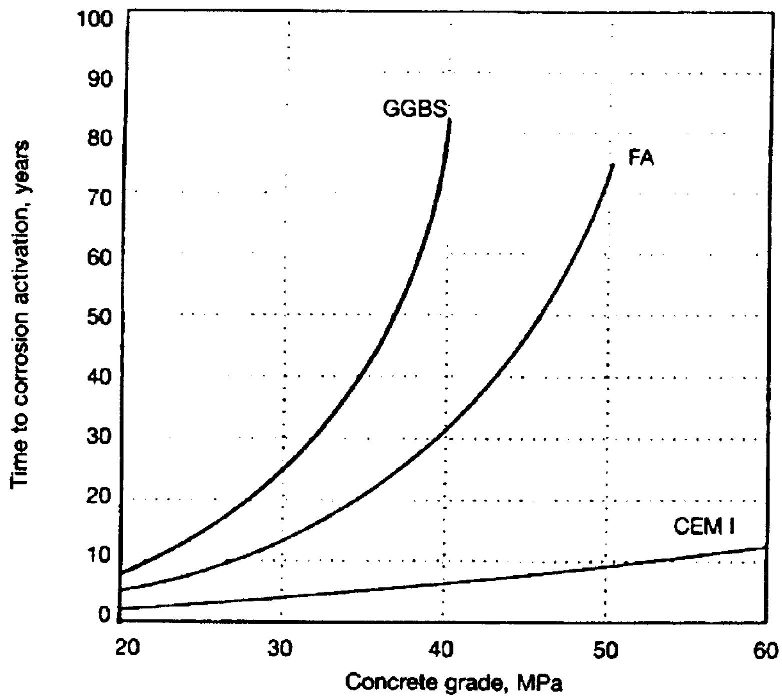


Figure 2.6: Model prediction of the time to corrosion activation for different concrete types [31]

- Radiolysis reactions can cause the vaporization of elements on the surface and in the concrete. This can cause high internal pressures in the concrete, accelerating corrosion and crack development.

The topic of concrete for radiation shielding is an extensive subject and the reader is referred to Kaplan's work in this regard [32].

2.4 Summary of Room Temperature Properties of Concrete

This chapter has provided a brief insight into some of the factors concerning concrete at ambient temperatures. Consideration of the chemical reactions of Portland cement paste and various commonly used extenders has been given. A brief outline of several alternatives for binders has been given, with a general discussion as to their possible merits and demerits, from which it was concluded that this project will focus on Portland cement concrete.

Common aggregates are then discussed, with the relationship between thermal properties and silica content being pointed out. This concept is particularly important in the context of this project, as will be discussed in Section 3.2.3.

A discussion of the concrete material and various important factors and properties is given, pointing out some of the key concepts that are relevant for concrete exposed to high temperature, including modulus of elasticity and transport properties. The response of a concrete to high temperatures will now be discussed in Chapter 3.

Chapter 3

The Effect of Temperature on Structural Concrete

This Chapter considers the effect that high temperature exposure has on concrete. The American Concrete Institute has set the limits for concrete exposure to temperature, in nuclear reactors, of approximately 65°C for operating temperatures and 176°C for accident temperatures in ACI 349 [3]. These limits place a significant constraint on the design of concrete nuclear structures, requiring extensive use of insulation materials to ensure compliance [10, 33]. This has stimulated a large amount of research in the field looking to extend the predictability and prove the ability of concrete to withstand higher temperatures. Research can be broadly split into two categories [14]:

- Short term transient temperature situations such as fires and jet engine blasts.
- Long term constant temperature situations such as process and heat energy applications.

Each of these situations has a different effect on the response of concrete to high temperatures. This dissertation is primarily interested with the second category, long term constant temperature applications. Consideration of literature relating to short term transient situations is however valid for two reasons; this body of research is extensive, and it should be possible to isolate specific factors that relate to the long term response of concrete.

Several comprehensive literature studies on the topic of high temperature concrete have been identified, with each focusing on slightly different aspects of the problem [6, 7, 33, 34, 35].

It is noteworthy that Bazant et al., in research relating to liquid metal fast breeder reactors [22], have suggested that Portland cement is suitable as a binder for operating temperatures of exposure between 300°C and 400°C and short term accident scenarios of up to 600°C.

3.1 The Different Environments of Heat Exposure for Concrete

Determining the response of concrete to high temperatures requires careful and considered analysis and testing. Pihlajavaara [36] has discussed this topic by describing eighteen factors that define the response of concrete to high temperatures, and providing criticism of research that does not sufficiently consider these factors. It is suggested that unless complete consideration of these factors is taken, testing should be avoided, as these results tend to be inconsistent and sometimes contradictory.

An illustrative example of the difference between transient and operational scenarios was given by Naus [14]. Fire situations are fundamentally transient in nature, with high thermal gradients and possibly high temperatures. It is reasonable to assume that the high rate of heating and thermal gradients produce significant thermal stresses in the material. Operational situations as may be found in power stations, chemical or process industries, are quasi-static in nature with stable thermal gradients and controlled temperature exposures on the concrete. These environments tend towards the steady state response of the material, with a greater effect on the chemical structure of the concrete.

The complexities around defining the mechanical response of a concrete to high temperatures were effectively discussed by Naus using the work of Schneider [14, 37, 38]. There are three main test parameters that can be used to generate data: heating, application of load, and control of strain [37]. These parameters can be divided into six testing regimes [37, 38]:

1. Stress-strain relationships (stress-rate controlled): tests can be used to establish stress-strain relationships, compressive and tensile strength, modulus of elasticity, and ultimate strain at collapse.

2. Stress-strain relationships (strain-rate controlled): tests can be used to establish properties stated above and mechanical dissipation energy.

3. Creep: Constant stress creep tests providing relationships between loading at specified different temperatures and strain.

4. Relaxation: Constant strain creep test providing relationships between load and constant strain at specified different temperatures.

5. Time dependent total deformation: provides failure temperatures and transient creep values for different stress levels at specified different temperatures.

6. Time dependent total forces: provides a relationship between restraint forces and temperature as a consequence of heating.

Naus goes on to state some of the reasons why it is difficult to interpret quantitatively available data on this topic:

- Samples were tested at temperature or after cooling.
- Moisture migration was either free or restricted.
- Samples were loaded or unloaded at temperature.
- Varying mix constituents and quantities.
- Different sample sizes and shapes.
- Samples were tested after various durations and environments of curing.
- Time at temperature varied.

These issues surrounding the interpretation of available literature support the need for a set of guidelines with which to assess a heating environment and concrete response.

3.1.1 A Set of Parameters to Assess the Environment of Heat Exposure

Two guidelines have been identified for analyzing concretes exposed to high temperatures, one by Pihlajavaara [36] and one by Lankard et al. [39].

In Table 3.1 [36], Pihlajavaara identified eighteen factors that influence the response of concrete to high temperatures. These range from factors that are intrinsic to the concrete mix design such as concrete strength class, aggregate selection and concrete composition, to environmental factors such as the level of carbonation of the concrete. Considering intrinsic and environmental factors together makes this set of parameters cumbersome to use.

Lankard et al. suggested a similar method to analyze a concrete exposed to temperatures, where a useful distinction was made between the environment of exposure and the effects this exposure has on concrete. Lankard et al. discussed six effects of temperature exposure [39]:

1. Alterations to the composition of the mineral species.
2. Alterations to the relative amounts of the mineral species.
3. Changes to the thermal properties of each of the mineral species.
4. Chemical reactions involving the mineral species with each other or with ambient media (gases, steel, water).
5. Volume changes caused by chemical changes.
6. Physical volume changes due to thermal expansion of the mineral species, including differential volume changes due to temperature differences in the concrete.

Table 3.1: Parameters for high temperature assessment suggested by Pihlajavaara [36]

1	Strength class of concrete
2	Thermal compatibility of cement and aggregate
3	Composition of cement and concrete
4	Temperature level
5	Temperature gradients and heating/cooling rates
6	Size of specimen or structure tested
7	Loading during temperature
8	Moisture content and its alterations
9	Moisture gradients and transfer rates
10	Duration at temperature
11	Degree of hydration and its alterations
12	Effect of carbonation
13	Temperature activated transformations
14	Previous history of concrete
15	Aging after temperature exposure
16	Condition of specimen on testing - hot or cold
17	Testing procedure
18	Reference strength - saturated, moist or dry

These events can all be affected, either directly or indirectly, by the factors that are suggested in Table 3.2 [39]. The parameters presented in Table 3.2 are effective at defining the heating environment that a concrete will be exposed to.

Table 3.2: Parameters for assessment of high temperature environments suggested by Lankard et al. [39]

1	Composition and relative proportions of concrete
2	Heating rate and final temperature
3	Heating conditions (temperature uniformity)
4	External stress conditions
5	The nature of the surrounding media (ability for moisture to escape)
6	Changes in the surrounding media
7	The duration of heating

There are however some omissions from the set of parameters, largely relating to intrinsic factors and environmental influences on the concrete, such as the concrete age at testing, level of carbonation etc., refer to Table 3.1 for more [36]. As such, in testing the effect of temperature exposure on concrete there are three considerations to be made:

1. The effect that temperature exposure has on the concrete, as outlined

by Lankard et al. in points 1 to 6 previously [39].

2. The environment of exposure for the concrete, as outlined in Table 3.2 [39].

3. The condition of the concrete being tested, as can be effectively determined using Table 3.1 [36].

Consideration of the condition of the concrete tested in this project is covered in Chapter 4 of this dissertation.

Some minor adjustments were made to the parameters as outlined below, with a discussion of each factor:

1. Concrete constituents and their quantities – Careful selection of binder and aggregate phases and their mix proportions has significant implications with the response of concrete to high temperatures.

2. Heating environment

    (a) Heating rate – A high heating rate can generate significant thermal gradients and pore pressures in concrete which can cause significant thermal stresses in the concrete.

    (b) Final temperature – The final (or target) temperature determines the impact of thermal expansion of the binder phase and the aggregate, as well as any chemical changes such as dehydration and chemical evolution of the constituents.

    (c) Thermal cycling – Repeated thermal cycling between room temperature and a target temperature can have a significant effect on final properties.

3. Duration of heating – The duration of heating determines whether the environment is transient or steady state. This has implications on the causes of property change.

4. Thermal differences – Thermal differences in the structure and concrete can lead to significant stresses in the material.

5. Stress conditions – The stress conditions of concrete (through pre- or post- stressing) carry significant implications in terms of all properties.

6. The nature of the surrounding media – This fundamentally determines the moisture state of the concrete and subsequently the primary effects at temperature on all properties. This factor also considers the effect of bond strength between the concrete and steel reinforcement.

7. Changes in the surrounding media – This factor considers the evolution of the surrounding media (such as moisture state and bond strength) during exposure to heat.

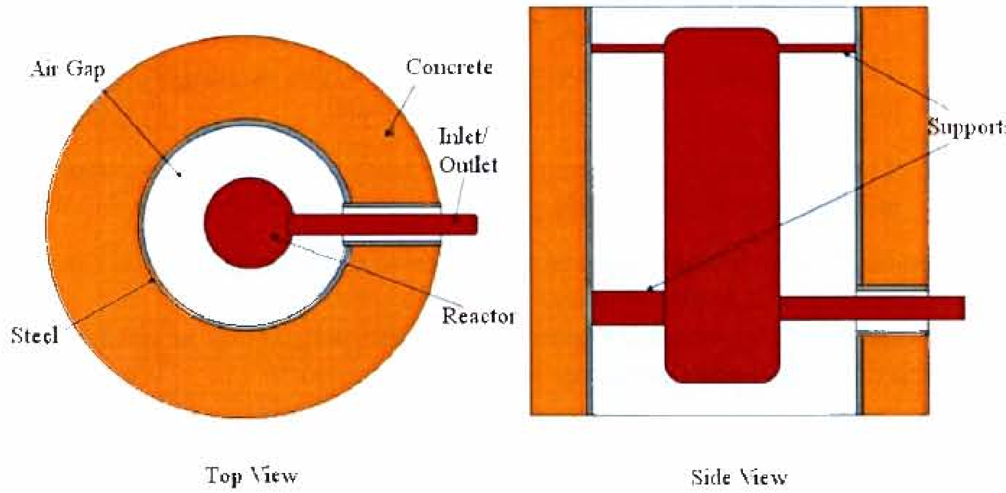


Figure 3.1: Schematic of PBMR housing, top and side views

This method is now used to assess the PBMR heating environment, to focus on the relevant areas of literature.

3.1.2 The Environment of Heat Exposure for the Pebble Bed Modular Reactor

Considering that there is more than half a century of extensive literature relating to concrete exposed to high temperatures, it became necessary to identify the areas of literature that are of particular relevance to this project. This was done by assessing the environment the PBMR would place on concrete according to the parameters discussed in Section 3.1.1. Strictly speaking this relates to the experimental Section of the project (Chapter 4), but is necessary to identify the subset of literature discussed in Section 3.2.

The first step in defining the environment of heat exposure is to consider where the concrete itself fits into the PBMR system. This is shown schematically in Figure 3.1. The reactor is at the centre of the housing, with an air gap, a steel liner and then the concrete under consideration.

Conventional methods of keeping concrete within the temperature limits imposed by the relevant codes for nuclear reactors include: active cooling systems between the steel liner and concrete, placement of foil reflectors and/or the use of insulating foam [9, 33]. A qualitative comparison of the heat distribution in the structure, in operating conditions with and without insulating systems, is given in Figure 3.2 suggesting the higher temperatures uninsulated concrete may experience.

With this identification of where the concrete is to be applied, an assessment according to the parameters identified in Section 3.1.1 is given below.

1. Concrete constituents and their quantities These are to be determined

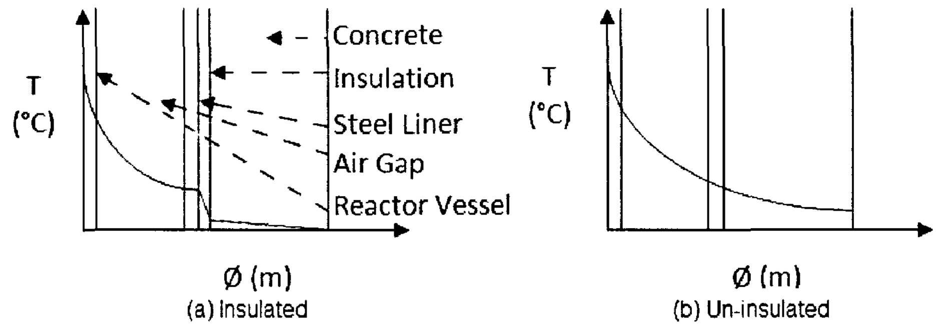


Figure 3.2: Qualitative comparison of temperature exposure of a) insulated and b) uninsulated concrete

for the reactor cavity structure as shown in Figure 3.1.

2. Heating environment

   (a) Heating rate – Due to the nature of the reactor design of pebble bed reactors, the maximum heating rate expected for the concrete is in the region of 7°C per hour [33]. This would be in the case of a Loss of Coolant Accident (LOCA), when the reactor is in operation.

   (b) Final temperature – Two final temperatures have been defined, 225°C for operating temperatures and 450°C in the event of a LOCA, as outlined in the project scope of research work [10].

   (c) Thermal cycling – The PBMR will undergo a series of maintenance shutdowns during its lifetime, indicating several thermal cycles for the concrete. An estimate of 8 thermal cycles, a shut down every 5 years for 40 operational years, would be reasonable.

3. Duration of heating – There are three scenarios relating to the duration of heating, with options (b) and (c) enveloping all LOCA scenarios:

   (a) Plant operates for its lifetime (40 years) at 225°C and is then decommissioned.

   (b) Plant experiences an excursion/LOCA on first heating. The LOCA takes the concrete to 450°C for approximately 30 days, with a gradual reduction of temperature from 450°C.

   (c) Plant operates for its lifetime and experiences an excursion/LOCA at 40 years.

4. Thermal differences – There will be significant thermal differences in the structure of the reactor cavity, both through the thickness of the concrete and at different heights. This is most effectively dealt with at the structural design level.

5. Stress conditions – The reactor cavity structure will likely be pre- or post-tensioned to between 10% and 30% of the compressive strength of the concrete.

6. The nature of the surrounding media – The steel liner on the inside of the reactor cavity prevents moisture from escaping on the hot face of the concrete, creating a 'sealed' environment as will be discussed in Section 3.2.1.3. The surrounding concrete only allows this moisture to migrate away from the hot face through the concrete. Consideration of the impact of steel reinforcement was also necessary.

7. Changes in the surrounding media – This is directly related to the long term service of the structure and required in depth assessment, especially in the context of moisture.

This set of environmental parameters allows the consideration of a smaller but more relevant area of literature. The mechanical, transport and thermal properties that were of interest to the project are now outlined.

3.1.3 The Properties of Interest

The design of any concrete structure generally requires assessment of several properties that fall into three broad categories, namely mechanical, transport and thermal. Those that are of primary interest to the structural engineer concerned with designing the reactor cavity structure include [33]:

- Mechanical properties
  - Compressive strength
  - Tensile strength
  - Modulus of elasticity
  - Poisson's ratio
- Transport properties
  - Moisture migration
  - Chloride transport
  - Air permeability
- Thermal properties
  - Coefficient of thermal expansion
  - Thermal conductivity
  - Specific heat capacity

- Thermal diffusivity

This is a comprehensive list of the properties that are relevant to the design of the reactor cavity structure.

One property not mentioned is the effect of creep at temperature. This property, although of interest, fell outside of the project criteria and was not considered in depth. For further reading on this subject the reader is recommended to consult the works of Bazant and Kaplan [7] and Kassir et al. [35]. The works of Khoury [34], Marzouk [40] and Lohtia [41] are also useful in this regard. Khoury has suggested that temperature has a linear influence on the creep of concrete with the stress conditions (10% to 30% compressive strength) expected for the PBMR [34].

Section 3.1 has appropriately prepared the reader for the in depth review of literature presented in Section 3.2.

3.2 The Effect of Temperature on the Properties of Concrete

To give an overview to start Khoury presented useful research shown in Table 3.3 [34]. Rather than being a comprehensive summary, this Table gives insight into some of the key aspects of temperature exposure:

1. The heating rate of the PBMR environment is well within the moderate influence level suggested by Khoury.

2. The temperature level has a significant influence on the properties of concrete.

3. Thermal cycling has a moderate influence on the properties of concrete.

4. The duration at temperature has a significant influence on property development.

5. Load levels below 30% of the cold strength, as will be expected with the tensioning of the structure, have a linear influence on the transient creep of a structure.

Further support of some of these conclusions will be presented in subsequent Sections. It should be apparent that there are several aspects that need consideration with the high temperature response of concrete.

Considering the amount of literature available, particularly relating to mechanical properties where no consistent set of models or functions have been developed, the set of parameters discussed in Section 3.1.1 will be used to present literature in Section 3.2.2. Properties with well developed models (such as thermal) will be considered in a more general context, presenting the effect of temperature on the property.

Table 3.3: Influence of Environmental Factors on Heated Concrete [34]

Factor	**Influence**	**Comment**
Temperature Level	*** **	Chemical-physical structure and most properties The properties of some concrete (e.g. compressive strength and modulus of elasticity) when heated under 20% - 30% load can vary less with temperature - up to about 500°C - than if heated without load
Heating Rate	** ***	<2°C/min: Moderate influence >about 5°C/min: Becomes significant, possibility of explosive spalling
Cooling Rate	* ** ***	<2°C/min: Negligible influence >2°C/min: Cracking could occur Quenching: Very significant influence
Thermal Cycling	** **	Unsealed Concrete: Significant influence mainly during first cycle to given temperature Sealed Concrete: Influence in so far as it allows longer duration at temperature for hydrothermal transformations to develop
Duration at Temperature	** ***	Unsealed concrete: Only significant at early stages while transformations decay Sealed concrete: Duration at temperature above 100°C leads to continuing hydrothermal reactions
Load-Temp. Sequence	***	very important - not usually appreciated
Load Level	*** ***	<30%: Linear influence on transient creep at least in range up to 30% cold strength >50%: Failure could occur during heating at high load levels
Moisture Level	** ***	Unsealed: Small influence on thermal strain and transient creep particularly above 100°C Sealed: Very significant influence on the structure of cement paste and properties of concrete above 100°C

***Large influence; ** Moderate influence; * Negligible influence

3.2.1 Chemical Composition and Physical Structure Changes with Temperature

One of the most important distinctions to make considering cement paste or concrete exposed to temperature are the different moisture states it may be in. There are fundamentally two states that a concrete can be heated under, unsealed and sealed as illustrated in Figure 3.3. An unsealed state is concrete from which moisture is allowed to freely escape, such as the surface of a massive concrete element. A sealed state is where moisture is effectively locked in the pores of the concrete either by the surrounding concrete, or, in the case of the PBMR, a steel liner on the hot face of the structure. There are a range of states between sealed and unsealed concrete, with the two states (sealed and unsealed) enveloping these.

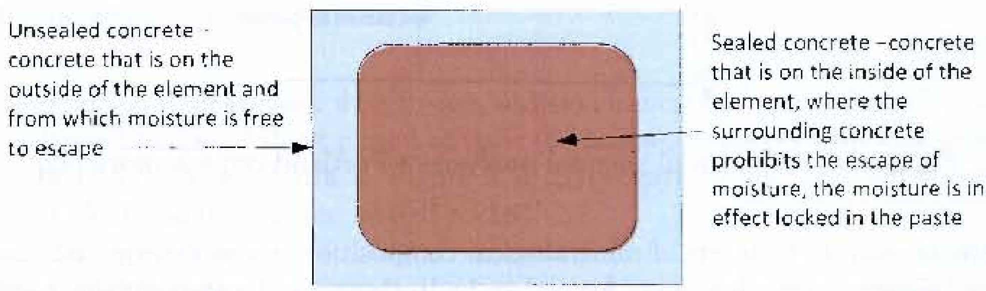


Figure 3.3: Sealed versus unsealed states

The response of a binder or concrete to these moisture states is significantly different, with the unsealed state response dependent on dehydration of the paste and/or paste aggregate interaction. The sealed state response is highly dependent on hydrothermal reactions.

Binder

Figure 3.4, by Lankard [42], is a representation of a differential thermal analysis of hardened cement paste for an unsealed state. This suggests the temperatures that the cement paste undergoes significant changes. The endotherm around 100°C is characterized by the loss of physically and chemically bound water from the cement paste. This dehydration is approximately 70% complete at 500°C, and dehydration is effectively complete around 850°C [43]. The products of the dehydration of CSH are mainly β-dicalcium silicate ($\beta - C_2S$), β-wollastonite ($\beta - CS$) and water. The endotherm around 500°C is caused by the decomposition of calcium hydroxide, forming products of calcium oxide (CaO) and water.

Considering the sealed response of a binder, Kropp et al. [44] have investigated the response of normal Portland cement paste, blast furnace slag cement paste and Portland or blast furnace slag cement paste modified with fly ash or

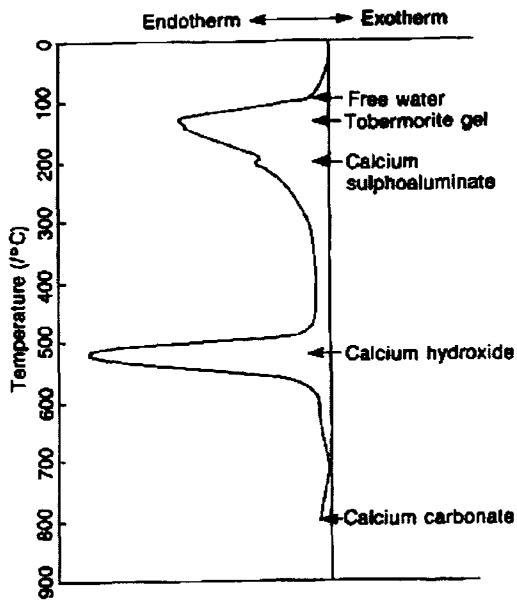


Figure 3.4: Differential thermal analysis of Portland cement paste [42]

ground quartz. In terms of mineralogical composition it was determined that the following new phases are formed in hydrothermally treated cement paste [44]:

1. Hydrogarnets (HG) - $C_3(A,F)SH_4$
2. Hydroxylellestadite (E) - $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$
3. αdicalcium silicate hydrate ($\alpha - C_2SH$) - $C_2SH_{0.3-0.1}$

Neat cement paste made with blast furnace slag cement (slag content 75%, W:C - 0.4) showed no phase changes up to 105°C, on exposure for up to 90 days. After 7 days of exposure to 180°C all three new phases were apparent, with all $Ca(OH)_2$ that was apparent in the unheated paste having disappeared. On exposure to 250°C there was an increased formation of the new phases, mainly $\alpha - C_2SH$.

Tests on neat cement paste made with Portland cement paste showed no change in mineralogical composition after exposure to 105°C. Exposure to temperatures above 150°C showed formation of hydrogarnets (HG), while exposure to 250°C showed formation of hydroxylellestadite (E) and $\alpha - C_2SH$. The $Ca(OH)_2$ content appeared unaffected by hydrothermal exposure (in contrast to blast furnace slag cement). Identical transformations were observed with concretes that had been pre-dried to a water content of 30% of the as cast water content, indicating that only small amounts of free water are required to support the phase transformations.

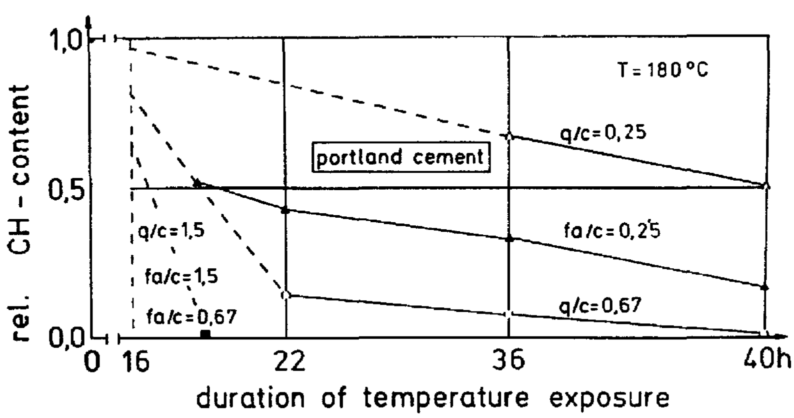


Figure 3.5: Relative CH content of Portland Cement paste with fly ash, after temperature exposure [44]

Tests on cement paste with fly ash addition indicated that all $Ca(OH)_2$ was consumed in a very short period of time (20 hours), in pastes with high quantities of fly ash, as shown in Figure 3.5. Hydrogarnets and 11Å tobermorite were identified in concrete heated to 180°C.

Pore Structure Neat cement paste experiences a significant increase in pore size distribution from 20nm at room temperature to between 100nm and 1000nm after hydrothermal exposure to temperatures in excess of 200°C [44], as shown in Figure 3.6 (a). This suggests high capillary porosity, while nitrogen adsorption tests indicated that the change in structure also happened in the CSH gel. The specific surface area of paste reduces with temperature, being less than 1/10 of its original value after exposure to 180°C due to the formation of crystalline phases.

Cement pastes with large amounts of fly ash demonstrate a retention, or small increase of capillary porosity, dependent on the amount of fly ash replacement as shown in Figure 3.6 (b). This indicates that pozzolanic reactions between free fly ash and CH occur. Kropp et al. [44] have however found that the required amount of fly ash to achieve this is large, as high as 66% of total binder content. The specific surface area of these pastes increases significantly with hydrothermal exposure as well, 75% with ground quartz and 300% with fly ash.

Aggregate

Generally, aggregates are stable up to about 500°C, and non-siliceous aggregates such as limestone are stable up to at least 600°C [7]. This effectively allows most conventional aggregates to be considered for use in this project. The most well known transformation reaction is the conversion of quartz (SiO_2) in siliceous aggregates from α-quartz to β-quartz gradually between 500°C

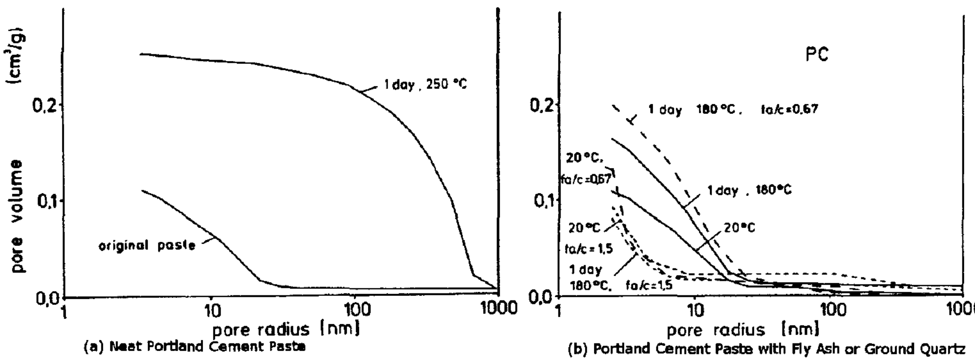


Figure 3.6: Pore Size Distribution of (a) Neat Cement Paste and (b) Neat Cement Paste with Fly ash Replacement [44]

and 650°C. This is accompanied by a total expansion of between 1.0% and 1.4%, with a significant increase in the rate of expansion occurring between 200°C and 300°C. Limestone aggregates also undergo a decarbonation reaction between 600°C and 900°C[50]:

1. $CaCO_3 \rightarrow CO_2 + CaO$

There have been instances of aggregates that are reactive at temperatures significantly lower than these. Carrette et al. [45] carried out long term tests for up to 8 months and temperatures up to 600°C. The specimens for 150°C experienced substantial deterioration after 1 month with cracking and decomposition of the aggregate (dolomite). Subsequent investigation and analysis unveiled an approximate 4% iron sulphide (pyrite) content in the aggregate. This decomposition seems to have been stifled at higher temperatures, but it was not ascertained to what degree this may have affected higher temperature results.

With these results in mind it is important to confirm that an aggregate is nonreactive up to the maximum temperature of 450°C.

Concrete

The different moisture states a concrete may experience with thermal exposure require special consideration as different factors influence the property development of a concrete in each state. In terms of the unsealed state, the following effects are observed:

- Dehydration of the cement paste. Up to 105°C all of the evaporable water in the concrete evaporates. Above this chemically bound water begins to evaporate from the cement paste, causing the paste to shrink [7]. This results in the densification of the solid phases and an increase in the pore size of the paste.

- The aggregate is generally considered as chemically stable at temperature and expands, non-linearly, with temperature [7].

- This combined expansion of the aggregate, dehydration and shrinkage of the cement paste develops micro-cracking in the concrete [39].

This dehydration of the cement paste and microcracking caused by thermal incompatibility of the aggregate and paste has a considerable effect on the properties of a concrete, as will be discussed from Section 3.2.2 onwards.

In terms of the sealed state, the following effects can be observed:

- With the prevention of the escape of moisture from concrete and the heating of concrete above 100°C, a situation of high vapour pressures develop in the concrete pores [7, 46, 47, 48].

- These vapour pressures can cause significant stresses in the pores, within the region of 0.5 to 1 MPa [7]. This could cause the development of micro-cracking in the concrete.

- The presence of high temperatures, calcium hydroxide ($Ca(OH)_2$) and moisture causes a change in the primary strength giving product, calcium silicate hydrate (CSH), of Portland cement [39]. The $Ca(OH)_2$ reacts with the CSH to form several new phases, with the most dominant being dicalcium-silicate-αhydrate that is more crystalline and has poorer mechanical properties [39, 44, 49]. This formation of crystalline phases can be counteracted with high quantities of fly ash replacement [17, 44].

This effect of micro-crack development and evolution of the CSH species has significant consequences in terms of properties of the concrete. Interestingly, Kropp et al. [44] point out that high quantities of fly ash replacement, though beneficial for hydrothermal exposure, lead to excessive shrinkage in an unsealed concrete with a subsequent deleterious effect on mechanical properties. Table 3.4 summarizes some of the chemical processes that can occur in the binder paste and aggregate as suggested by Schneider and Diedrichs [50].

Summary of chemical and physical changes A summary of the chemical and physical changes that are significant at temperatures includes:

- Cement paste dehydrates with temperature exposure, resulting in changes in the chemical constituents of the paste, densification of the solid phases, an increase in porosity and shrinkage of the material.

- Conventional aggregates are generally chemically stable up to the temperatures of interest, and most expand non-linearly with temperature.

- There are two moisture states that a concrete can be heated under, sealed and unsealed.
  - Unsealed concretes experience dehydration of the cement paste and expansion of the aggregate, likely causing microcracking that will affect properties.

Table 3.4: Estimated Heats of Transformation and Decomposition for Quartzite and Limestone Concretes Exposed to Elevated Temperatures [50]

Temperature (ºC)	Transformation or Decomposition Reaction	Heat of Transformation Reaction per Unit Mass ($KJ\,kg^{-1}$)	Mass of Material Transformed or Decomposed per m³ of Concrete ($kg\,m^{-3}$)	Heat of Transformation or Decomposition per m³ of concrete ($KJ\,m^{-3}$)
30 - 120	Release of evaporable water	Heat of evaporation of water $2238 KJ\,kg^{-1}$ (endothermic reaction)	130 kg of water	290×10^3
30 - 300	dehydration of non-evaporable or chemically bound water in cement gel	Heat of hydration of $\beta - C_2S$ $250 KJ\,kg^{-1}$ (endothermic reaction)	78 kg of hardened cement paste	20×10^3
120 - 600	Release of remainder of evaporable and non evaporable water	Heat of hydration, not less than $2238 KJ\,kg^{-1}$ (endothermic reaction)	About 60 kg of water	135×10^3
450 - 550	Decomposition of $Ca(OH)_2$ to $CaO + H_2O$	Heat of decomposition $1000 KJ\,kg^{-1}$ (endothermic reaction)	not more than 40 kg of $Ca(OH)_2$	40×10^3
570	Transformation from α to β quartz	Heat of transformation of SiO_2 $5.9 KJ\,kg^{-1}$ (endothermic reaction)	1500 kg SiO_2 in quartzite concrete 200 kg SiO_2 in limestone concrete	8.8×10^3 1.2×10^3
600 - 700	Decomposition of CSH and formation of $\beta - C_2S$	Heat of decomposition $500 KJ\,kg^{-1}$ (endothermic reaction)	240 kg C_2S in hardened cement paste	120×10^3
780	Recrystallization of unhydrated cement	Heat of recrystallization $50 KJ\,kg^{-1}$ (exothermic reaction)	100 kg unhydrated blast furnace slag cement	5×10^3
1100 - 1200	Melting of concrete	Heat of melting $750 KJ\,kg^{-1}$ (endothermic reaction)	2100 kg quartzite concrete 1500 kg limestone concrete	1575×10^3 1125×10^3

  - Sealed concretes experience the same effects as unsealed concretes (including dehydration of the cement paste) as well as the development of high pore pressures and a change in the chemical structure of the main strength giving product of cement.

- The use of high quantities of fly ash or ground quartz has been shown to reduce the impact of hydrothermal exposure on the chemical and physical structure of cement paste [44]. Such high quantities of fly ash replacement do however lead to excessive shrinkage in unsealed concretes exposed to high temperatures.

With this discussion on the chemical and physical aspects relating to temperature exposure carried out, it is now appropriate to discuss the properties of interest.

3.2.2 Mechanical Properties

The primary mechanical properties of interest are strength, modulus of elasticity and Poisson's ratio of concrete. Results from literature appear varied and sometimes contradictory, dependent on variations in the set of parameters presented in Section 3.1.1.

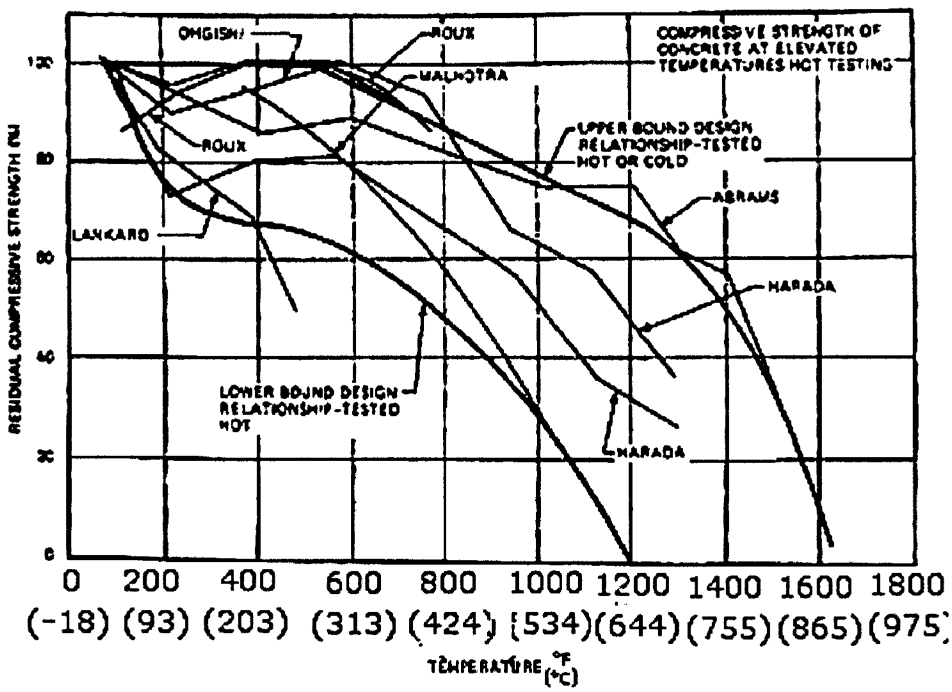
Several authors have suggested the use of a statistical approach to modeling the mechanical properties of concrete at high temperatures [35, 51]. These models definitely have use in the context of well defined concrete mix designs and heating conditions, however, there is limited broader applicability to concrete structures exposed to temperatures. As such a more qualitative approach to determining properties is required.

Compressive Strength

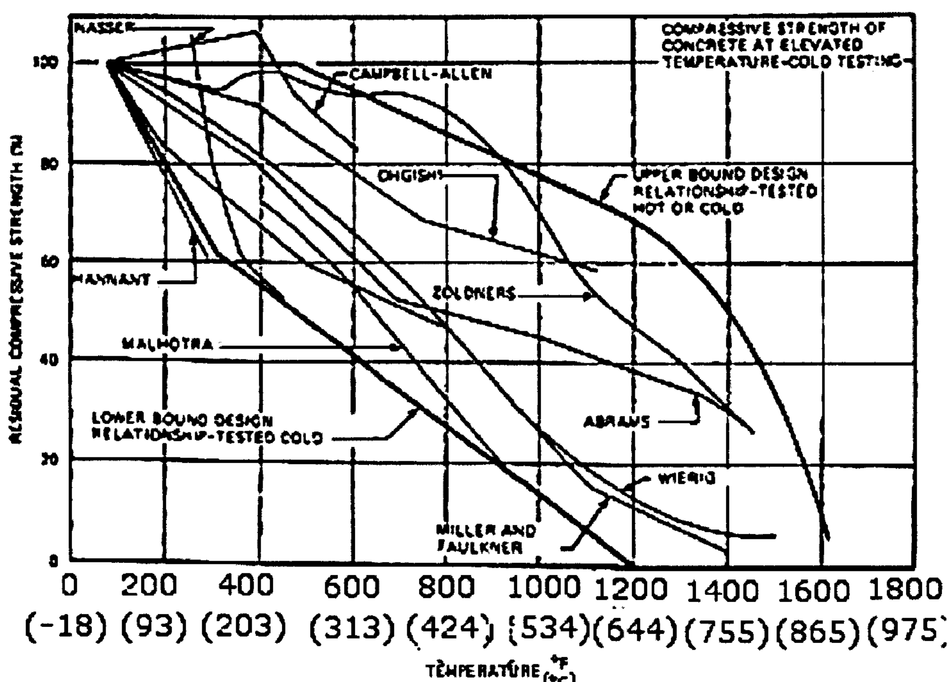
An excellent summary of some of the broad range of data available in terms of strength is given by Freskakis [52] in Figure 3.7. This is presented for both the hot and cold compressive strengths, for a range of sealed and unsealed data.

This Figure demonstrates the broad range of strength response of concrete to high temperatures, dependent on changes to the set of parameters outlined in Section 3.1.1. An interesting point made by Kropp et al. [44] is that strength loss after exposure to elevated temperatures only becomes apparent if 'sufficiently slender' specimens are used. This is particularly important in unsealed conditions, supported by the data shown in Figure 3.8 [44] for concretes heated for 7 days at 250°C in an unsealed state. This furthermore supports the point made by Pihlajavaara [36] of the need for consistency across tests.

Concrete Constituents The strength properties of a concrete at high temperatures are highly dependent on the concrete constituents and their relative quantities. In the context of concrete design for high temperatures there are several parameters that are desirable:



a) Hot compressive strengths



b) Cold compressive strengths

Figure 3.7: Effect of temperature exposure on compressive strength of concrete tested: (a) Hot and (b) Cold [52]

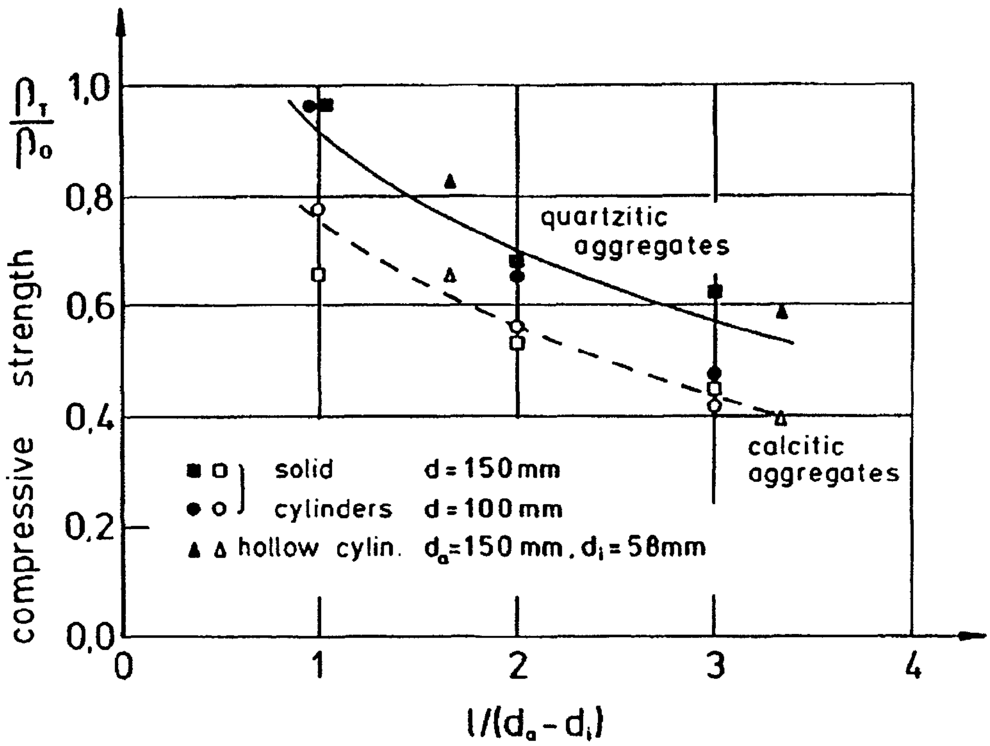


Figure 3.8: Compressive Strength Ratio as a Function of Slenderness [44]

- Stable, positive or limited negative strength development at temperature of the binder phase.
- Selecting an aggregate with a low coefficient of thermal expansion to minimize strength loss due to excessive development of micro-cracking.

Considering the effect of temperature on the binder, and the associated hydrothermal reactions that occur, the most pertinent examples are those of Lankard et al. [39] and Ghosh and Nasser [49].

Lankard et al. [39] found that with specimens subjected to saturated steam pressures (a sealed environment), the primary effect was a change in the mineralogy of the cementitious compound. It was also suggested that the response of the concrete to temperatures was highly dependent on the moisture state of the concrete, and whether the moisture was allowed to freely evaporate. The hydrothermal reactions entail a reaction between calcium hydroxide (CH) with the strength giving calcium silicate hydrate (CSH) to form lime rich highly crystalline CSH. Residual tests by Lankard et al. [39] on concrete with no extenders show a significant reduction when exposed to 232°C, as shown in Figure 3.9. This is in agreement Kropp et al. [44], who explain the phase changes that occur (as discussed in Section 3.2.1.1), and conclude that the increased porosity and misalignment of the newly formed coarse crystalline particles lead to a significant decrease in strength.

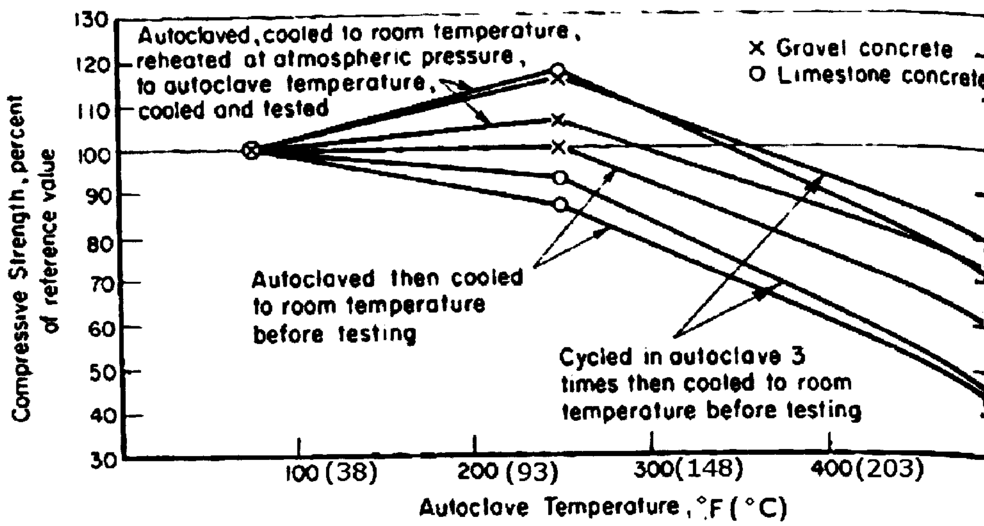
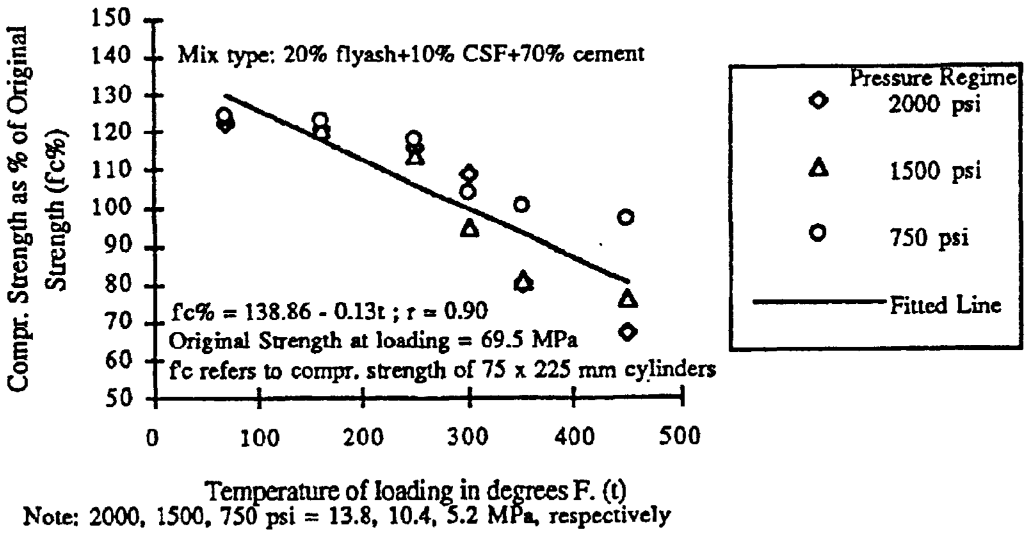


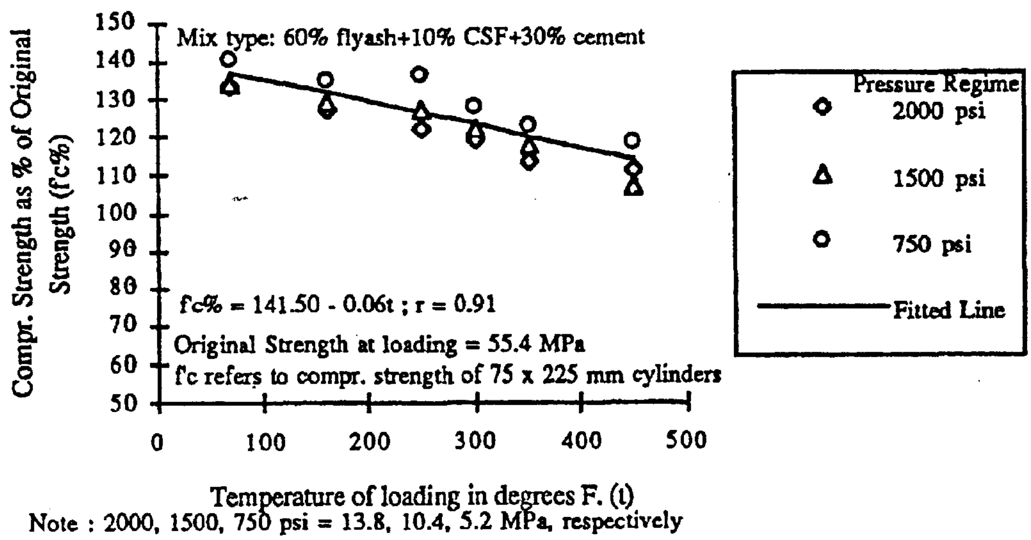
Figure 3.9: Effect of test conditions on the compressive strength of autoclaved gravel and limestone concrete [39]

Two papers that also illustrate the deleterious effect temperatures have on sealed concrete with low fly ash contents are those of Nasser and Lothia, and Nasser and Marzouk [53, 54]. Although these concretes were tested at very early stages in their curing cycle (28 days and 1 or 14 days respectively), there is a clear indication of loss of strength above temperatures of 150 °C. These findings were strongly supported by Ghosh and Nasser [49], who demonstrated with scanning electron microscope photographs and energy dispersion spectra that there was a significant chemical change in a concrete heated to 232 °C with 20% FA and 10% CSF. This concrete demonstrated a significantly reduced residual compressive strength when compared to a similar concrete with 60% FA and 10% CSF, as shown in Figure 3.10 [49]. These tests were under both pressure and temperature loading for 90 days, and are applicable when considering the response to stress conditions as well.

From this, it becomes apparent that the use of high quantities of pozzolans such as FA may be beneficial in sealed concrete. In the context of unsealed concretes, for short periods of heat exposure the use of pozzolans has been supported by the work of Poon et al. [55], who demonstrate a beneficial effect on residual strength when compared to concretes with lower contents of pozzolans. This is presented in Table 3.5, with concretes containing 40% fly ash having higher compressive strengths after 400 °C than at room temperature.



(a) 20% FA, 10% CSF, 70% Portland Cement



(b) 60% FA, 10% CSF, 30% Portland Cement

Figure 3.10: Compressive strengths of concretes with a) 20% fly ash and b) 60% fly ash replacement after temperature and pressure exposure [49]

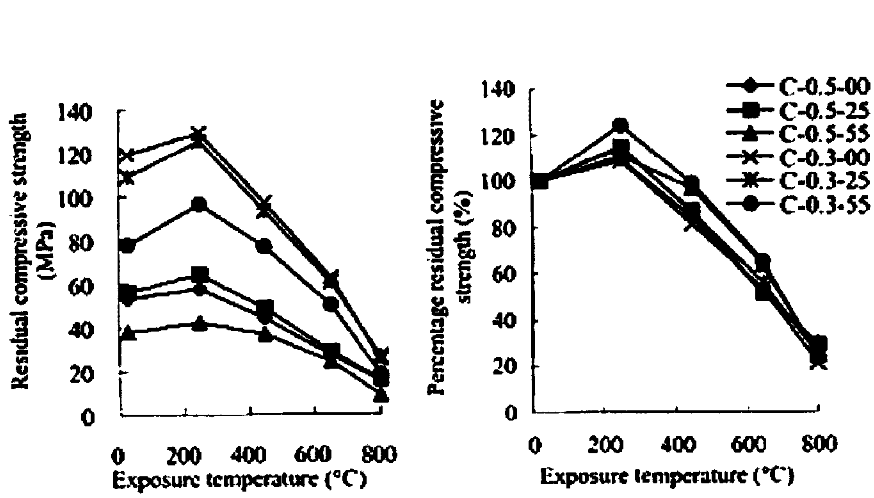


Figure 3.11: Residual Compressive Strengths of PC - FA mixes [16]

Table 3.5: Unstressed Residual Compressive Strengths of High Strength Concretes with Different Extenders [55]

	Compressive Strength - MPa (%)				
Mix	20°C	200°C	400°C	600°C	800°C
Control	91.3 (100)	88.0 (96)	81.5 (89)	53.0 (58)	21.9 (24)
5% Silica Fume	106.1 (100)	105.5 (99)	98.7 (93)	55.2 (52)	22.3 (21)
10% Silica Fume	119.9 (100)	117.7 (98)	104.3 (87)	52.8 (44)	19.2 (16)
20% Fly Ash	96.6 (100)	110.2 (114)	92.9 (96)	59.8 (62)	27.0 (28)
30% Fly Ash	102.8 (100)	124.6 (121)	100.7 (98)	68.9 (67)	32.9 (32)
40% Fly Ash	107.7 (100)	131.5 (122)	112.2 (104)	61.4 (57)	32.3 (30)
10% Silica Fume + 20% Fly Ash	123.9 (100)	135.3 (109)	116.5 (94)	63.2 (51)	23.5 (19)
30% Blast Furnace Slag	111.9 (100)	126.7 (113)	108.5 (97)	59.3 (53)	30.2 (27)
40% Blast Furnace Slag	115.5 (100)	133.3 (115)	114.9 (100)	70.5 (61)	33.6 (29)
Values outside brackets are in MPa, values inside brackets are in %					

This is further supported by Xu et al. [16] who illustrate, as shown in Figure 3.11, that after short term exposure to a temperature of 450°C a FA replacement in an unsealed concrete of 55% can provide 98% of the unheated strength.

The research of Seeberger et al. [17] supports strength improvement for longer periods of exposure. It is demonstrated that, after 28 days of heating, a fly ash:cement (FA:C) ratio of 0.3 provides approximately a 10% improvement of compressive strength when compared to a (FA:C) ratio of 0.12 with a quartzitic unsealed concrete. There does however seem to be an upper limit to the beneficial effect of extenders in unsealed conditions for long periods of heating [44], with the binder experiencing greater shrinkage than one without extenders leading to greater microcracking and strength loss. Sanack et al. [56] have demonstrated that the use of condensed silica fume in concretes exposed to rapid heating lead to a greater loss of properties, likely related to the development of excessive pore pressures through the refinement of the concrete microstructure caused by silica fume.

Moving back to sealed concretes, Seeberger et al. [17] also provide an interesting illustration of the beneficial effect of using high quantities of FA with hydrothermally treated quartzitic concrete. Their findings illustrate an improvement of strength that develops over time, reaching approximately 125% after 28 days at 250°C. This suggests that there is a hydrothermal effect occurring, in that with high temperatures, high moisture content and the presence of unreacted FA, further formation of CSH occurs.

When Seeberger et al. [17] focus on limestone concretes it becomes apparent that these concretes require a significantly greater amount of FA to experience a similar improvement in strength in hydrothermal conditions. Indeed, this paper focuses on attempting to utilize limestone for its good coefficient of thermal expansion properties while minimizing the negative effects of an increased availability of CaO. CaO reacts with CSH to form dicalcium-silicate-αhydrate (that has poor mechanical properties) [39, 49]. It is quite clearly illustrated that the high quantities of FA required to ensure that limestone aggregate does not react with the CSH in sealed conditions, reduces the unsealed residual strength of the concrete.

The comparison between limestone and siliceous aggregate concretes was also considered by Savva et al. [57]. Unsealed tests were carried out on concrete that had various types of fly ash at either 10% or 30% loading that had been allowed to mature for 3 years. Figure 3.12 illustrates the beneficial effects of siliceous aggregates in terms of residual compressive strength up to 450°C. Above this temperature the quartz in the aggregate undergoes transformation from its α to β phase, with a subsequent thermal expansion which damages the concrete.

Interesting data with respect to the choice of aggregate is given by Abrams, shown in Figure 3.13 [58]. This graph shows the unsealed hot strengths of concretes with either expanded shale, calcareous or siliceous aggregates. Within the temperatures considered (up to about 450°C) the choice of aggregate appears to be insignificant, but as the siliceous aggregate approaches the conversion point of α-quartz to β-quartz at 570°C, there is a significant reduction in strength.

Several researchers have considered the effect of adding fibres into a concrete, with two primary fibres of interest, polypropylene and steel [22, 59, 60, 77]. Polypropylene fibres have been considered in the context of creating addi-

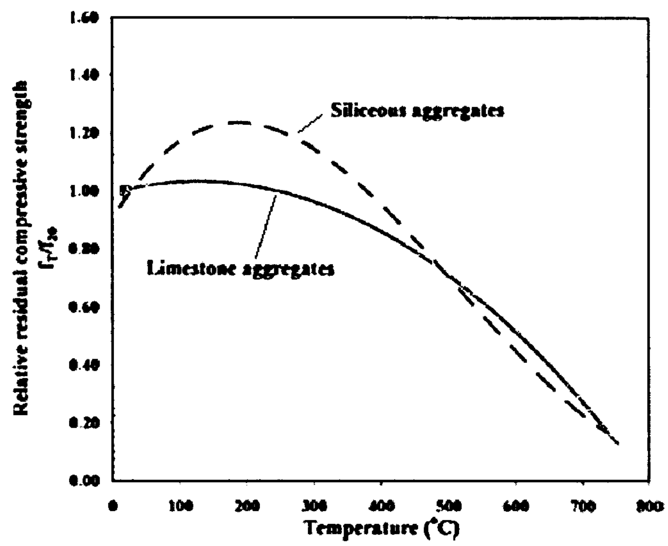


Figure 3.12: Relative Residual Compressive Strengths of Limestone and Siliceous Aggregate Concrete [57]

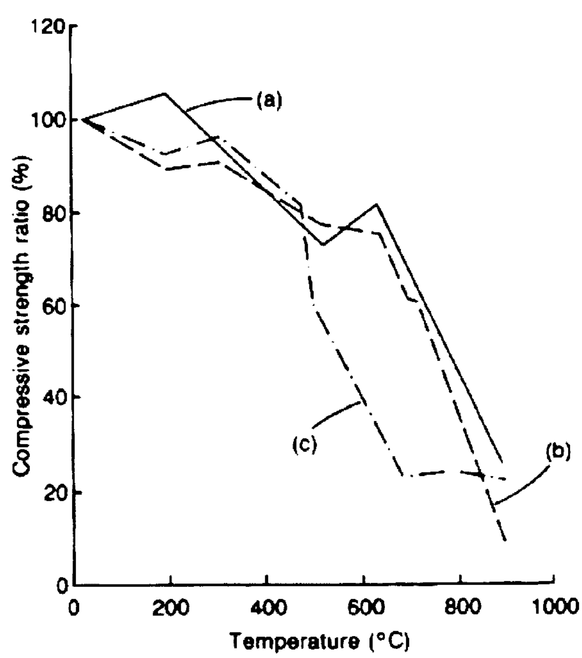


Figure 3.13: Effect of aggregate type on compressive strength during heating as a function of temperature; a) expanded shale light weight concrete; b) calcareous aggregate concrete; c) siliceous aggregate concrete [58]

tional, interconnected porosity in high strength concretes as the fibres melt at 170°C, with a view to managing the development of pore pressures in the concrete at high temperatures [60]. The fibres reduce pore pressures in concrete exposed to high thermal gradients, indicating that they are beneficial for damage limitation in fire situations. This effect has been suggested as suitable for managing sealed environments in operating temperature conditions, with the stress strain characteristics of the concrete above the melting temperature of polypropylene fibres tending towards that of a concrete without polypropylene fibres [60]. Steel fibres have been considered in the context of arresting micro-crack development [59, 77]. This has been supported by compressive strengths that demonstrate a slight improvement in maximum strength when compared to a concrete without fibre addition, at 600°C [59]. More notably these tests demonstrated a marked improvement of sustained stress in high strain, post maximum strength conditions (i.e. the failure region of the stress strain curve) [59].

Surrounding Media and Moisture Conditions As has already been clearly illustrated, the nature of the surrounding media has a direct effect on the moisture state of the concrete and thus a direct effect on the response of a concrete to temperature. In the context of strength, there is a significant difference between the sealed and unsealed characteristics.

It is difficult to draw clearly defined responses of concrete to sealed or unsealed environments, as the response is inherently dependent on the constituents of a concrete. This is appropriately illustrated by Lankard et al. [39] showing a reduction in strength of a sealed concrete compared to an unsealed concrete, due to deleterious hydrothermal reactions, while Seeberger et al. [17] demonstrated improved strengths for sealed concretes over unsealed concretes with the use of FA.

The main trends that can however be drawn for the response of either sealed or unsealed concretes to temperature, are in the difference between hot and cold (residual) testing. An appropriate illustration of this is given by Bazant and Kaplan's [7] interpretation of Lankard et al.'s data [39] in Figure 3.14.

From this diagram it becomes apparent that the trends between hot and cold testing, for sealed and unsealed concretes, are inverted. Considering sealed concrete, it is likely that the hot strength of the concrete will be between 10% and 15% lower than the cold strength of the concrete. This is possibly due to the presence of high vapour pressures in pores and flaws increasing the rate of micro-crack development as the samples are loaded to failure [7].

When one considers the response of unsealed concrete it becomes apparent that the hot strength of the concrete is higher than that of the cold strength. This is most likely due to the differential shrinkage between the dehydrated cement paste and the aggregate on cooling of the concrete [7]. The difference between hot and cold unsealed concrete strengths was also illustrated by Malhotra [61] as shown in Figure 3.15 on page 49.

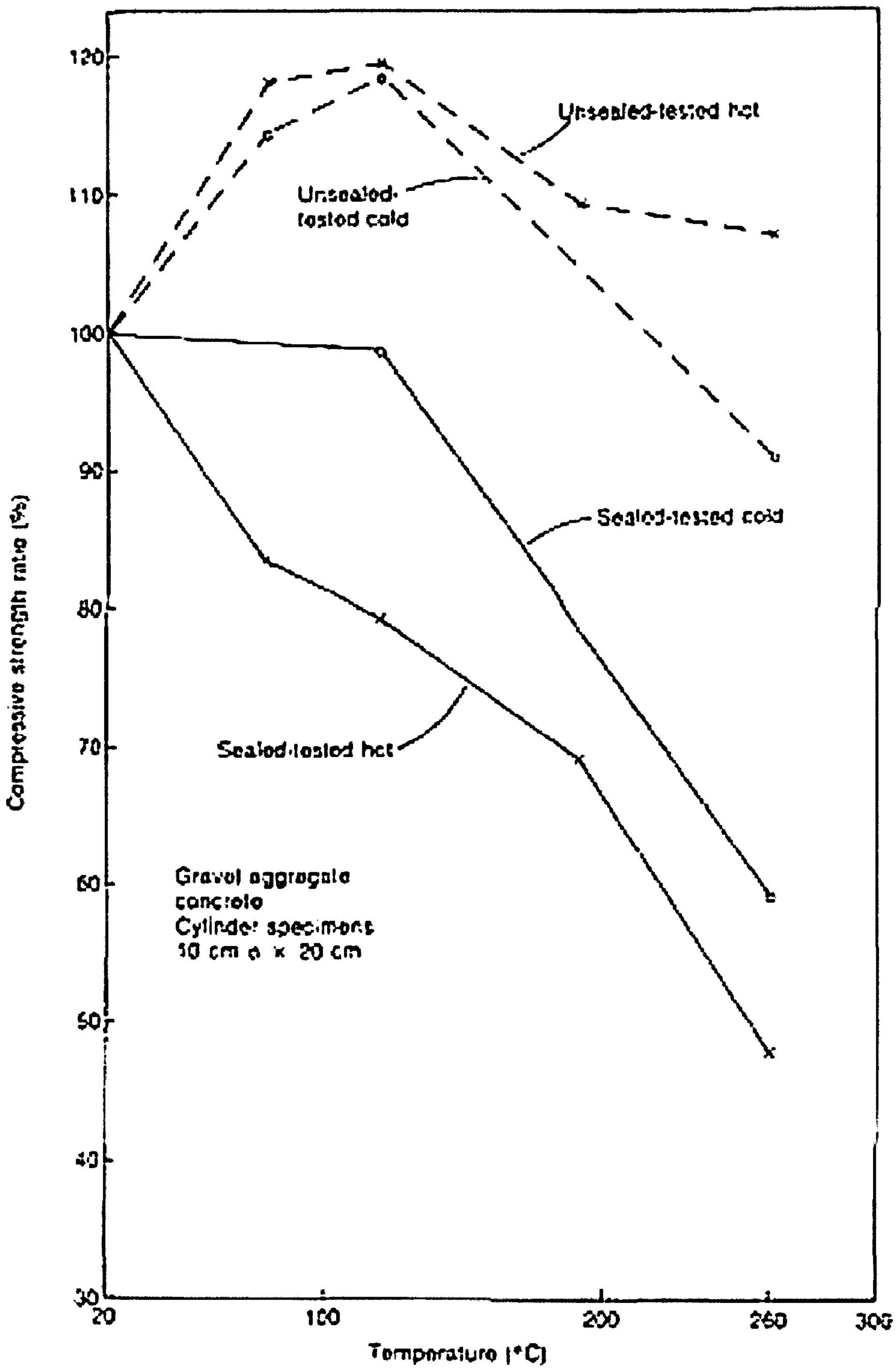


Figure 3.14: Compressive strength as a percentage of initial strength before heating as a function of temperature, for various test conditions [39]

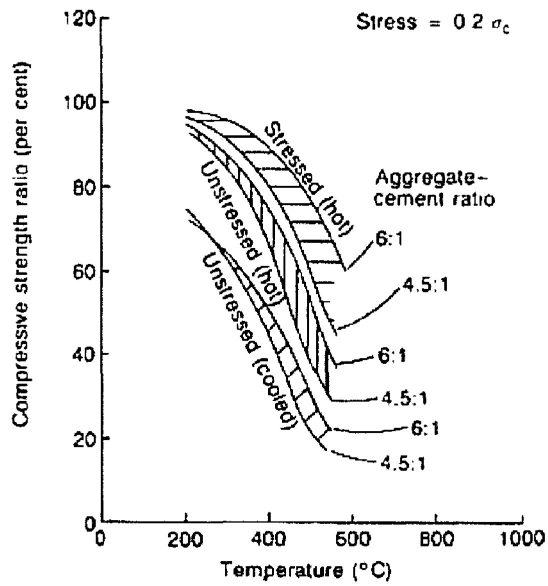


Figure 3.15: Dependence of compressive strength of concrete at temperature

Temperature conditions The immediate thermal factors such as heating rate, final temperature, and thermal cycling, have a significant effect on the strength response of a concrete to temperature.

Rate of heating There are limited data available to quantify the effect of the heating rate on the response of a concrete to high temperatures. It has been suggested that provided the heating rate is not high enough to produce significant thermal gradients in the concrete, it has a secondary effect on the strength of the concrete [39]. Khoury suggests that below a heating rate of 2°C/min this becomes a moderate effect [34]. Naus [14] discussed work by Mohamedbhai [62], who carried out some tests comparing quick and slow heating of basalt concretes, which indicate that there is a significant effect within the temperature range this project is interested. This data proves difficult to understand and draw conclusions from as 'quickly' and 'slowly' heated were not clearly quantified.

It should however be restated that even in an accident scenario that the PBMR is unlikely to experience temperature gradients significantly above 10 °C per hour, which is well below the limits of moderate influence suggested by Khoury [34]. When one considers the work of Xu et al. [16] and Poon et al. [55] with heating rates of 1°C/min and 2.5°C/min, and that these concretes demonstrated improvements in strength up to 450 °C, it is likely that the heating rate has a limited effect on the concrete strength.

Maximum temperature The final temperature that the concrete is exposed to clearly has a significant effect on the compressive strength. Good examples of this in terms of unsealed concretes have already been presented with the work of Xu et al. [16] (refer to Figure 3.11 on page 44) and Poon et al. [55] (refer to Table 3.5 on page 44). Abrams [58] clearly illustrates the effect that final temperatures have on the hot and residual strengths of unstressed concretes made with different aggregates in Figure 3.16.

Abrams work clearly illustrates the quartz transition at 570°C for siliceous concretes, further supported by the significant reduction of strengths found by Xu et al.[16] and Poon et al. [55] between 400°C and 600°C.

There is limited sealed data for temperatures above 250°C. Most of the significant work has been done up to approximately this temperature. Lankard et al. [39] provided data for hot and residual strengths for a gravel concrete in hydrothermally sealed conditions that clearly illustrates a steady reduction of strength up to 232°C.

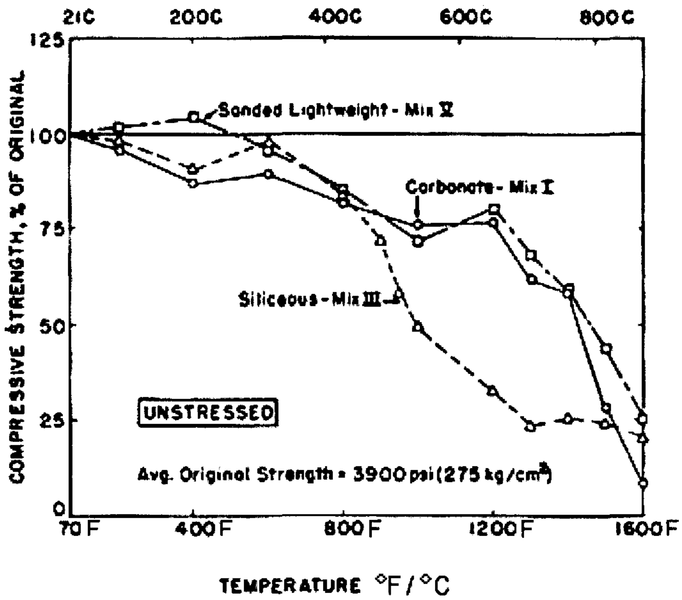
It again becomes necessary to illustrate that the response of the concrete to a specific temperature is highly dependent on the mix design, as supported by Seeberger et al. [17] finding an improvement in the residual strengths of concretes exposed to 250°C with high FA contents.

The influence of thermal cycles The effect of thermal cycling is as varied as any of the other responses. Bazant and Kaplan [7] suggest on assessment of a large group of data from various references, that thermal cycling generally results in a progressive reduction of compressive strength dependent on the number of cycles and final temperature per cycle.

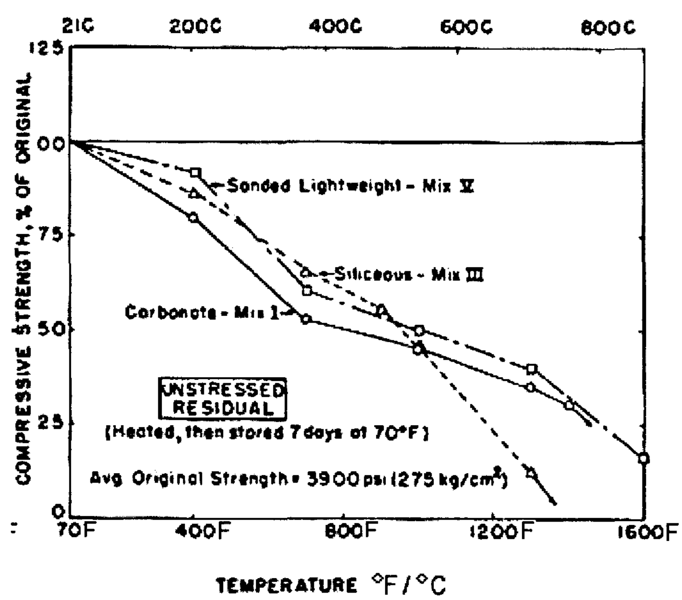
An interesting set of data in this regard is the work of Bertero and Polivka [63] who demonstrate both a reduction in strength for sustained temperatures and thermal cycles to 150°C for a sealed limestone concrete, as shown in Figure 3.17. Their findings for unsealed limestone concrete were that thermal cycling had little effect. It becomes necessary to again suggest the likelihood of hydrothermal reactions with limestone concretes producing a CSH gel with lower strength properties, as shown by Seeberger et al. [17].

When one considers the effect of thermal cycling on siliceous aggregates, Davis [64] reported that for a gravel concrete with cycles between 39°C and 200°C, there was a 10% loss in strength for 1 cycle and a 27% reduction after 20 cycles. Weigler and Fischer [65] demonstrated for an unsealed quartzite concrete that had been preloaded, that there was no effect with 3 cycles to 300°C, and a 50% reduction when the maximum temperature was raised to 600°C (above the α-quartz to β-quartz transition point).

Time at temperature The response of a concrete to the duration of heating is dependent on whether one considers sealed and unsealed concretes. Considering unsealed concretes, the largest change occurs in the rise to temperature. This is appropriately represented by the work of Kottas et al. [66] as shown in Figure 3.18 (a). This demonstrates that there is still some effect of the time at temperature with the response of the concrete, but this is limited.



(a) At temperature tests



(b) Residual Tests

Figure 3.16: a) At temperature and b) residual compressive strengths of concretes made with different aggregates [58]

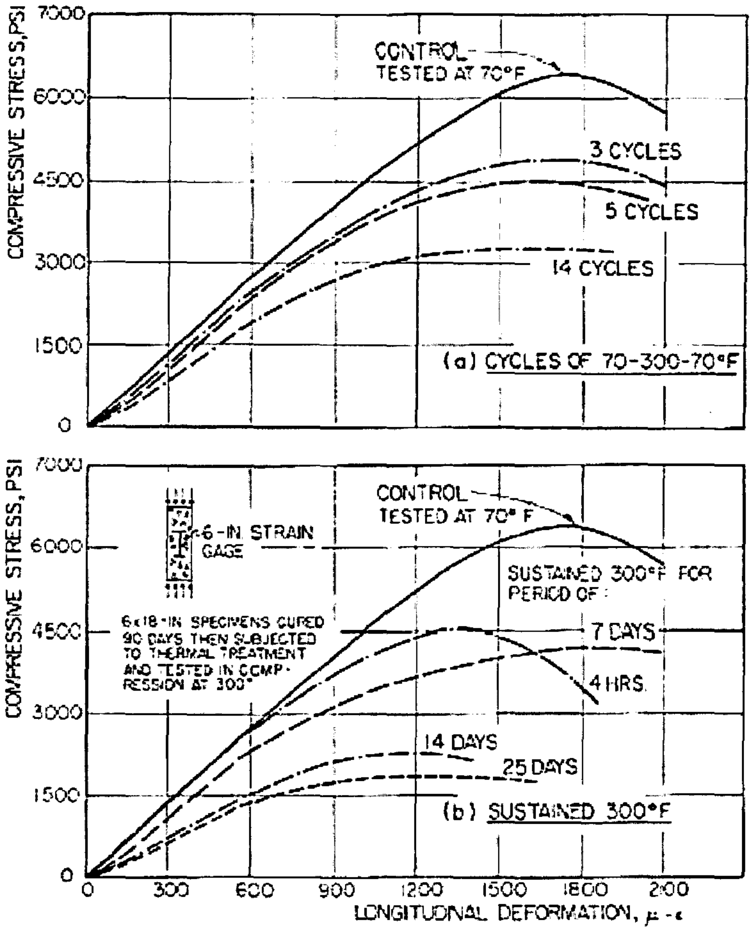
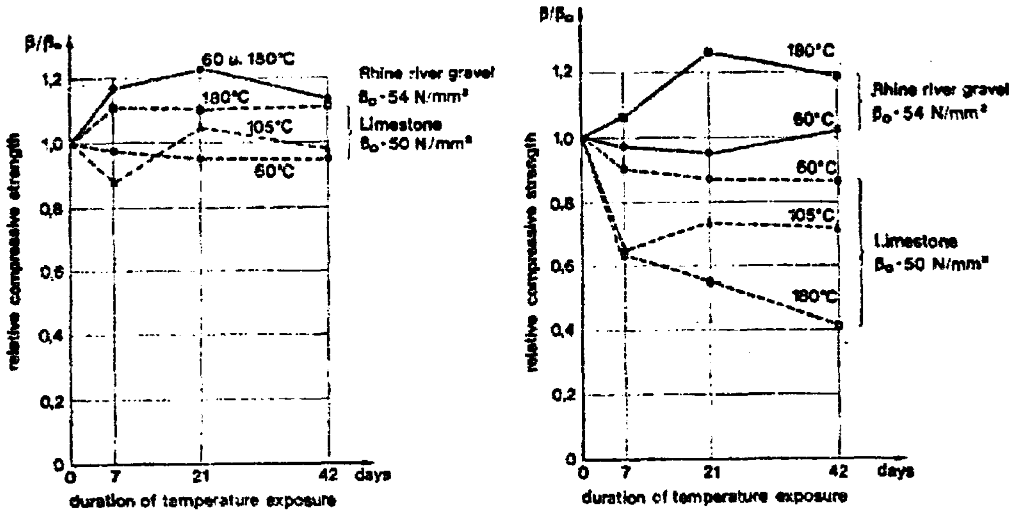


Figure 3.17: Influence of thermal cycling on $\sigma - \varepsilon$ response of sealed concrete tested at 300°F (149°C) [63]



(a) Unsealed (b) Sealed

Figure 3.18: Relative strength development of (a) unsealed and (b) sealed concrete exposed to elevated temperatures [66]

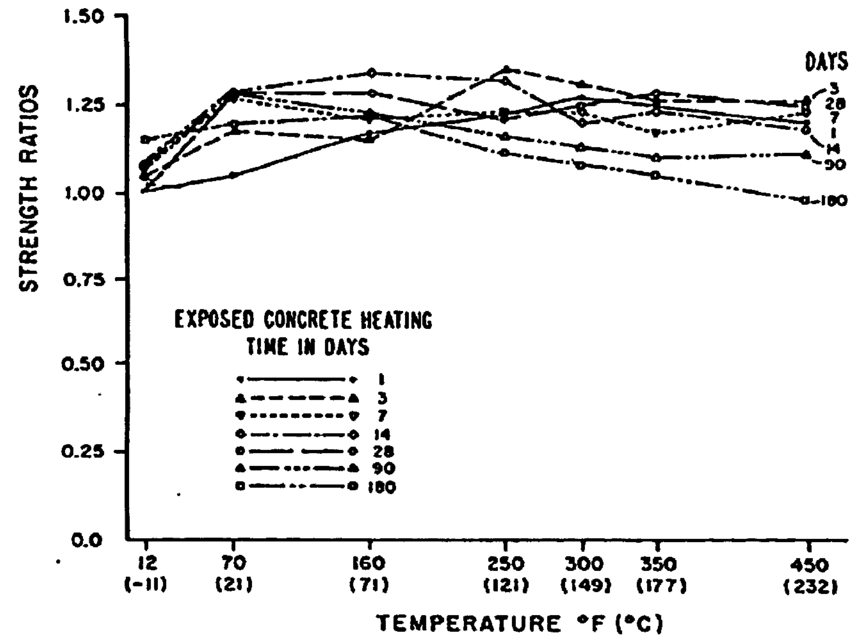
The improvement in unsealed strengths is supported by Nasser and Chakraborty, as shown in Figure 3.19 (a). This figure also demonstrates a time dependent relationship of strength at 232°C that ranges over 20% to 25% for up to 180 days of exposure [67].

The work of Suzuki et al. [68], as shown in Figure 3.20, demonstrates that with comparatively mild temperatures of 65°C, 90°C and 110°C, the change of strength for unsealed concretes over long durations of heating of up to 3.5 years is limited.

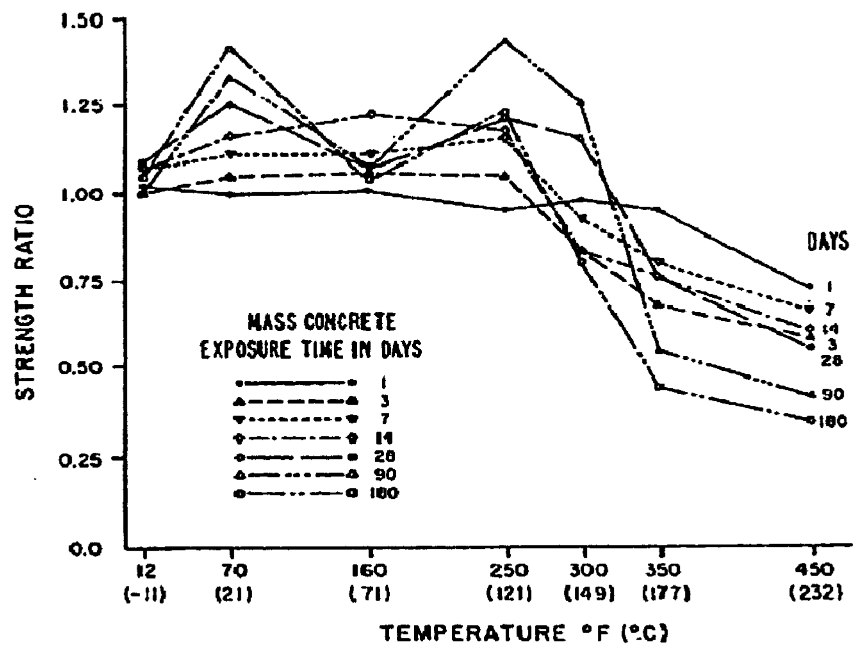
This work does however illustrate effectively the effect that long periods of exposure can have on sealed concretes, with a strength ratio in excess of 150% for a sealed concrete at 90°C after 3.5 years. Nasser and Chakraborty [67] clearly demonstrated a significant time effect in the context of sealed concrete with a loss of in excess of 50 % strength over 180 days at 232°C, with a clear trend of deterioration as shown in Figure 3.19 (b). This concrete contained a 25% FA replacement ratio with a dolomite and hornblende aggregate.

Kottas et al. [66] demonstrated a marked difference between the time dependent responses of limestone and Rhine river gravel concretes in a sealed environment, with the limestone showing a significant reduction, see Figure 3.18 (b). This suggests that hydrothermal reactions such as those discussed by Lankard et al. [39] are occurring at higher temperatures with limestone aggregate concretes.

Seeberger et al. [17] demonstrated that the use of high FA contents in a sealed quartzitic concrete yield a significant strength gain of about 25% over 28 days as illustrated in Figure 3.21. Indeed, it appears that the strength gain



(a) Unsealed



(b) Sealed

Figure 3.19: Relationship of (a) unsealed and (b) sealed compressive strength and temperature of concrete [67]

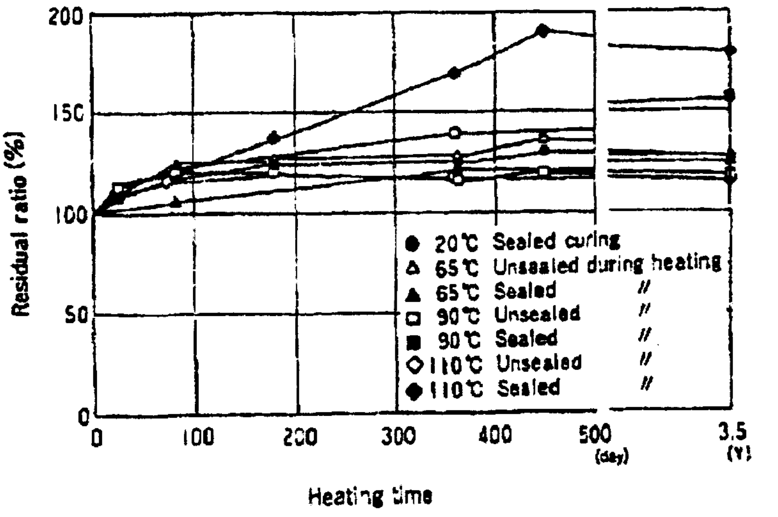


Figure 3.20: Compressive strength of sealed and unsealed concretes exposed to various temperatures for up to 3 ½ years[68]

was most significant over the first 7 days of exposure to temperatures. This same concrete demonstrated an unsealed residual strength of about 90% after 7 days of exposure at 225°C.

Preloading concrete The stress condition of a concrete during heating has a significant positive effect on the strength properties of a concrete. When one considers unsealed concretes, the presence of a pre-loading of 0.4 σ_c has been shown by Abrams [58] to maintain the unheated compressive strengths to in excess of 400°C for siliceous aggregates and 600°C for limestone concretes. This is due to the compressive preload preventing the development of microcracking through differential thermal expansion of aggregate and cement paste. These results are shown in Figure 3.22. The stressed results were for concretes tested at temperature in an unsealed environment.

This agrees with the findings of Malhotra [61] who carried out tests on unsealed concrete shown in Figure 3.15 on page 49. No literature has been identified for sealed concretes heated under stress.

Conclusions on compressive strength The following conclusions were drawn for the response of compressive strength of a concrete to high temperatures:

- A broad range of values are attainable, dependent on material constituents and quantities, the heating environment, time at temperature and prestress applied to the concrete. Some concretes demonstrate an improvement in strength around 250°C, after which there is generally a loss in strength [52].

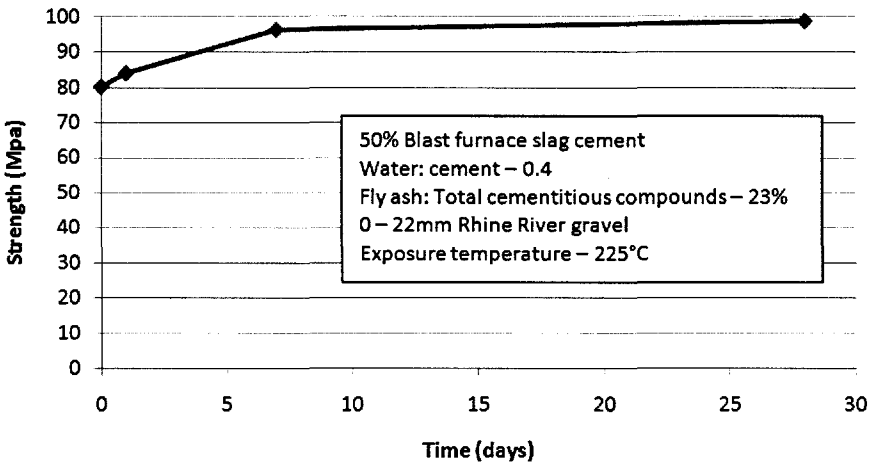


Figure 3.21: Strength development over time at 225°C of hydrothermally treated quartzitic concrete [17]

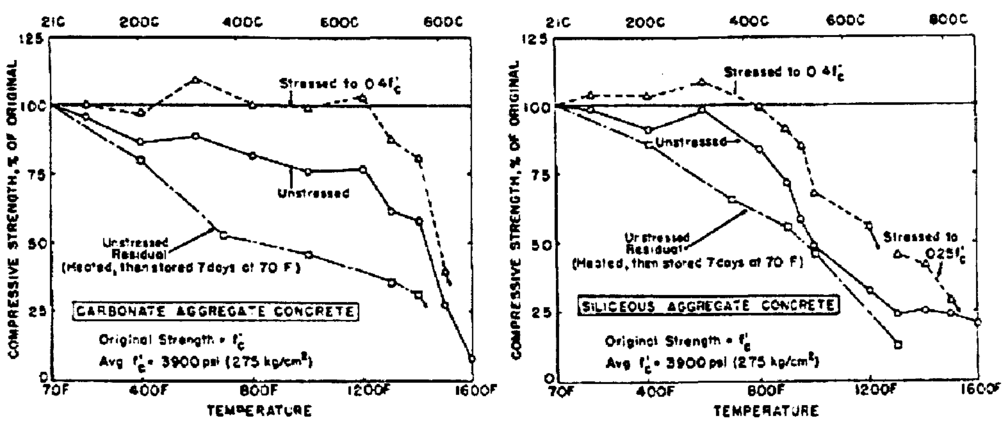


Figure 3.22: Effect of Exposure Temperature on Residual Strength of Carbonate and Siliceous Aggregate Concretes [58]

- In terms of material constituents the following conclusions can be made:
  - Portland cement with extenders, especially fly ash and ground granulated blast furnace slag, provide a beneficial effect when compared to plain Portland cement concretes [16].
  - Aggregates with a low coefficient of thermal expansion are ideal, however limestone appears to encourage deleterious hydrothermal reactions at high temperatures [17].
  - The use of fibres such as polypropylene and steel can provide beneficial effects at temperature. Polypropylene fibres may allow for release of excess pore pressures [60], while steel fibres act as microcrack arrestors [59].
- In unsealed concretes the primary change in strength is due to dehydration of the cement paste and differential expansions between the cement paste and aggregate. With careful selection of the aggregate a concrete can provide a strength roughly equivalent to the room temperature strength at 450°C for at least short periods of heating [16, 55].
- In sealed concretes the primary change in strength is due to a change in the CSH gel to a more crystalline species. The prevalence of this reaction can be counteracted with the use of high quantities of extenders that consume excess $Ca(OH)_2$ [17, 49, 44].
- The strength at temperature is highly time dependent, with a deterioration generally being the case at temperatures in the range of 180°C to 250°C [67]. This can be counteracted in sealed concretes with the use of extenders, that appear to cause an improvement in strength for at least the first 28 days of heating [17, 66].
- The application of prestress to unsealed concretes improves the retention of compressive strength at temperature [58, 61]. No literature has been identified relating to sealed environments and prestress.

Flexural and Tensile Strength

The flexural and tensile strength of concrete that has been exposed to high temperatures also experiences a variety of factors that contribute to property deterioration. Here a short summary of the expected trends has be given. Much of the information concerning tensile strength was collected from the work of Bazant and Kaplan [7].

Broadly speaking the tensile strength of concrete is reduced with temperature, without the increase up to about 250°C that can be experienced by compressive strength. This reduction is generally greater than the reduction experienced by the compressive strength although there is also considerable scatter in the results as shown by Figure 3.23 [7].

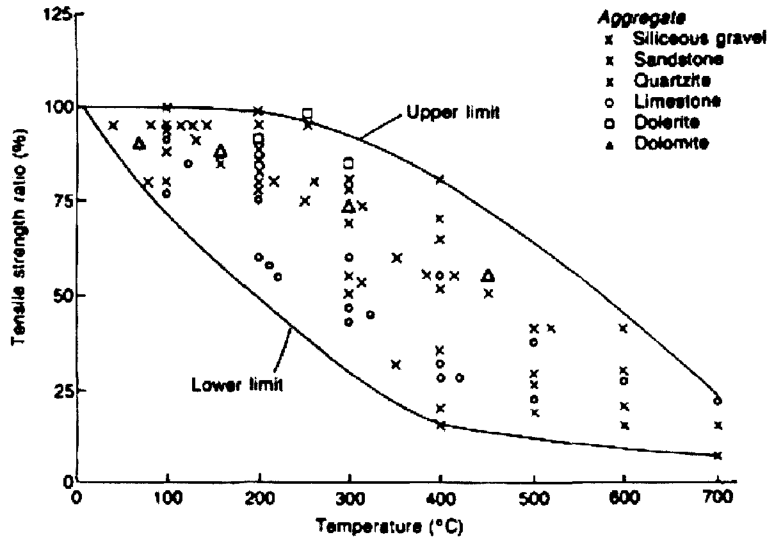


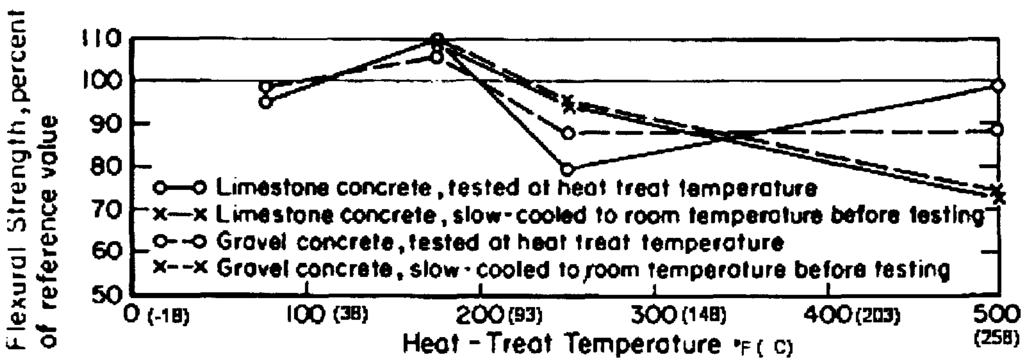
Figure 3.23: Splitting tensile strength (as a percentage of initial strength before heating) of Portland cement concretes with conventional aggregates, at various temperatures [7]

The concrete constituents have a considerable effect on the tensile strength of the concrete. It has been reported that concretes with high cement contents (rich mixes) have a greater reduction than concretes with lower cement contents (lean mixes) [61, 69]. In terms of aggregates, it is difficult to draw clear conclusions although there is evidence that siliceous aggregate concretes retain their properties better than limestone concretes [38, 70].

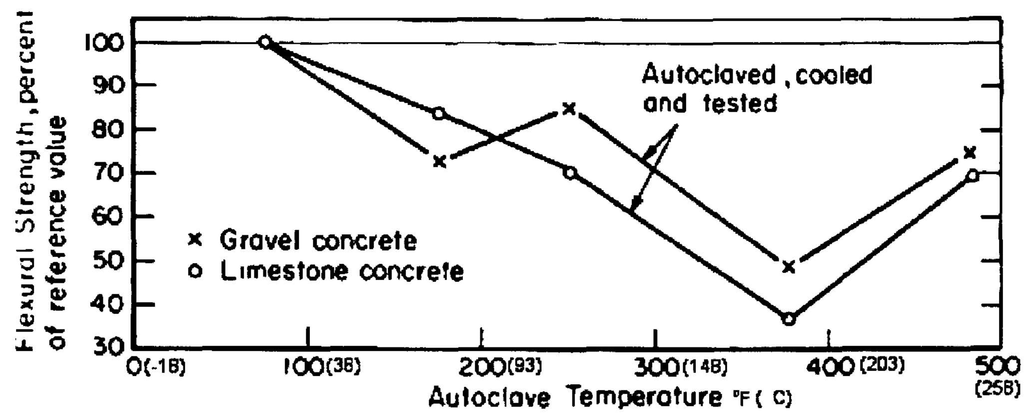
Considering the moisture state of the concrete, there has been limited testing for tensile strength on concretes that have been exposed to both sealed and unsealed conditions. The research of Lankard et al. [39], relating to flexural strength, included data for both environments, as presented in Figure 3.24, with image (a) presenting the at temperature and cooled responses of unsealed concretes and image (b) presenting the values for cooled autoclaved concretes. Considering the likelihood of hydrothermal reactions, this data suggests that sealed concretes experience a greater deterioration of tensile strength with temperature. No literature has been identified for concretes with high extender contents in sealed environments.

In terms of the heating rate, there has been no literature identified that can illustrate the effect that this has on the properties of the concrete. It is however reasonable to extend the work of Khoury [34] to this section, in that very high heating rates will probably cause significantly greater damage to the concrete than lower heating rates. The development of high pore pressures and thermal stresses ultimately causes localized tensile failure of the concrete, leading to property loss and spalling.

It is clear that the final temperature that the concrete is exposed to has



(a) Flexural strength of unsealed limestone and gravel concretes after prolonged temperature exposure, at temperature and after cooling



(b) Flexural strength of sealed (autoclaved) limestone and gravel concretes after prolonged temperature exposure

Figure 3.24: Flexural strengths for limestone and gravel concretes for (a) unsealed at temperature and cooled conditions and (b) cooled autoclaved concretes [39]

a considerable effect on the tensile strength of the concrete as supported by Lankard et al. in Figure 3.24 [39]. It is also apparent that there is not the increase in strength that is achievable with compressive strength up to about 250°C.

Thermal cycling has a similar effect on the tensile strength as with compressive strength, in that generally the greatest deterioration happens with the first few cycles [64, 71, 72, 73]. The effect of subsequent cycles is debatable, with some authors suggesting a continued deterioration [72], while others suggest a fundamentally stable response after the first cycle [64].

Considering the effect of the duration of heating, Harada et al. [70] and Carrette et al. [45], suggest that above 150°C the tensile strength experiences a progressive deterioration with time.

There has been no data identified that considers the effect that the applied stress conditions such as prestressing has on the tensile strength of the concrete.

Conclusions on flexural and tensile strength The following conclusions can be made with regard to flexural and tensile strength:

1. Tensile strength generally reduces with exposure to temperature.
2. Siliceous aggregates (i.e. amorphous igneous aggregates) appear to retain properties better than limestone aggregates.
3. Sealed concretes possibly experience a greater reduction of strength, due to hydrothermal reactions.
4. It has been suggested that there is a progressive deterioration of strength with duration of heating.

Modulus of Elasticity and Stress-Strain Characteristics

A summary of some research relating to modulus of elasticity (E) was outlined by Freskakis in Figure 3.25 [52]. This summary clearly suggests that there is a significant reduction of the modulus with temperature. At the temperatures being considered for this project, these could range from between 10% and 65% for 225°C and 50% and 85% for 450°C.

Material components One of the main contributors to the modulus of a concrete is the modulus of the aggregate, as shown in Figure 3.26 [74].

This Figure suggests that, in the temperature range of interest (up to 450°C), siliceous aggregates provide the best response. Considering the conclusions made in the context of strength, basically that limestone aggregates need to be avoided, this therefore further supports the use of siliceous aggregates. Considering that limestone aggregates can be deleterious in terms of strength, the use of siliceous aggregates is further supported.

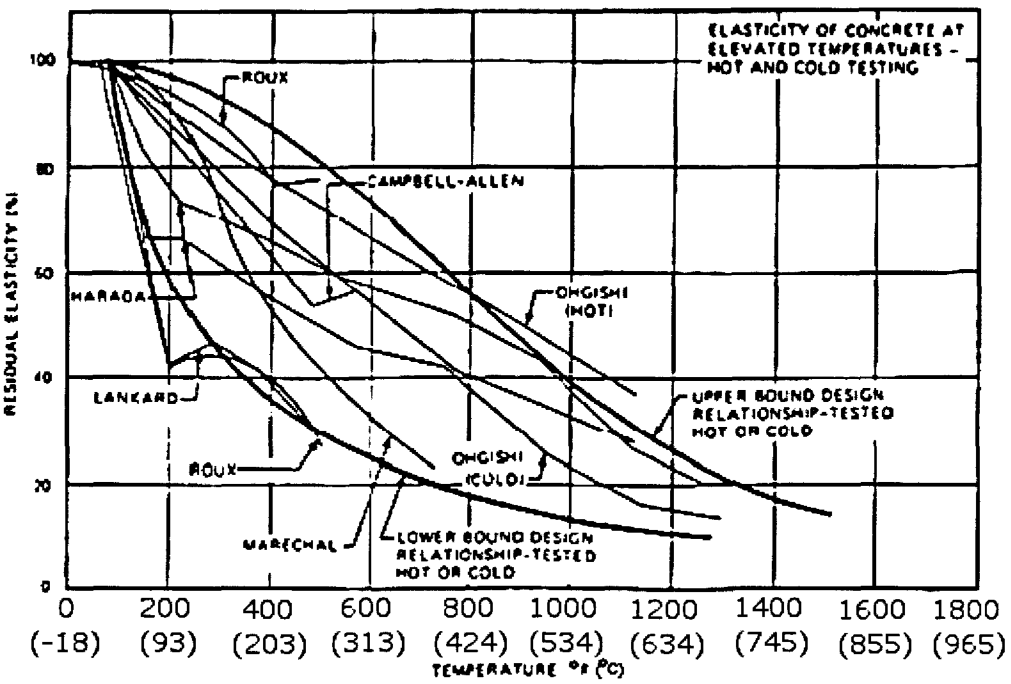


Figure 3.25: Effect of Temperature on the modulus of elasticity of Concrete: Hot and Cold Results [52]

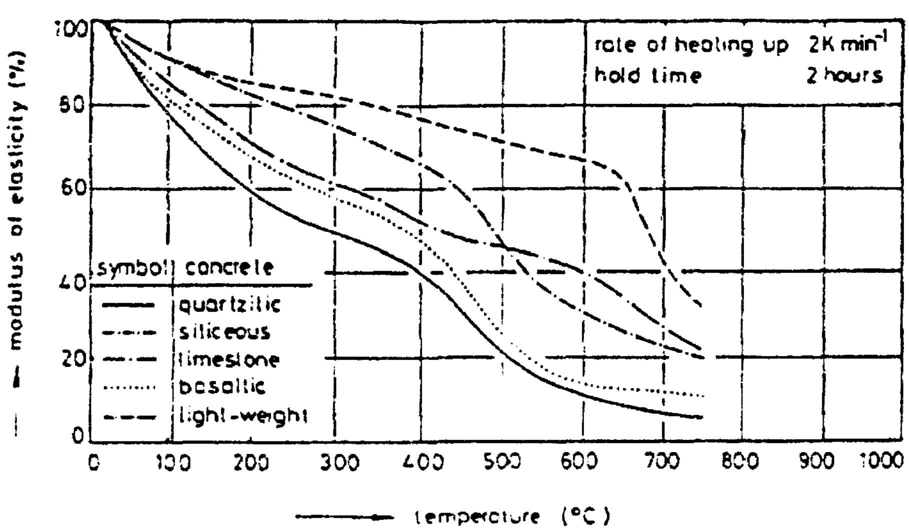


Figure 3.26: Modulus of Elasticity of Different Concretes at Elevated Temperature [74]

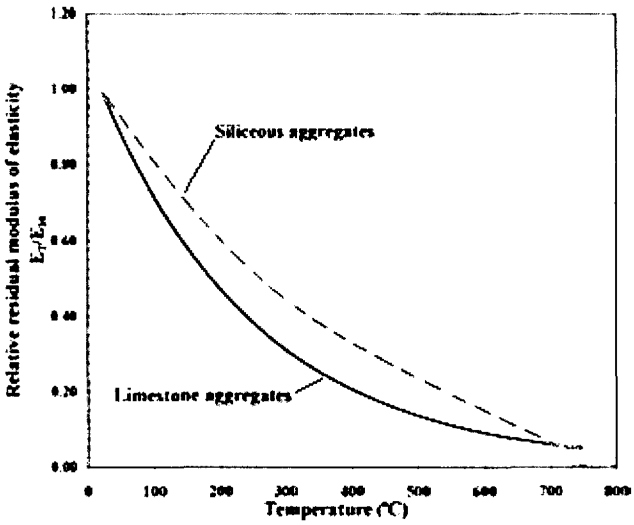


Figure 3.27: Relative Residual Modulus of a) Limestone and b) Siliceous Concretes [57]

Savva et al. [57] assessed the modulus of elasticity for unsealed limestone and siliceous aggregate concretes containing up to 30% FA, that broadly agree with the findings of Schneider [74], demonstrating less degradation of modulus of elasticity with siliceous aggregates. Shown in Figure 3.27.

This work also becomes interesting when considering the siliceous results and the different fly ash replacement ratios. Tests were done with Megapolis fly ash, which has a low calcium content, and significant pozzolanic activity and Ptolemaida fly ash with a high calcium content and therefore significant pozzolanic and hydraulic activity. Savva et al.'s [57] data suggests that the modulus of concretes with higher quantities of FA experiences a greater reduction with temperature. This is in agreement with the findings of Ghosh and Nasser [49], presented in the discussion on stress conditions shortly. This is a difficult characteristic to explain, considering high quantities of fly ash improve strength retention with temperature.

Moisture state As with the strength of concrete, the nature of the surrounding material and the moisture state of the concrete has a significant effect on the modulus and stress strain characteristics. It is likely that modulus is also affected by the hydrothermal reactions discussed in the strength section, supported by Kottas et al. in Figure 3.28, who demonstrate a remarkable deterioration of modulus and stress strain characteristics for sealed limestone concrete at 180°C [66]. This is adequately supported by the very low failure stress for the sealed concretes at this temperature.

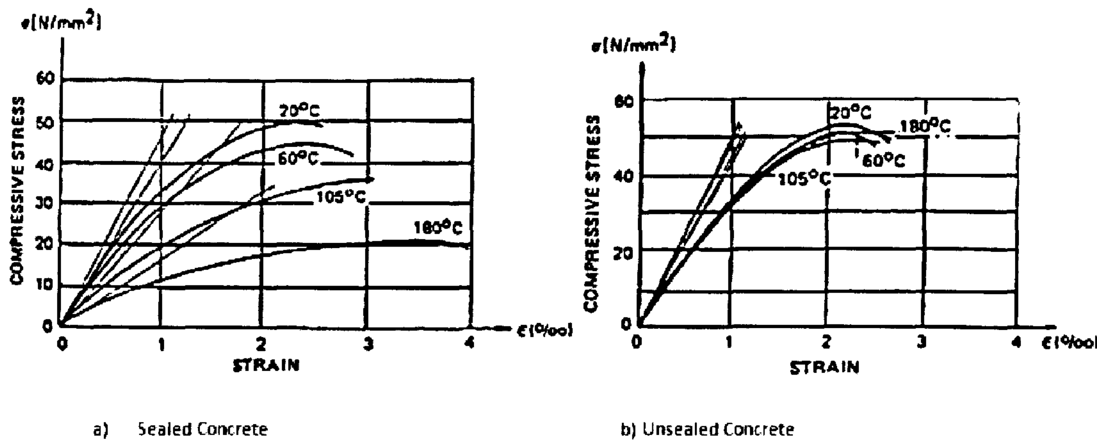


Figure 3.28: Stress-Strain Diagrams of Sealed and Unsealed Limestone Concrete [66]

Lankard et al. [39] provide some interesting data to compare the effect of moisture state on the hot modulus and the residual (cooled) modulus. Figure 3.29 is for a gravel concrete, with the left hand figure presenting unsealed at temperature and residual results while the right hand image presents the sealed at temperature and residual results.

It should be apparent from this that there is a significant difference between the sealed and unsealed modulus and stress strain characteristics of a concrete, with the sealed state experiencing a much greater reduction in properties both at temperature and after exposure to temperature above 200 °C. After exposure to about 150°C the residual modulus appears to be unaffected, while the at temperature modulus appears to be between 30% and 50% of its reference value above 93°C.

Heating environment There has been no data identified on the effect of heating rate on the modulus and stress strain characteristics of a concrete.

In terms of the final temperature, possibly the best reference is Figure 3.25 on page 61 which indicates the effect, and broad range of values possible, that the final temperature has on the modulus of concrete. An appropriate representation of the effect that the temperature has on the stress strain response of an unsealed quartzitic concrete is exposed to is given in Figure 3.30 on page 65 [75].

Clearly, as unsealed quartzitic concrete is exposed to temperatures in excess of 265°C the modulus deteriorates, probably due to differential thermal expansions of the cement paste and the quartzitic aggregate causing micro-crack development, which accelerates significantly as the temperature approaches the α-quartz to β-quartz transition temperature of 575 °C. Weigler and Fischer [65] provided some insight into the difference of the stress strain behaviour at temperature and after cooling. It was clearly indicated that there is no

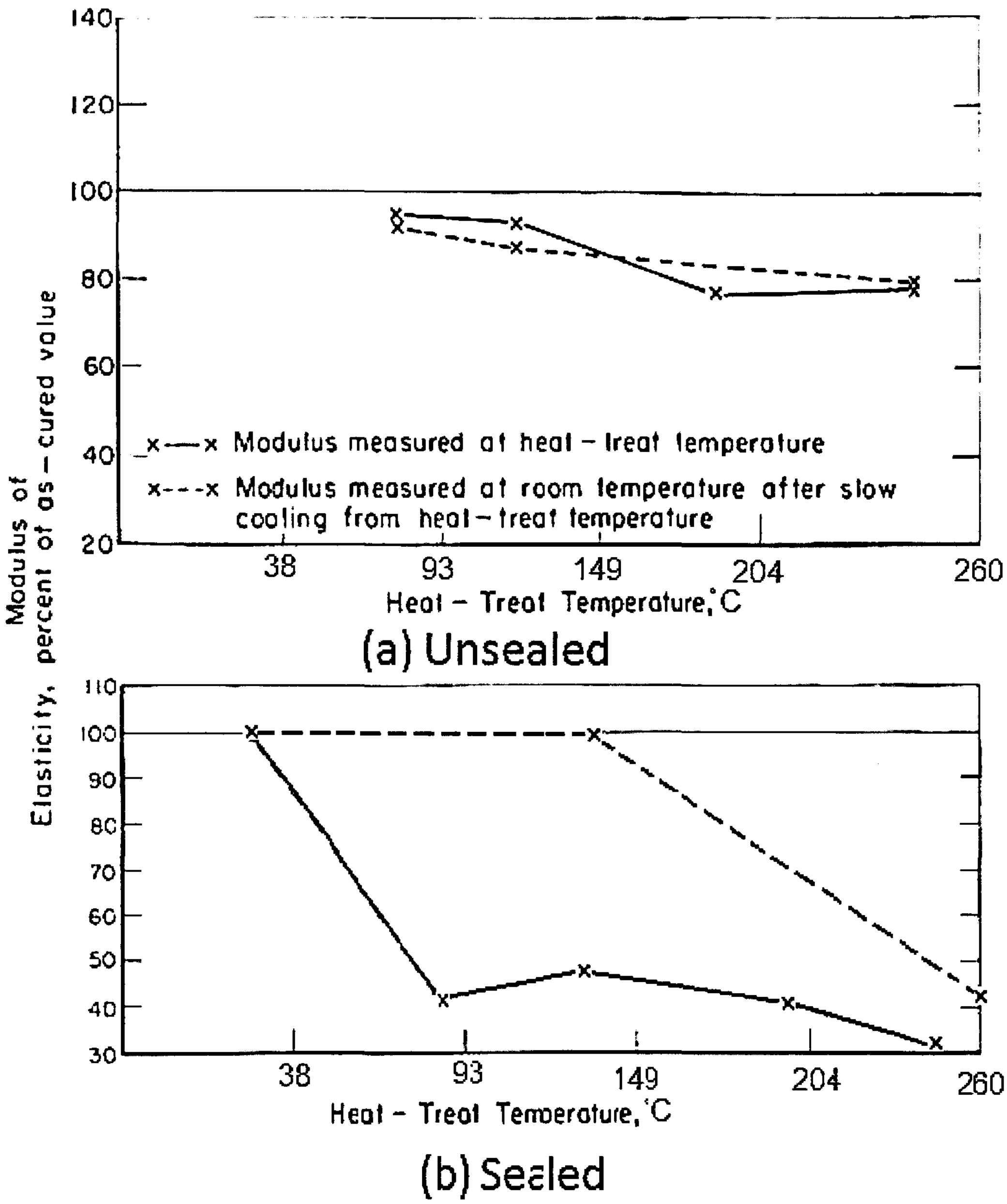


Figure 3.29: Modulus of elasticity of gravel concretes tested at temperature and after cooling: (a) unsealed (b) sealed [39]

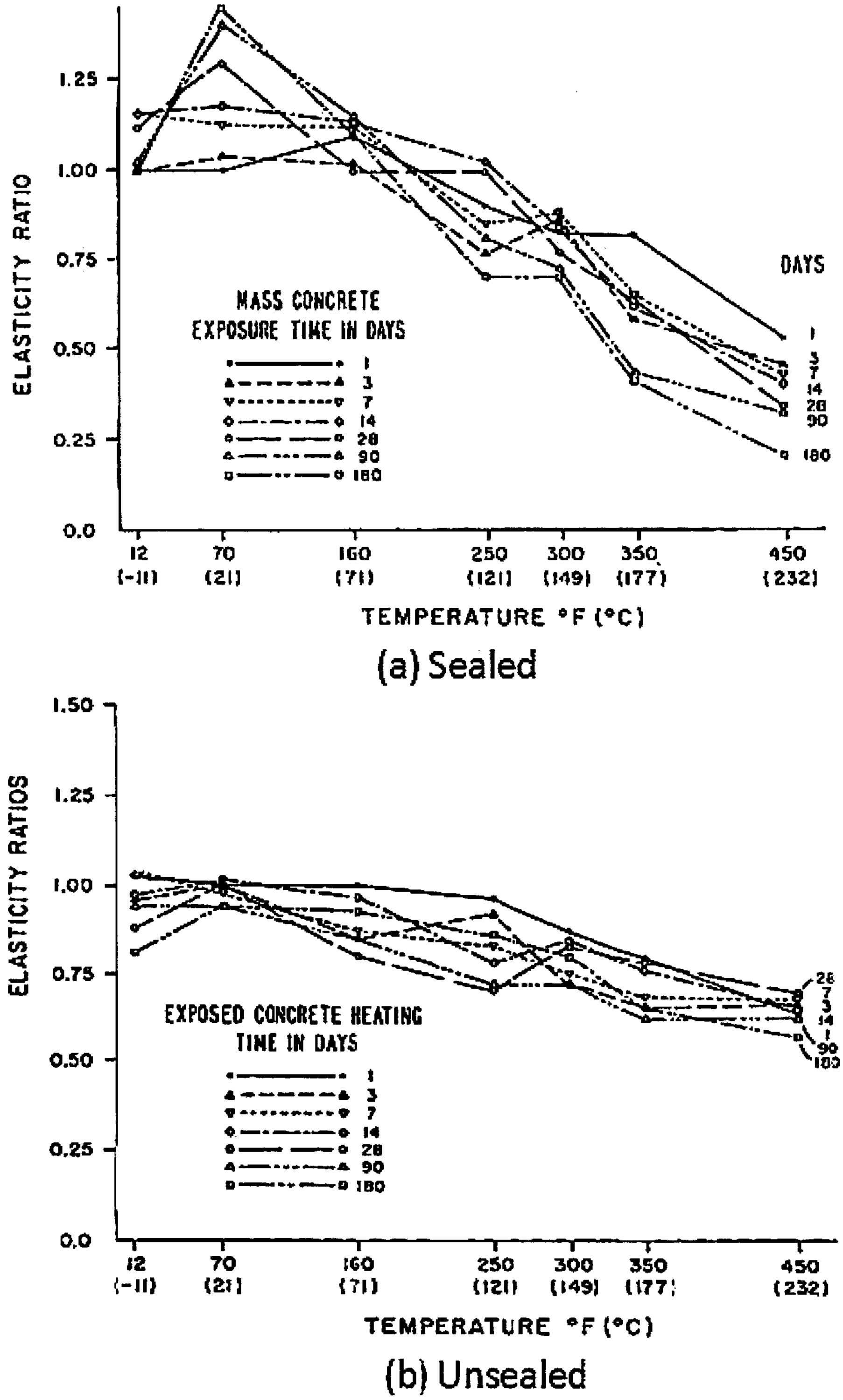


Figure 3.31: Relationship of Modulus of Elasticity and Temperature for (a) sealed and (b) unsealed concrete[67]

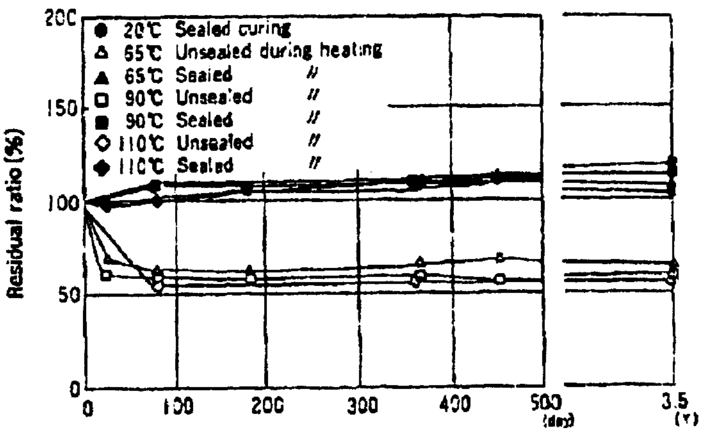


Figure 3.32: Long-term (3.5 year) heating effect on modulus of elasticity [68]

The conclusions drawn in the Suzuki et al. study included [68]:

- Loss of modulus for unsealed specimens was probably due to the formation of micro-cracks.
- Changes in modulus stabilized after about 90 days and changed little up to 3.5 years.
- Loss in modulus in unsealed specimens is directly proportional to moisture loss in the sample.

A series of experiments to assess the drying effect of high temperature exposure on the relative modulus of unsealed concretes made with several different aggregates was carried out by Kasami et al. [76]. Considering these results are for a 90 day period of heating, it appears from this data that long term exposure suggests the use of amorphous igneous aggregates such as basalt over calcareous limestone, as shown in Figure 3.33.

Confining Stress The application of a compressive stress to a concrete has a beneficial effect on the modulus and stress strain characteristics, as with the compressive strength of the concrete, appropriately demonstrated by Schneider in Figure 3.34 on the next page [38].

From this graph it becomes apparent that the application of a prestress of approximately $0.3\sigma_{ult}$ facilitates little change in the modulus between 250°C and 450°C (as the graphs have the same slope up to approximately $0.5\sigma_{ult}$). The prestress also facilitates some retention of strength, although there is a significant drop in maximum stress between 225°C and 450°C.

Ghosh and Nasser [49] investigated the effect of different fly ash replacement ratios on concrete under a confining stress and exposed to temperature, with results shown in Figure 3.35 on page 70. These results support the data of Savva et al. [57], in that higher replacement ratios of fly ash lead to a greater

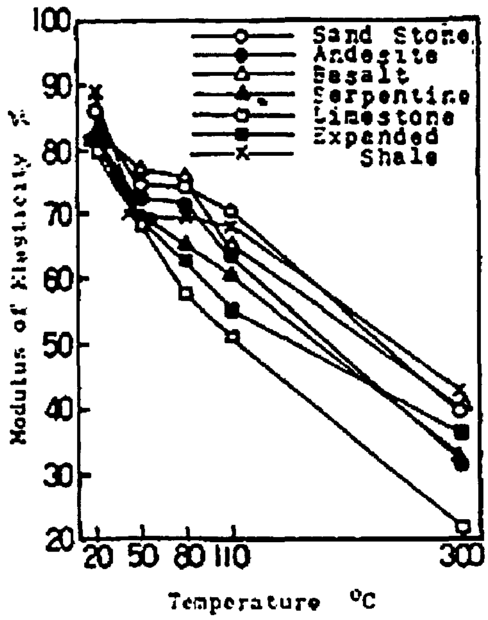


Figure 3.33: modulus of Heated Concrete with Different Aggregates [76]

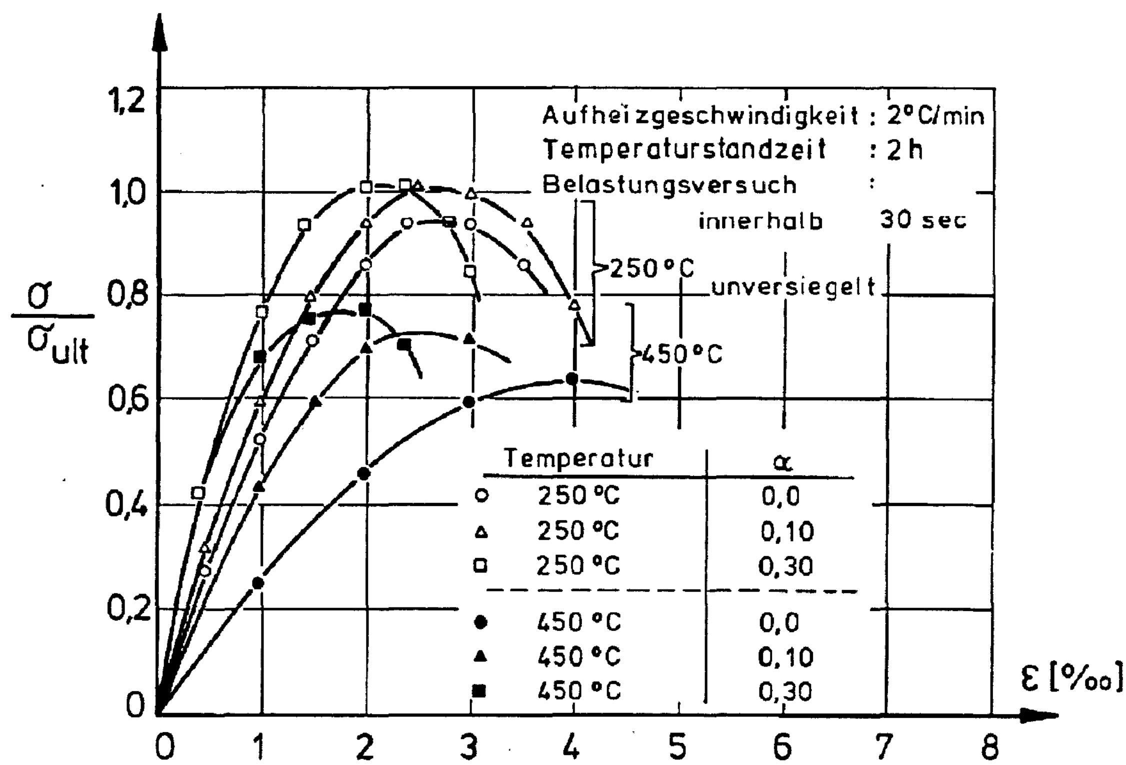


Figure 3.34: Stress- Strain Characteristics of Normal Concrete with Loading during the Heating Period [38]

reduction in modulus. This is interesting considering the high quantities of fly ash also appear to improve the strength retention with concrete at temperature.

Conclusions on modulus of elasticity The following conclusions were drawn on the modulus of elasticity of concrete exposed to high temperatures:

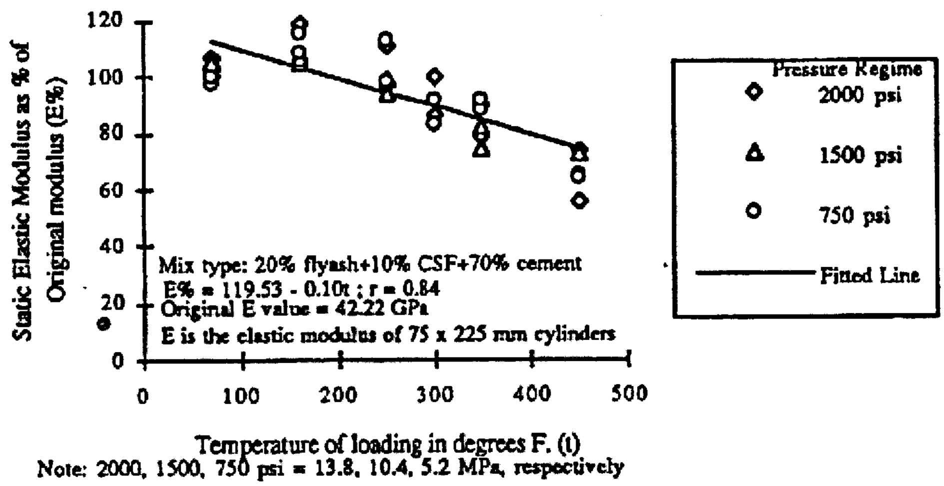
- Modulus generally deteriorates with temperature, with no gain up to 250°C as may be expected from compressive strength.
- When considering the effect of material constituents on the modulus response, the following deductions can be made:
  - The use of siliceous and amorphous igneous aggregates provides a beneficial response over calcareous aggregates. [38, 76].
  - The use of extenders has a deleterious effect on the retention of modulus [49, 57].
- Sealed environments provide a large deterioration both at temperature and with residual (cooled) tests when compared to unsealed concretes [39, 66].
- Modulus generally deteriorates with length of temperature exposure, probably related to hydrothermal reactions with the CSH gel [67]. However an improvement in modulus has been shown to develop at temperatures of 110°C up to 90 days, after which the modulus stabilizes [68].
- Prestress generally improves the retention of modulus and stress-strain characteristics [38].

Poisson's ratio

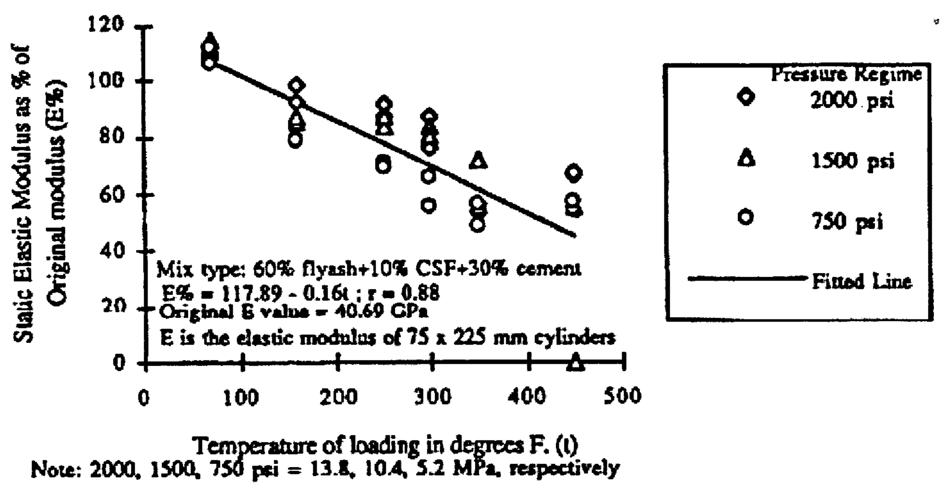
There is limited data available on the effect that temperature has on the Poisson's ratio of concrete, and the existing literature is indefinite and sometimes contradictory [14]. It has been suggested that the Poisson's ratio decreases with temperature [14, 77] whilst others state that below 400°C it is in the range of 0.11 – 0.25, and increases above 400°C [14].

If one considers the Poisson's ratio from the context of the microstructural response of concrete to temperature, as suggested by Bazant and Kaplan [7], the rupture of bonds on heating is an applicable theory. This is in agreement with the data for Maréchal, who observed a drop in the ratio from 0.28 at room temperature to 0.1 at 400°C, as shown in Figure 3.36 [78]. Generally the Poisson's ratio reduces as the concrete dries as shown in Figure 3.37 by Lau and Anson testing unsealed concrete [77].

Bertero and Polivka suggest that with sealed specimens the drop with temperature in Poisson's ratio is small, from 0.2 to 0.18, largely because of the retention of moisture [63]. This is in broad agreement with Hirano et al. who



(a) 20% FA, 10% CSF, 70% Portland Cement



(b) 60% FA, 10% CSF, 30% Portland Cement

Figure 3.35: Static Elastic Modulus under temperature and pressure loading of (a) 20% Fly Ash, 10% Silica Fume, 70% Portland Cement and (b) 60% Fly Ash, 10% Silica Fume, 30% Portland Cement [49]

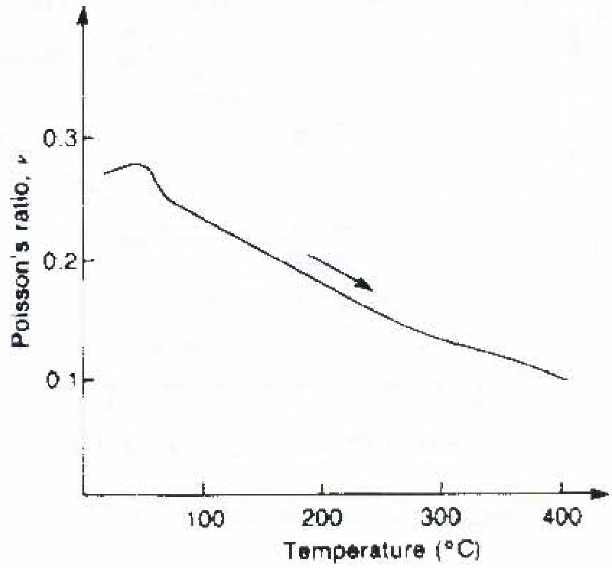


Figure 3.36: Variation of Poisson's ratio of Portland cement quartzite concrete with temperature [78]

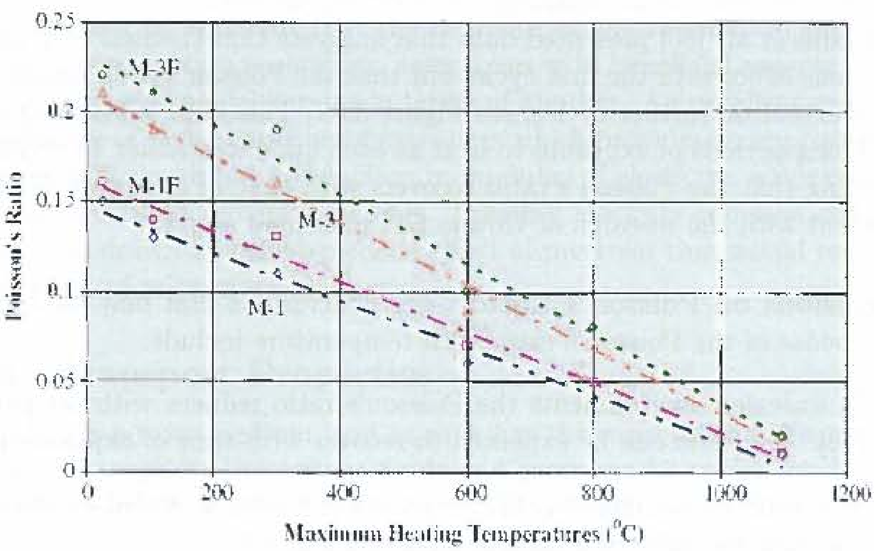


Figure 3.37: Poisson's Ratio with respect to Temperature [77]

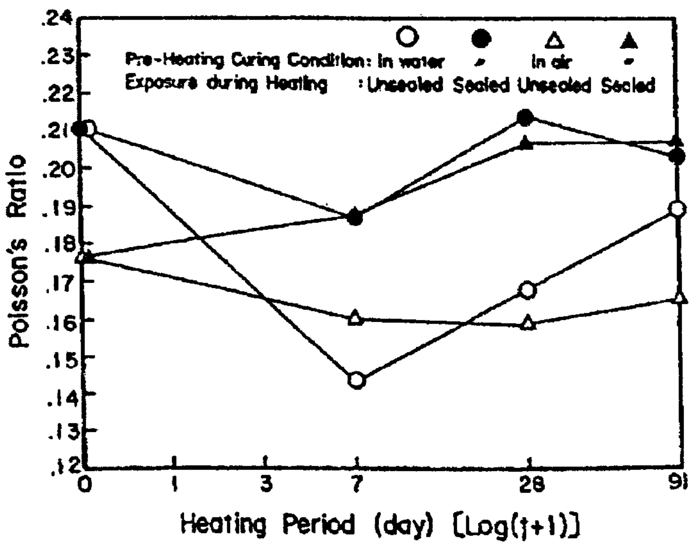


Figure 3.38: Poisson's Ratio Results [79]

presented the effect of duration of heating at 175°C in Figure 3.38 [79]. This Figure broadly suggests that the Poisson's ratio varies dependent on the curing conditions and moisture state on heating of the concrete.

It has been suggested by Bazant and Kaplan [7] that the presence of a confining stress or pressure on the concrete will likely support the retention of the unheated Poisson's ratio. This is on the basis that confining pressures will reduce the development of micro-cracking, which has a similar effect on the strength and stress strain characteristics of the concrete.

Abrams et al. [80] presented data that suggests that thermal cycling has a deleterious effect with the first cycle, but that the Poisson's ratio recovers to a certain extent on further cycles, see Figure 3.39. This data is also representative of long periods of exposure to heat as each cycle was either 14 or 28 days, suggesting that the Poisson's ratio recovers with time of exposure. This is in agreement with the research of Hirano [79] presented above.

Conclusions on Poisson's Ratio The conclusions that may be drawn on the response of the Poisson's ratio with temperature include:

- In unsealed environments the Poisson's ratio reduces with temperature [78]. The ratio can be expected to recover with time of exposure [80].
- The ratio is relatively unaffected by temperature in sealed environments but may increase with time of exposure [63, 79].
- Prestress or a confining stress on the concrete will likely assist in the retention of the ratio, due to the prevention of microcracking [7].

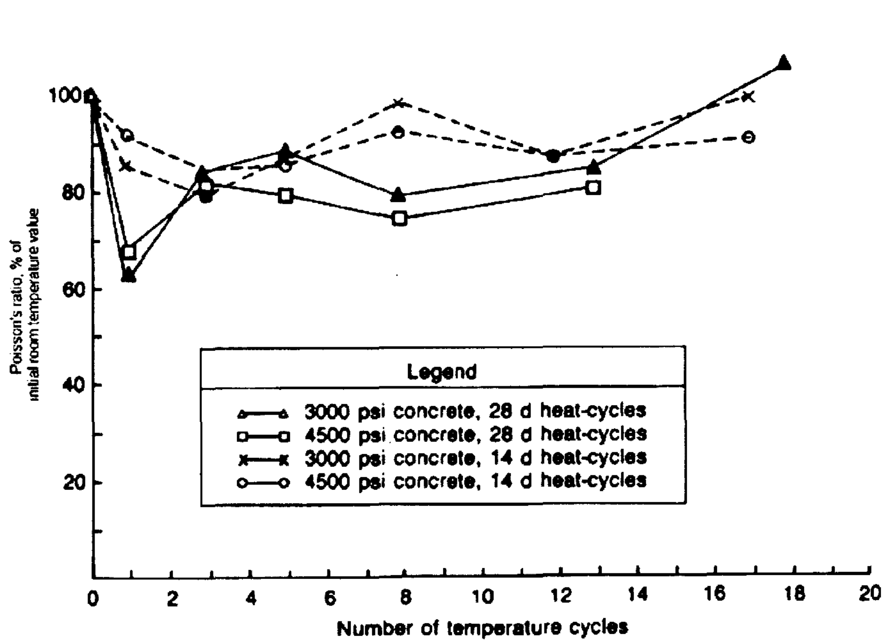


Figure 3.39: Variation of Poisson's ratio of basalt aggregate concrete with number of thermal cycles from ambient to 176°C [80]

- Thermal cycling of unsealed concretes causes a marked reduction in Poisson's ratio on the first cycle, recovering with further cycles and time at temperature [80].

The discussion on the Poisson's ratio concludes the mechanical properties section. It should be apparent that the response of any mechanical property of interest to temperature is complex, sometimes with beneficial aspects in terms of one property being deleterious in terms of another. An excellent example of this is the use of high quantities of extenders which provides an improvement of compressive strength but a reduction in modulus of elasticity, when compared to normal Portland cement concretes. Possibly the only common conclusion that may be drawn was the beneficial effect of prestress that would reduce the development of microcracking.

3.2.3 Transport Properties

Concrete is a porous medium, and as such has the capacity to transport fluids and gases through it. Deleterious fluids and gases can be transported towards steel reinforcement, leading to corrosion, which is one aspect that determines the lifetime of a structure. For a more comprehensive discussion on this topic the reader is referred to Fulton's Concrete Technology [12], however it is pertinent to state that in the context of carbonation and chloride transport, the objective is to design a concrete that hinders the ingress of these materials. This applies equally well in the context of high temperatures and nuclear reactors, as nuclear reactors are frequently built next to the ocean, providing extensive exposure to chlorides, and temperature generally has a deleterious effect on the properties of concrete.

In the context of durability and water ingress, generally the target is to reduce the ability for a concrete to absorb water. In a heated concrete this situation becomes more complicated as the water that is in the concrete vaporizes and causes significant vapour pressures. It then becomes ideal to allow these vapour pressures to escape.

Pore pressure development and water migration

Moisture content and migration Concrete as a porous medium generally contains a fully saturated solution of $Ca(OH)_2$ in its capillary and gel pores. At ambient temperatures and average relative humidity, massive structures can take many years for the capillary and gel water to evaporate from the structure [12], noting that the moisture content of a concrete is the sum of the moisture in the cement paste and aggregate. Generally the water that evaporates from a concrete at or below 105°C is called evaporable (or not chemically bound) water [7].

Above this temperature to about 500°C water that is chemically bound in the cement paste evaporates. The pore water is a mixture of gaseous and liquid forms above 105°C, which creates significant pressures in the pores of the concrete. Hungerford et al. [81] have reported that residual water contents for concretes exposed to 100, 200, 300, 400, 500 and 600°C are 16, 12, 8, 3, 2 and 0% by weight of dry concrete respectively.

There has been some work carried out to determine the time taken for a concrete to dehydrate at a specific temperature. Roux [73] reported mass loss results on specimens with dimensions 273 x 76 x 76 mm, heated to 70, 100, 150, 250, and 400°C respectively. For the specimens at 70 and 100°C the concrete took more than 80 hours to dry, whereas, at temperatures of 150, 250 and 400°C the times to reach equilibrium were approximately 25, 20 and 15 hours respectively.

These data become useful when one considers the environment being considered, namely a massive wall that is sealed on the hot face. Thus water will have to migrate through the concrete to escape on the cold face of the wall. Bazant and Thonguthai [82, 85] have developed a mathematical model for the migration of water under temperature loadings. In their findings it is suggested that although the moisture content is dependent on the temperature and moisture concentration, the migration and transfer of the moisture is principally governed by the gradient of pore pressures in the concrete.

Pore Pressures The evaporation of water, inside the concrete, can create significant pore pressures. In unsealed concretes, this becomes a relevant problem in high thermal gradient situations (such as fires) and can even cause

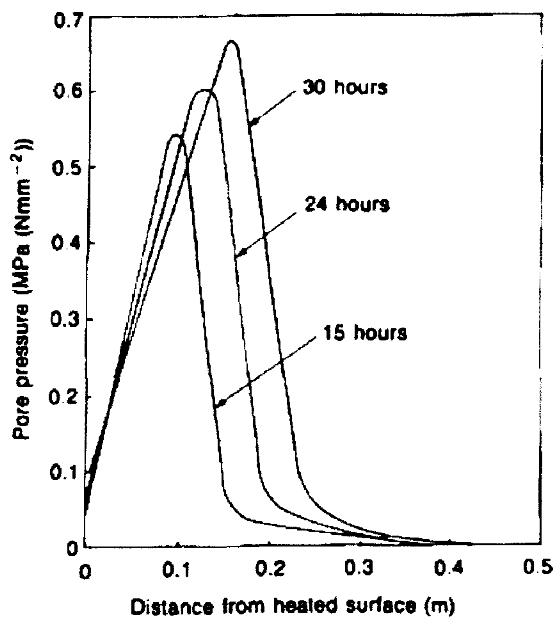


Figure 3.40: Profiles of pore pressure in massive Portland cement concrete blocks at various durations of heating [83]

spalling of the concrete as the moisture migration and pressure causes microcracking. Zhukov and Shevchenko [83] carried out thermal spalling tests on massive Portland cement concrete specimens, with one unsealed face heated while the pore pressure distribution through the specimen was measured, as presented in Figure 3.40 adapted by Bazant and Kaplan [7].

The work of Sullivan and Akhtaruzzaman [84] similarly suggested that pore pressures can be significant in a structure, while experimental data suggested that pore pressures were generally less than 1 MPa. Considering these pressures in the context of the tensile strength of concrete, it is apparent that pore pressures can cause local tensile failure under high thermal gradients and loads. An interesting representation of this concept, including the different effects a sealed and unsealed heated face have, is given by Bazant and Thonguthai [85] with an implementation of their finite element model to rapid heat exposure. As shown in Figure 3.41 the model suggests that in an unsealed state the maximum pore pressures occur a short distance from the heated face, whereas in a sealed state, the maximum pressures occur against the steel liner. This model also suggests maximum pore pressures in excess of 2 MPa.

These data are of limited relevance to the PBMR. By its nature, even in a LOCA accident, the heating rate would be significantly lower than those required to cause such situations. Of greater interest is the steady state response of a concrete to long term temperature exposure, and the implications this has on the moisture content and pore pressures. Significant research in this regard

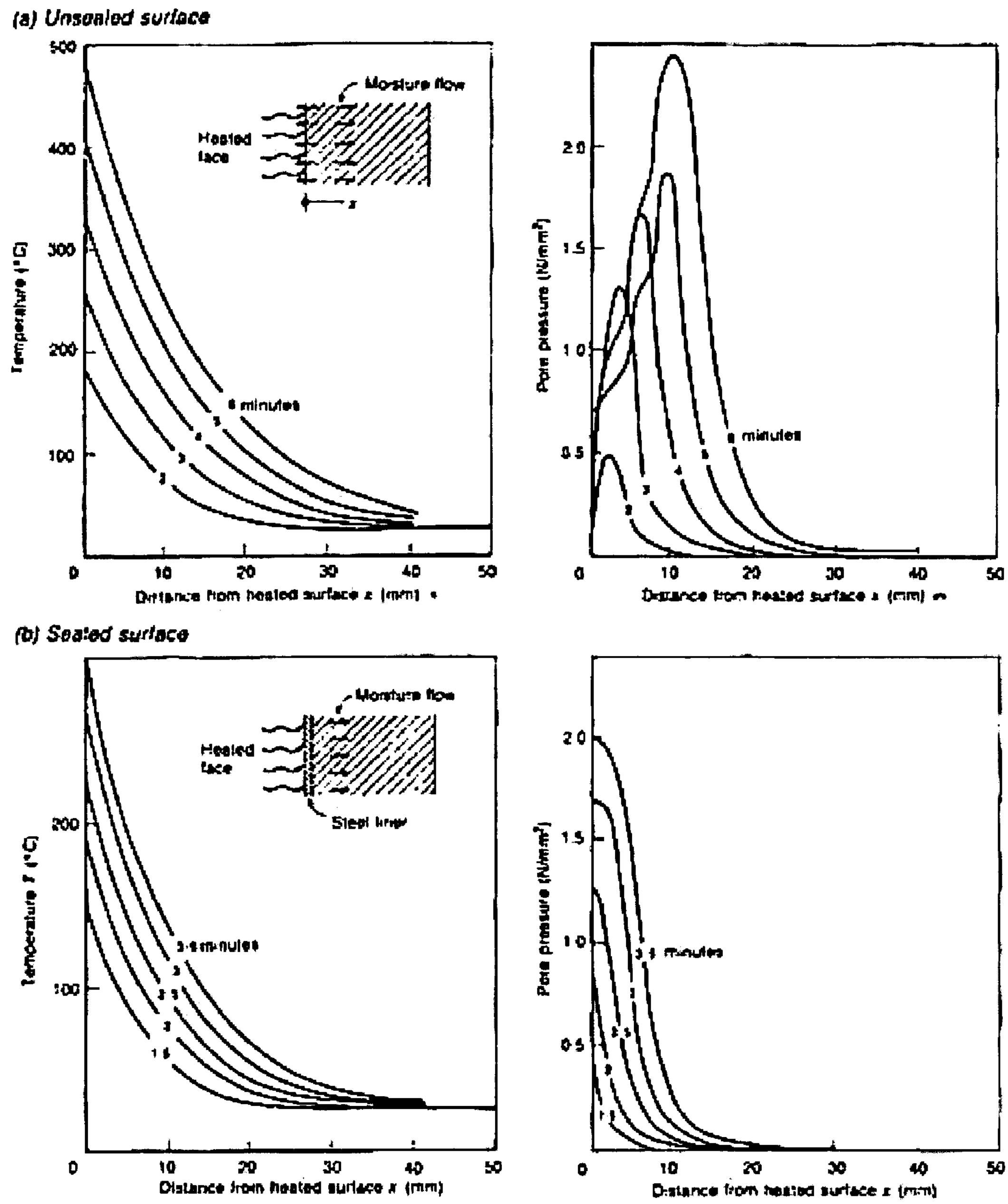


Figure 3.41: Relation between temperature and pore pressure, and distance, x, from heated surface. Thermal conductivity = 1.67J/m s °C, permeability = 10^{-12} m/s, saturation water content = 100kg/m^3, water/cement ratio = 0.50, unit mass of concrete = 2400kg/m^3, rate of heating = 80°C/min [85]

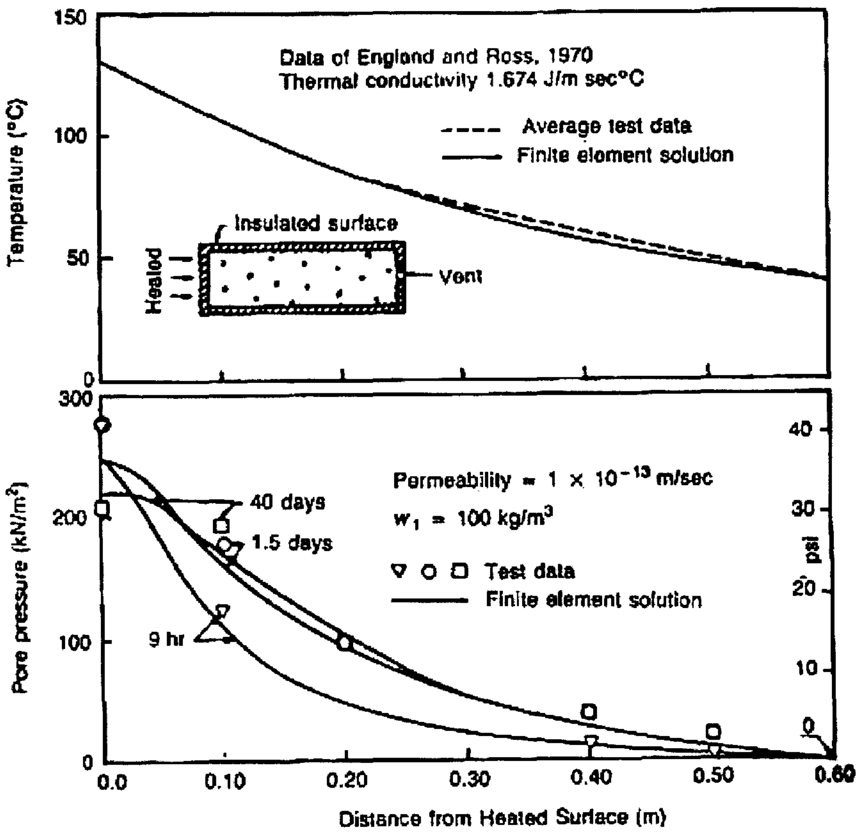
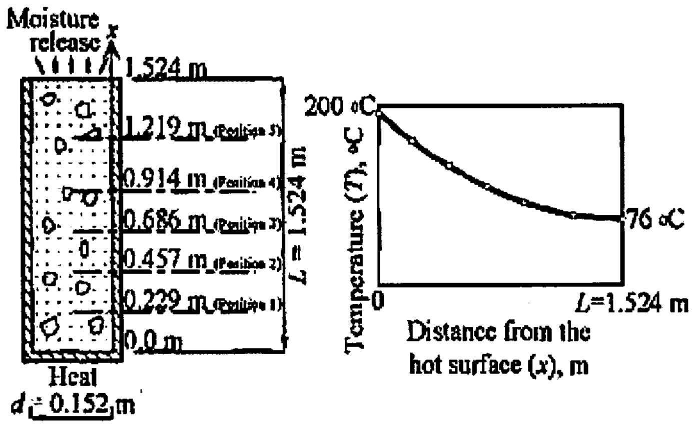


Figure 3.42: Fits of temperature and pore pressure distributions measured by England and Ross [46] (from [7] after Bazant and Thonguthai [82])

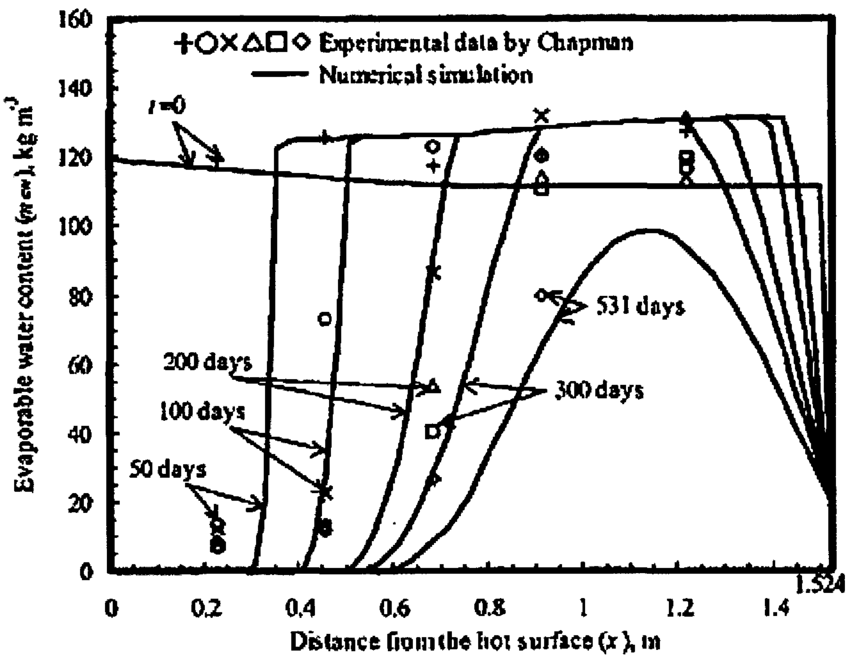
is that of England and Ross [46] and Chapman and England [47]. Figure 3.42 contains data points of concrete with a sealed face exposed to a temperature of 135°C compared to the model of Bazant and Thonguthai [82], which shows maximum pore pressures in the region of 0.2 to 0.3 MPa [7].

Ichikawa and England [48] have developed a model for pore pressures and moisture migration that was compared against the experimental work of Chapman and England [47]. The work of Chapman is specifically relevant considering that the hot face of the concrete was both sealed and exposed to 200°C for up to 531 days. A representation of the experimental set up is given in Figure 3.43 with the comparison between the developed model and experimental data for the moisture migration for up to 531 days.

It is important to note that there is still some moisture content within 0.2 m of the heated face for the first 50 days. The pore pressure development over time, shown in Figure 3.44 on page 79, demonstrates a reasonable correlation for the maximum pressures between the model and the experimental data of Chapman [47] for up to 300 days. The maximum pore pressure measured (t = 0) was in the region of 0.65 MPa.



a) Test specimen and temperature distribution



b) Comparison of simulated and experimental water content

Figure 3.43: a) representation of experimental set up and b) comparison between FEM model and data for water contents [48]

Xu et al. [16] reported data on the increase of porosity of unsealed concretes made with varying replacement ratios of fly ash of 0%, 25% and 55% and two different water:cement ratios of 0.3 and 0.5. These data suggest that lower water:cement ratios significantly reduced porosity, while higher replacement levels of fly ash had a minor effect of increasing porosity, and there is a reasonably stable increase in porosity with temperature up to 650°C. Of specific interest is that the porosity of a concrete exposed to 450°C with a water to cement:ratio value of 0.3 and fly ash replacement of 55% had a porosity of about 22%, which was in the region of a concrete not exposed to any temperature with a water:cement ratio of 0.5 and 0% fly ash replacement. This suggests that the increase in porosity, for a concrete with high fly ash content, is limited in the temperature ranges of interest for this project.

Interestingly Bazant and Thonguthai [82] suggest that above 100°C there is an increase in permeability by about two orders of magnitude. A suggested hypothesis for the cause of this is a reduction of the surface energy of capillary and gel pores because of the heating, causing the widening of necks in pores that would, at room temperatures, inhibit the migration of moisture.

Chloride transport

There has been limited work identified on the chloride ion durability of concretes exposed to temperature. The work of Xu et al. [16] provided some interesting insights into the chloride transport behaviour of concretes with varying replacement of fly ash (0%, 25% and 55%) and two different water:cement ratios (0.5 and 0.3), as shown in Figure 3.45. Figure (a) illustrates that both lower W:C ratios and higher FA replacement ratios provide a beneficial effect of inhibiting the transport of chlorides. This data suggests that a high proportion of FA in the region of 55% and a low W:C ratio can provide a concrete with lower chloride diffusivity after exposure to 450°C than an ordinary Portland cement concrete with a higher W:C ratio not exposed to high temperatures.

However the relative residual total charge passed, illustrated in Figure 3.45 (b), suggests that the presence of FA leads to a greater relative deterioration with exposure to temperature (i.e. after 450°C concrete with 0% replacement of fly ash allows 3 times as much charge to pass as unheated concrete, while concrete with fly ash allows between 4 and 6 times as much charge to pass after exposure to 450°C).

Conclusions on Transport Properties

The following conclusions can be drawn for the transport properties of concretes that have been heated to high temperatures:

- The PBMR has a situation whereby the hot face of the concrete is against a steel liner, which will prevent moisture from escaping this face. This creates high pore pressures in the concrete and forces moisture to migrate

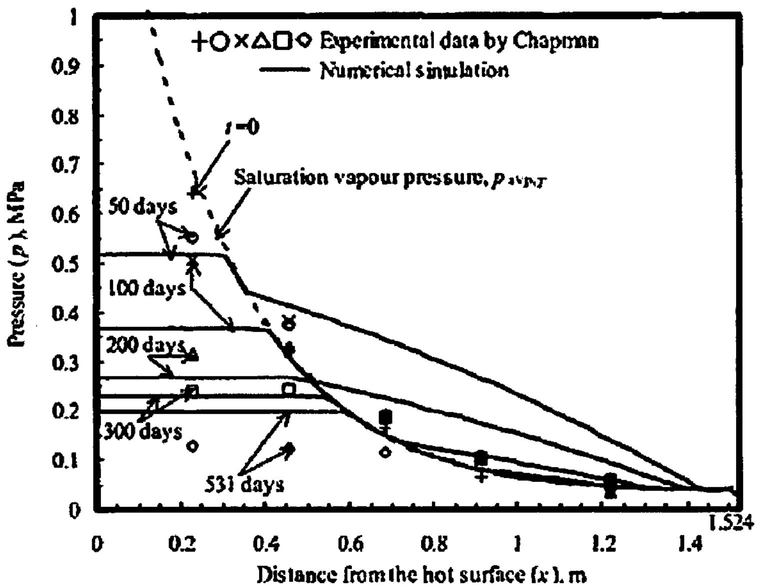


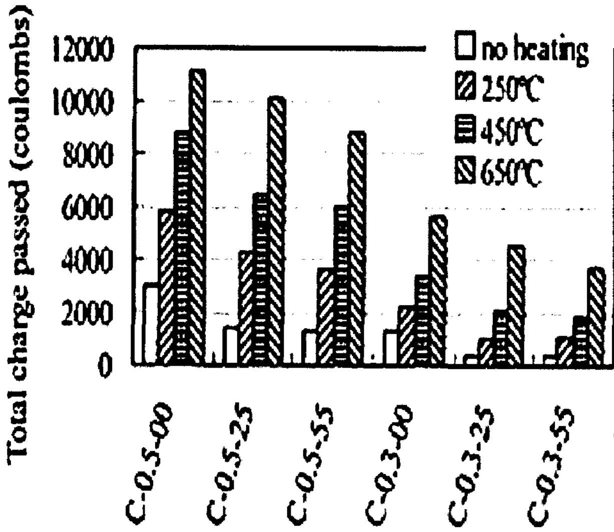
Figure 3.44: Comparison of simulated and experimental pressure distributions at various times [48]

Interestingly experimental results indicate that pore pressures are several orders of magnitude below the saturated steam pressures suggested in the ASME water tables [7]. This suggests that the pore space available to capillary water greatly increases with both temperature and pressure. Bazant and Thonguthai [82] suggest that this is due to a significant change in the porosity and permeability of a concrete above 100°C.

Porosity

There is a significant change in the pore size and size distribution with temperature [82]. It is believed this is because of an increase in pore space and more significantly a decrease in the adsorbed water in the solid phase of the binder. As Portland cement dehydrates at high temperatures it releases water molecules that are chemically bound at room temperature, causing a densification of the solid phase of the material and subsequent increase in porosity. The amount of water that is released with the dehydration of the cement has been found by several authors with a significant contribution from Harmanthy and Allen [43, 86].

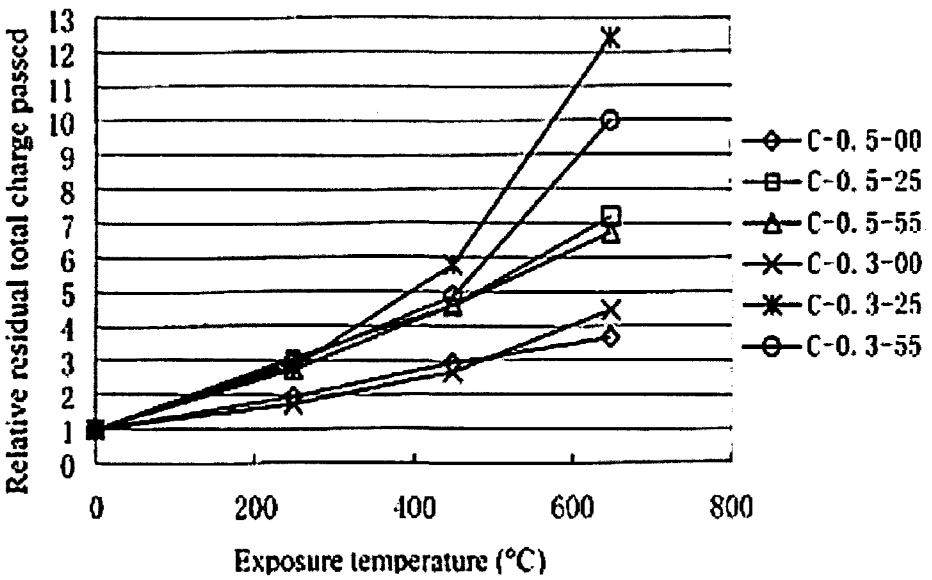
Kropp et al. [44] have investigated the development of pore size distribution with temperature for neat Portland cement pastes and pastes with significant extender addition in a sealed state, as shown in Figure 3.6 on page 36. It is apparent that hydrothermal reactions govern the pore size distribution of concrete heated in a sealed state, with the addition of siliceous materials such as fly ash reducing the impact of temperature.



Chloride ion penetrability based on charge passed

Charge Passed (coulombs)	Chloride Ion Penetrability
>4,000	High
2,000-4,000	Moderate
1,000-2,000	Low
100-1,000	Very Low
<100	Negligible

(a) Total charge passed



(b) Relative residual charge passed

Figure 3.45: (a)total charge passed and (b) relative charge passed by concretes with water:cement ratios of 0.3 or 0.5 and fly ash replacement ratios of 0%, 25% and 55% [16]

creates high pore pressures in the concrete and forces moisture to migrate through the wall of the concrete to escape on the cold face of the structure [82, 85].

- Concrete dehydrates relative to the temperature it is exposed to, allowing the development of further pore pressures in the concrete [73].
- High rates of heating can create significant pore pressures in concrete, where pressures in excess of 1 MPa are possible [83, 85]. This situation does not directly apply to the PBMR, where lower rates of heating can expect maximum pore pressures in the region of 0.6 MPa at temperatures of 200°C, gradually reducing over time [47].
- The high pore pressures near the hot face of the concrete are the primary driving mechanism for moisture migration through the wall [82]. At 200°C it could take moisture migration in excess of 500 days to reach equilibrium in a 1.5 m thick wall, with little or no moisture content in the hot region of the concrete [48].
- This implies that the concrete tends towards an unsealed state after a significant period of time in a sealed state of high pressure and water content.
- Lower water:cement ratios reduce porosity, while the use of extenders slightly increases the porosity [16]. Porosity increases with temperature exposure, largely related to dehydration of the binder causing densification of the solid phases of the concrete.
- A significant increase in permeability above 100°C can be expected, possibly due to smoothing of pore surfaces due to high surface energy [82].
- Chloride ion transport can increase up to 6 times with exposure to 450°C [16].

Considering the literature studied in this Section, it is apparent that high temperatures dehydrate the binder phase, cause the development of high pore pressures and the migration of moisture through the concrete. This has significant implications on the other properties of the concrete, with pore pressures and moisture migration possibly assisting microcrack development, and ultimately tending the concrete towards an unsealed state. Lower water:cement ratios appear to reduce both the porosity and chloride ion transport, while high extender contents significantly reduce chloride ion transport, when compared to concrete without extenders.

3.2.4 Thermal Properties

The thermal properties of a concrete exposed to temperature are particularly significant in the design of the reactor structure. As such, these properties need to be considered in depth. Fortunately, there is a significant body of literature available on this subject, with a certain degree of certainty and correlation with the results (unlike many of the mechanical and transport properties of a concrete). The thermal properties that are of interest are:

- Coefficient of thermal expansion
- Specific heat capacity
- Thermal conductivity

Of these, possibly the most important property from a material view is the coefficient of thermal expansion, while the specific heat capacity and thermal conductivity are relevant for the escape of heat from the structure (a structural design issue). Kugeler [33] has presented several models for these properties that were verified and validated against much of the literature discussed in this Section.

Coefficient of Thermal Expansion (CTE)

The coefficient of thermal expansion in a material is the normal linear strain caused by a change in temperature. As concrete is considered to be isotropic, where small differences between perpendicular planes is ignored, the CTE is considered to be a volumetric change, in that a unit volume of material expands the same amount in all directions. The CTE is significant in the context of a structure because different areas of concrete will likely be exposed to different temperatures, which will in turn create differential thermal expansions. This will cause stresses between these areas that can cause micro-cracking and even spalling.

The CTE of a concrete is directly related to the type of aggregate that is used, with aggregates with lower CTE values giving concrete with lower values. The interaction between the CTE characteristics of the aggregate and paste provide insight into the thermal limits that suit a concrete. First, consider the expansion/contraction characteristics of Portland cement as presented by Bazant and Kaplan [7] in Figure 3.46 using data from Harada et al., Philleo, Cruz and Gillen and Crowley [70, 87, 88, 89].

When one compares this with the expansion characteristics of common aggregates, shown in Figure 3.47 [7], it becomes apparent that up to approximately 200°C there is a reasonable correlation between the paste and aggregate. Above this temperature the paste and aggregate diverge in expansion.

This matched thermal expansion up to 200°C coupled with densification of the CSH phase correlates well with the improvement, or at the very least retention, of strength experienced by concrete around these temperatures. Above this temperature the cement paste begins to contract, while the aggregate accelerates in expansion, indicating the differential thermal expansions that would be happening on a micro-structural level. This would likely cause the

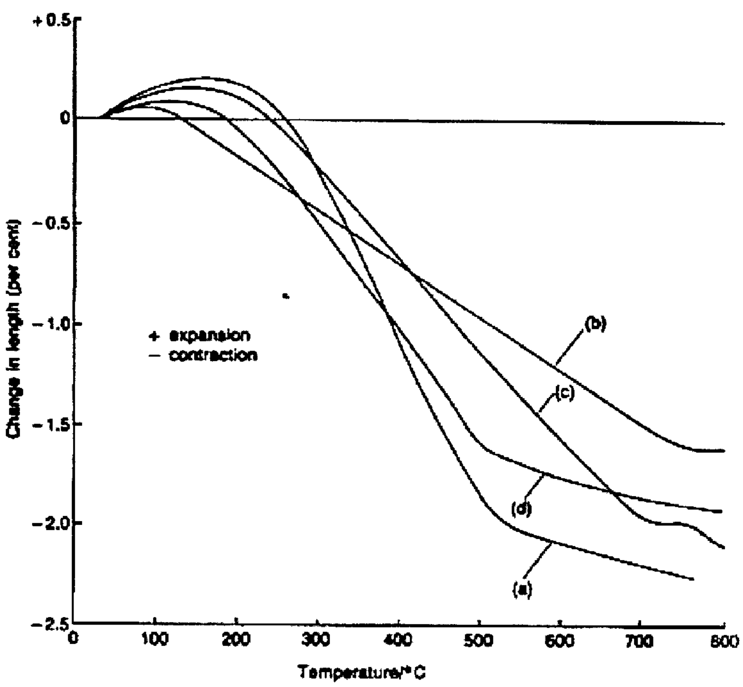


Figure 3.46: Length change of Portland cement paste specimens at various temperatures. a) Philleo; b) Harada et al.; c) Cruz and Gillen; d) Crowley [70, 87, 88, 89]

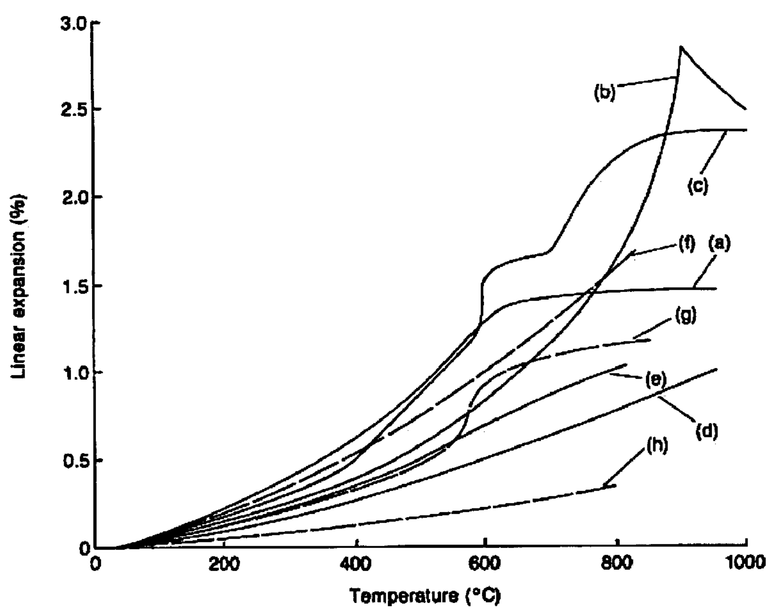


Figure 3.47: Linear thermal expansion of various rocks with temperature: (a) sandstone; (b) limestone; (c) granite; (d) anorthosite; (e) basalt; (f) limestone; (g) sandstone; (h) pumice [7]

development of micro-cracks in the concrete, with a subsequent loss in mechanical properties, even at 450°C.

Figure 3.48 illustrates this point effectively, where aggregates with high silica contents and therefore high CTE values cause concrete to expand more than concrete with aggregate of a lower CTE value [7]. It also illustrates the point that up to about 200°C the cement paste and aggregate expand with reasonable correlation, but above this temperature the CTE characteristics of the aggregate dominate. This is even more clearly illustrated by the CTE of the quartzite concrete, with a significant jump at the transition of α-quartz to β-quartz around 575°C accompanied by a large expansion in the volume of the aggregate.

Some values for the effect that temperature has on coefficient of thermal expansion are presented in Table 3.6 [90].

Table 3.6: Coefficient of thermal expansion at elevated temperatures for concrete made with different aggregates [90]

Type of aggregate in concrete	Coefficient of thermal expansion (10^{-6}°C^{-1})		
	Below 300°C	300-600°C	600-800°C
Granite	0.71	10.4	15.9
Serpentine	4.14	4.1	1.3
Limonite	4.86	4.5	4.2
Haematite	5.94	11.5	16.2
Steel Shot	4.20	8.5	16.2
Iron and Steel Scrap	5.1	7.2	8.6

Dimensional instability When concrete is exposed to high temperatures and subsequent cooling, the concrete generally exhibits a net expansion or contraction, i.e. it is dimensionally unstable on exposure to high temperatures [7]. This is due to several factors, dehydration of the cement paste and development of micro-cracking being two of the biggest contributors. Figure 3.49 is a good illustration of this, given by Harmanthy and Allen [86], who reported the dimensional changes of either a siliceous or expanded slag aggregate concrete on heating to 1000°C and after cooling.

An interesting point to note in this Figure is the net effect that the quartz transition has on the expansion properties of a siliceous concrete, causing a residual expansion as opposed to a net contraction found for the expanded slag concrete. Zoldners [91] has reported the residual linear deformations of several concretes that further support the observation of the impact that silica content has on concrete expansion. Sandstone and gravel aggregate concretes expanded significantly more than limestone concretes, while an expanded slag concrete (thus a lightweight concrete) experienced a net contraction.

Khoury et al. [92] presented some data on the residual expansions of different types of concrete exposed to 600°C. Lightweight, basalt, limestone and

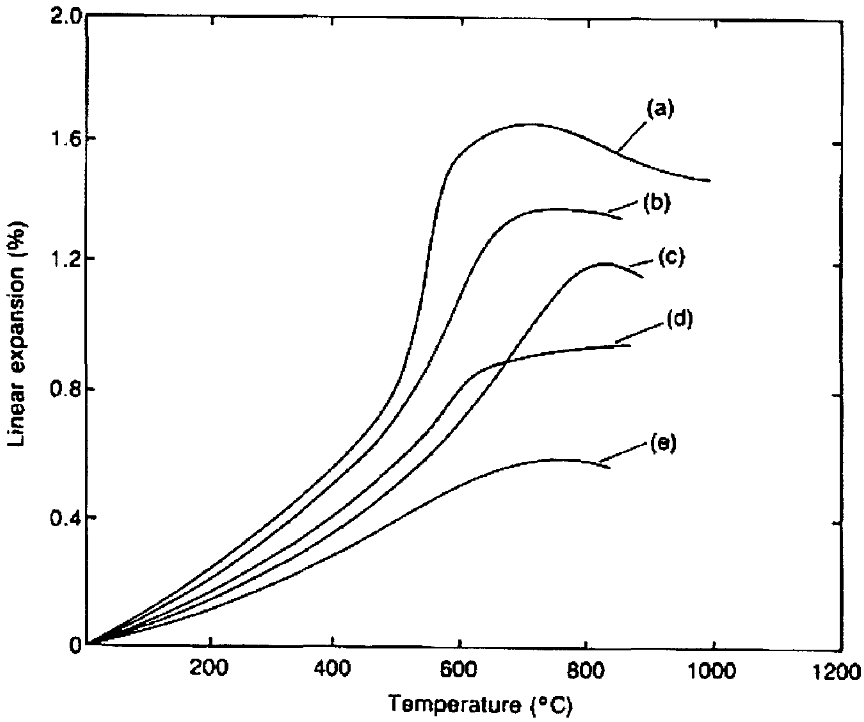


Figure 3.48: Linear thermal expansion of concretes made with various conventional aggregates as a function of temperature [7] (adapted from Schneider [38]): a) quartzite; b) sandstone; c) limestone; d)basalt; e) expanded slag

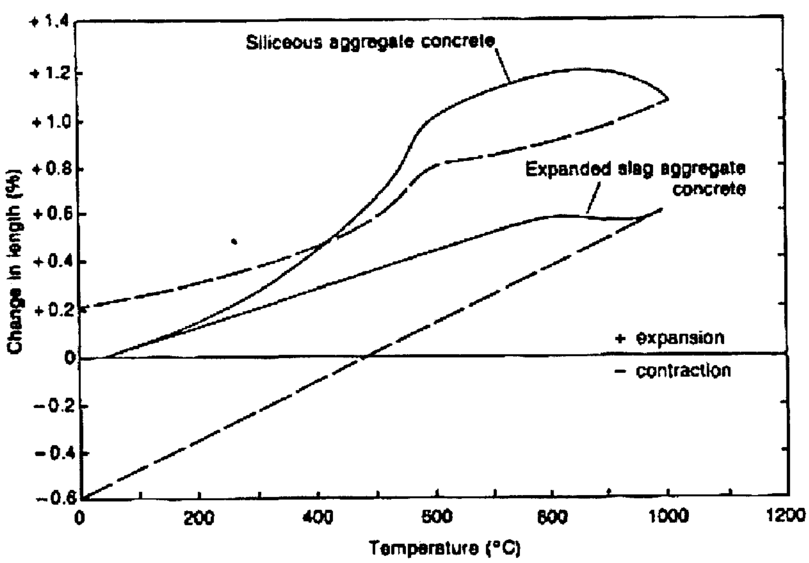


Figure 3.49: Length change of concrete specimens made with various aggregates during heating - cooling cycles [86]

siliceous gravel aggregate concretes were tested, with a net shrinkage of 0.4%, approximately 0% and expansions of 0.55% and 1.15% respectively. This clearly demonstrates that lightweight aggregate concretes allow the cement paste to control the expansion properties of the concrete, while conventional concretes are largely dominated by the expansion properties of the aggregate, where silica content is a reasonable indicator of the expansion characteristics.

The dimensional instability of a concrete after exposure to one thermal cycle suggests that there will be different expansion responses of the concrete on subsequent thermal cycles. It appears that thermal cycling can lead to a phenomenon called thermal growth, namely a gradual permanent expansion of the concrete [23, 78, 93].

Sullivan [94] has stated the importance of recognizing that the expansion properties on subsequent cycles of heating will be different to those of the first cycle, and suggests that these cycles follow the cooling curve of the first cycle. The phenomenon of thermal growth does however suggest that there will be a certain amount of hysteresis with each heating cycle, largely caused by the differential thermal expansion properties of the paste and aggregate [7].

Other Thermal Properties of Interest

The other thermal properties of concrete that are of significant interest are those of specific heat capacity (C_p) and thermal conductivity (K). These properties have little significance in the context of the mechanical and transport properties of the concrete, but are important in the context of designing the structure for thermal management and escape of heat. These properties are particularly significant in an accident situation, where the thermal diffusivity (D $= K/C_p\rho$) determines the temperatures reached in the wall and how quickly these temperatures are reached.

Specific heat capacity (C_p) Specific heat is the amount of heat required per unit mass to change the temperature by one degree, and the SI units are $Jkg^{-1}K^{-1}$. Generally concrete C_p values are in the region of 0.5 to $1.13Jkg^{-1}K^{-1}$ at normal temperatures [23]. Carman and Nelson [95] have suggested that the specific heat of concrete at normal temperatures is not affected by aggregate type, mix proportions and age. It has been suggested that the main factor affecting the specific heat of concrete at normal temperatures is the moisture content at the time of heating because water has a high C_p of $4.19Jkg^{-1}K^{-1}$ [7]. Up to about 150°C the moisture content plays a large role in the specific heat of a concrete; with concrete that is initially wet, heating to 90°C can cause a rapid but temporary increase by two to three orders of magnitude due to the vaporization of free water [96, 97]. At about 150°C C_p values are similar to initially dry concretes, and increase linearly with higher temperatures [96]. Zoldners [91] found the mean specific heats between 25°C and 400°C for four different concretes, gravel, limestone, sandstone and expanded slag, to be 0.959, 0.988, 0.976 and $0.930 Jkg^{-1}K^{-1}$ respectively. This is in broad agreement with Figure 3.50 [7].

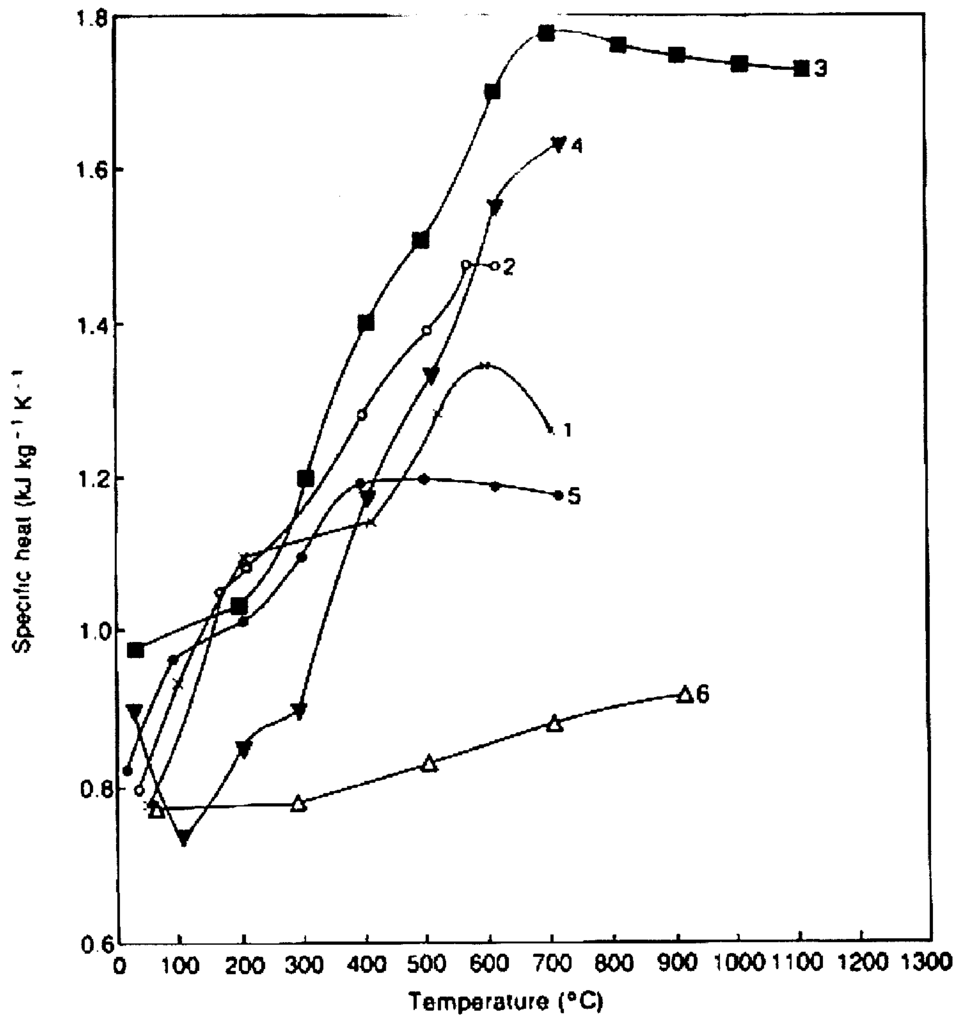


Figure 3.50: Effects of temperature on measured specific heats of various concretes [7]: (1) Limestone aggregate concrete [86]; (2) Siliceous aggregate concrete [86]; (3) Siliceous aggregate concrete [98]; (4) Limestone aggregate concrete [98]; (5) Limestone aggregate concrete [99]; (6) Granite aggregate concrete [100]

Thermal Conductivity (K) Thermal conductivity is the ability of a material to conduct heat. It represents the uniform flow of heat through a material of unit thickness over a unit area subjected to a unit temperature difference between the two opposite faces. Generally used units for thermal conductivity are $Wm^{-1}{}^{\circ}C^{-1}$. At normal temperatures the thermal conductivity of concrete depends on the water content of the concrete and the conductivity values for the aggregate. Blundell et al. [96] reported the thermal conductivity of concrete between 5°C and 25°C made with different aggregates that shows some correlation with the silica content of crystalline aggregates, as shown in Table 3.7. Zoldners [101] suggested that concrete that has been air dried to moisture content less than 50% of saturated concrete would experience a 25% reduction in conductivity.

Table 3.7: Thermal conductivity for saturated concrete at temperatures between 5 and 25°C ([7] after [96])

Aggregate type		Thermal Conductivity for Concrete ($Wm^{-1}°C^{-1}$)
1	Siliceous rocks e.g. Quartzite and sandstone	2.4 - 3.6
2	Igneous crystalline e.g. Granites and gneisses Sedimentary carbonate e.g. Limestone and dolomite	1.9 - 2.8
3	Igneous amorphous e.g. Basalts and dolerites	1.0 - 1.6

Harmanthy [43] has calculated the thermal conductivities of four oven dried concretes for between 25°C and 1000°C using aggregates of quartz, anorthosite and two lightweight expanded shales. These concretes had densities of 2.295, 2.333, 1.417 and 1.173$g\,cm^{-3}$ respectively, with the quartz representing crystalline aggregate and anorthosite representing amorphous aggregate. These are envelope values of concrete, considering Figure 3.51, the area between graphs (a) and (b) represents the envelope of conventional concrete and the area between graphs (c) and (d) represents the envelope of lightweight concrete.

Various determinations of non oven dried concrete are given in Figure 3.52 [7]. This graph indicates that there is a reasonable correlation between concretes up to around 300°C. Above these temperatures, Kugeler has collated a large amount of data that suggests significant variation in concrete response [33].

Thermal Diffusivity (D) Thermal diffusivity is an indication of the rate at which temperature changes can occur in a material. It is thus a useful value when considering the transient response of a material to temperature. Diffusivity can be calculated from D = $K/C_p\rho$, where K is thermal conductivity, C_p is specific heat capacity and ρ is density.

At normal temperatures the thermal diffusivity of a concrete is largely dependent on the diffusivity of the aggregate, ranging from $0.68 \times 10^{-6} m^2 s^{-1}$ for basalt concrete to $1.89 \times 10^{-6} m^2 s^{-1}$ for quartz aggregate concrete [7]. Harmanthy and Allen [86] have suggested upper and lower limits for normal weight concretes made with siliceous and calcareous aggregates, and lightweight concretes as shown in Figure 3.53 on page 91. Tests carried out by Abrams et al. [80] on oven dried normal concrete indicated a near linear decrease of about

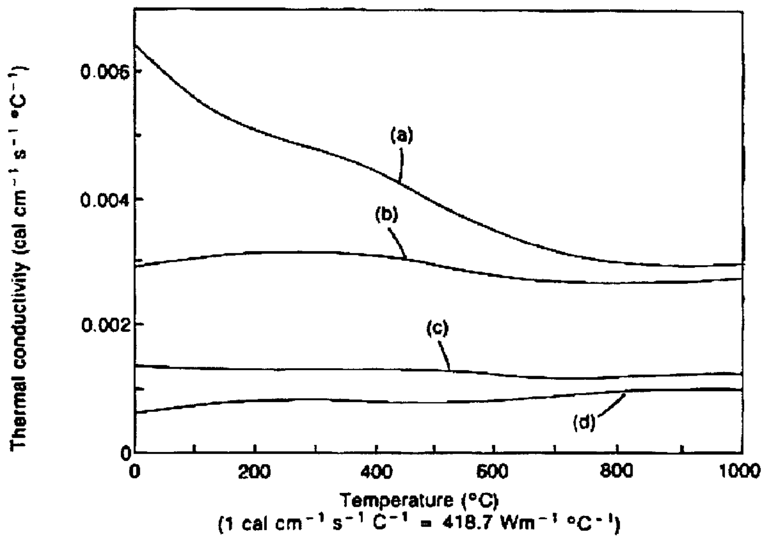


Figure 3.51: Thermal conductivity of various oven-dried concretes as a function of temperature [43]: (a) quartz concrete aggregate; (b) anorthosite aggregate; (c) expanded shale aggregate A; (d) expanded shale aggregate B

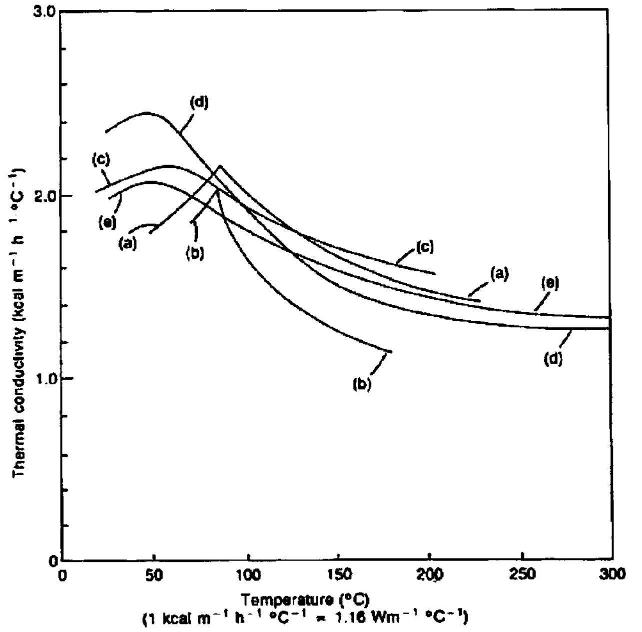


Figure 3.52: Thermal conductivity of various concretes that were not oven-dried before test, as a function of temperature [7]: (a) limestone aggregate concrete [102]; (b) barites aggregate concrete [103]; (c) gravel aggregate concrete [103]; (d) quartzite aggregate concrete [78]; (e) quartzite aggregate concrete [78]

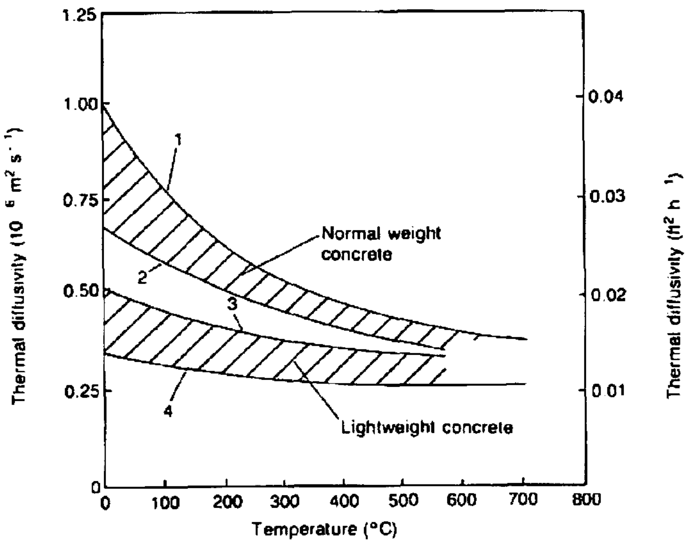


Figure 3.53: Effect of temperature on thermal diffusivity of concrete made with siliceous and calcareous aggregates and with lightweight aggregates [86]

30% on heating to 650°C, while on subsequent cooling there was a permanent decrease of diffusivity of about 25%.

Figure 3.54 is a collection of data on concrete done by various authors as presented in the work of Bazant and Kaplan [7]. Clearly, although there is a significant variation in actual values, the fundamental trend of a gradual reduction in thermal diffusivity with temperature is apparent. There is also reasonable correlation with the boundaries suggested by Harmanthy and Allen.

Conclusions on Thermal Properties

There is an extensive body of literature available on the thermal properties of heated concretes that demonstrates a reasonable correlation. The conclusions that can be drawn include:

- Coefficient of thermal expansion is governed by the expansion properties of the cement paste and aggregate. Up to about 200°C the paste and aggregate have similar expansions, above which the paste begins to shrink and the aggregate expands. The aggregate dominates the expansion of normal weight concretes at these temperatures, while cement paste dominates the expansion of light weight concretes [7].

- Concrete generally experiences a net contraction or expansion, dependent on the final temperature the concrete is exposed to and the type of aggregate used [7, 91].

- The concrete will follow a different path of thermal expansion with subsequent heating cycles after the first, probably similar to the cooling path

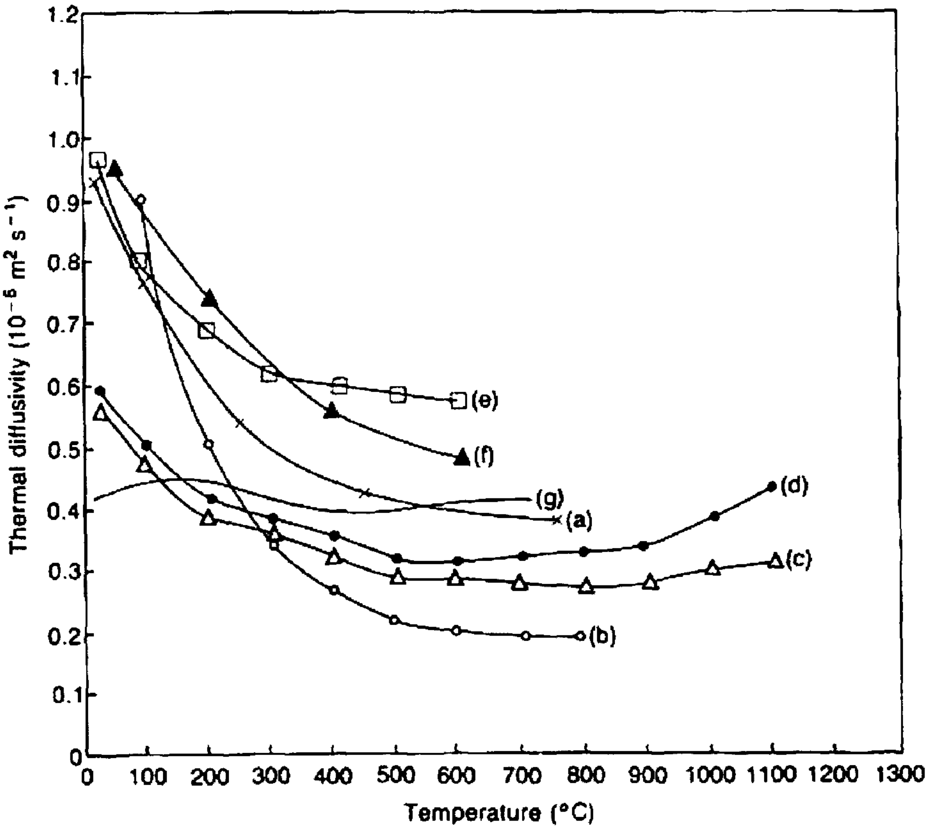


Figure 3.54: Thermal diffusivity of Portland cement concrete made with siliceous aggregates as a function of temperature [7]: (a) siliceous aggregate concrete [70]; (b) Limestone aggregate concrete [104]; (c) Limestone aggregate concrete [98]; (d) siliceous aggregate concrete [98]; (e) siliceous aggregate concrete [105]; (f) granite aggregate concrete, basalt concrete [38]; porous shale aggregate concrete [38]

of the first cycle. The concrete will also probably expand with thermal cycling according to the phenomenon of thermal growth [94].

- The specific heat capacity appears to be quite variable with temperature, but is largely governed by the water content of the concrete up to 150°C. Above this temperature the concrete response is the same as dried concretes, with aggregate playing a significant role [7].
- The thermal conductivity of a concrete is largely related to the crystalline nature, and silica content, of the aggregate used [96]. For normal weight concretes that have not been oven dried there is a reduction from about 100°C to 300°C, after which the conductivity appears to be relatively stable [7].
- Thermal diffusivity is a measure of the ability for temperature changes to occur in a material. The diffusivity generally reduces with temperature [7].

There is clearly a significant body of literature available concerned with the thermal properties of the concrete. As has already been mentioned, much of this literature has been correlated into models of each of the properties, as presented by Kugeler [33].

3.2.5 The Effect of Temperature on Steel Reinforcement

All of the data for this section was collected from Nuclear Regulatory Commission Literature Study carried out by Naus [14]. The effect of pre-stress on concrete at high temperatures is beneficial, as has already been clearly illustrated, however steel itself and the bond strength between the cement and steel, are affected by high temperatures, and need consideration. Although this topic is not necessarily directly related to the project, it is significant in terms of the greater ability to design the structure and as such becomes useful to include here.

The Effect of Temperature on Steel

When one considers the response of steel to high temperature, Figure 3.55 contains the stress-strain characteristics, modulus of elasticity and yield strength (all with respect to temperature) [106]. This Figure clearly illustrates that although the temperatures under consideration for the project have little effect on the residual properties of the steel, there is some effect on the properties of the steel at the temperatures of interest (225°C and 450°C). A good example of this is the change in modulus of elasticity up to 450°C. This will have consequences in terms of pre- or post- stress in the structure. This set of data appropriately addresses the mechanical properties of interest for steel.

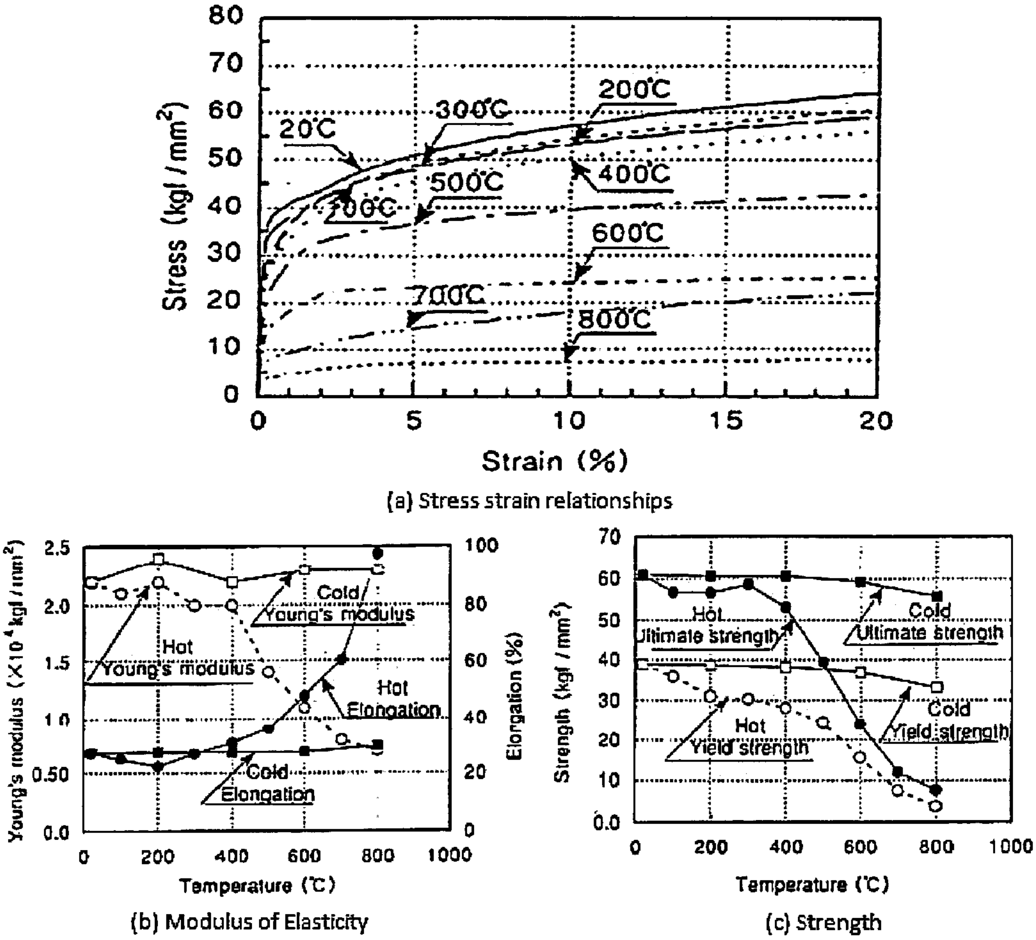


Figure 3.55: Response of reinforcing steel to high temperatures: (a) stress strain characteristics, (b) Modulus of elasticity, (c) strength [106]

Figure 3.55 illustrates that at 225°C the effect of temperature on reinforcing steel is limited. Apart from the yield strength which demonstrates about a 25% reduction, all other properties demonstrate only a slight decrease. There is a greater change when the steel is exposed to 450°C. All of the properties appear to experience a significant, deleterious change at this temperature, including a drop in yield and ultimate strengths and modulus of elasticity. This could have implications on the response of a structure exposed to these temperatures.

The thermal properties were effectively considered up to the melting point of steel by Schneider et al. [74], as shown in Figure 3.56. Ultimately, matching of the thermal responses of all of the constituents of a structural concrete under high temperatures will lend itself to improved properties of the concrete material and the overall structure.

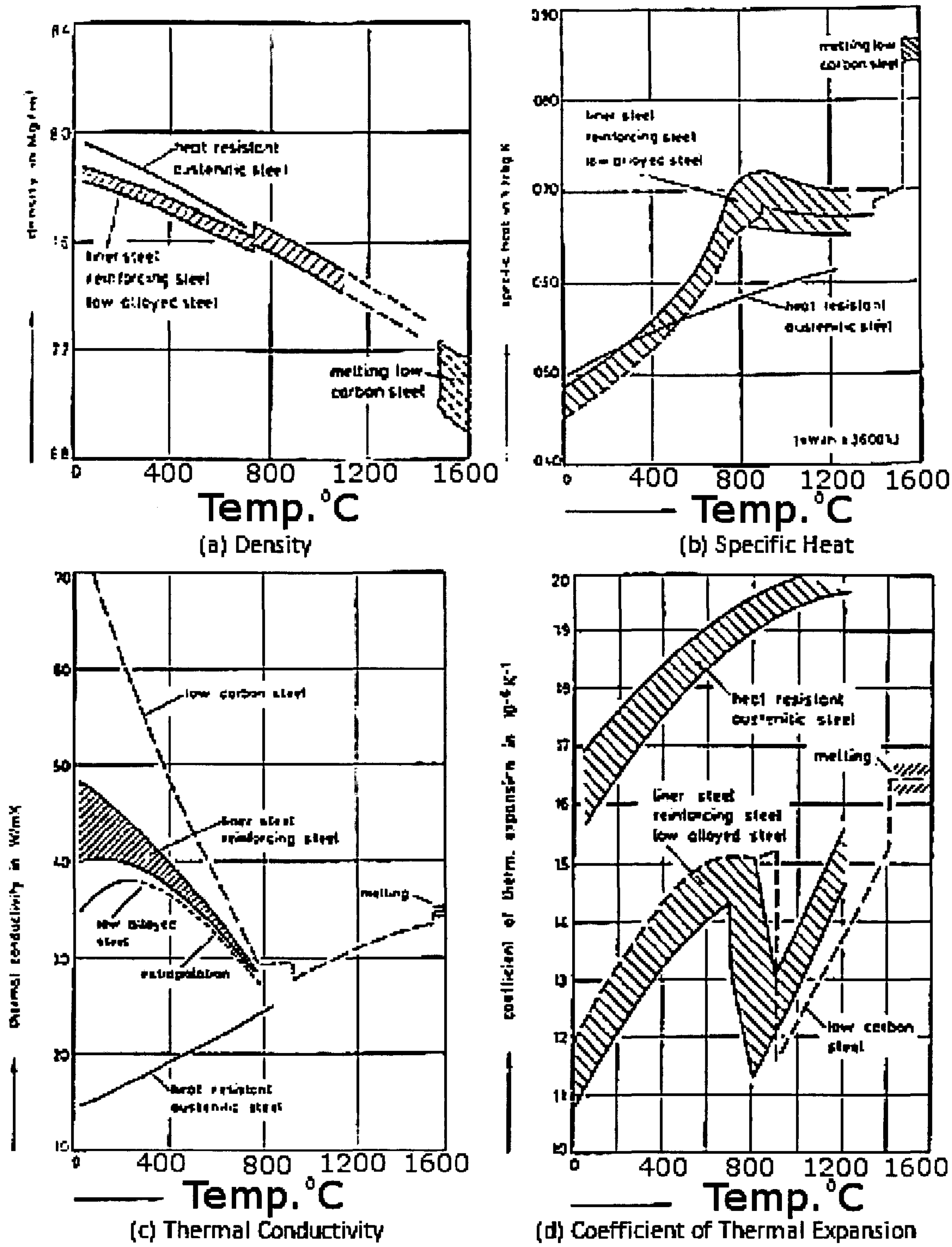


Figure 3.56: Thermal properties of structural steel: (a) Density, (b) Thermal conductivity, (c) Specific heat, (d) coefficient of thermal expansion [74]

Bond Strength Between Concrete and Steel with Temperature

While the properties of the steel are important, in terms of pre-stressed concrete, the bond strength between the steel and concrete is of equal or even greater significance. The bond between steel and concrete primarily arises out of friction and adhesion with the cement matrix [12]. In terms of bond strength the primary focus of literature appears to have been on comparing ribbed and plain round bar, with ribbed bar showing a significant improvement in high temperature property retention over plain round bar. Figure 3.57 indicates the response between plain and ribbed bars [107].

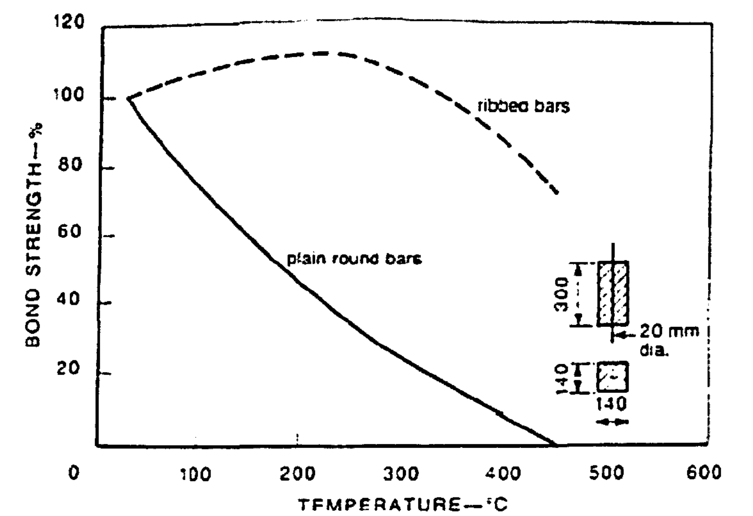


Figure 3.57: Bond Strength of Ribbed and Plain Round Bars [107]

This figure clearly emphasizes the necessity of using ribbed bars in a concrete design for high temperature. The diameter of steel bar has a small effect, with the optimal selection in terms of bond strength being highly dependent on the target temperature while not considering the effect the temperature has on the mechanical properties of the steel [108]. Figure 3.58 supports this point, and the necessity to use ribbed bars, with the conclusion that 12 mm ribbed bar is probably the most ideal.

The selection of aggregate has a substantial effect on the bond strength of a concrete, as shown by Figure 3.59 [110]. With the exception of limestone aggregates that had a bond strength in excess of the room temperature bond strength to about 300°C and above 90% for 450°C, the bond strength for all other aggregates tested was approximately 80% at 450°C.

The effect of different curing conditions (sealed/unsealed; water/air) on bond strength for extended periods of heating at 175°C is shown in Figure 3.60 by Hirano et al. [79]. This Figure indicates that bond strength increases with time in sealed conditions, while unsealed conditions have lower bond strength.

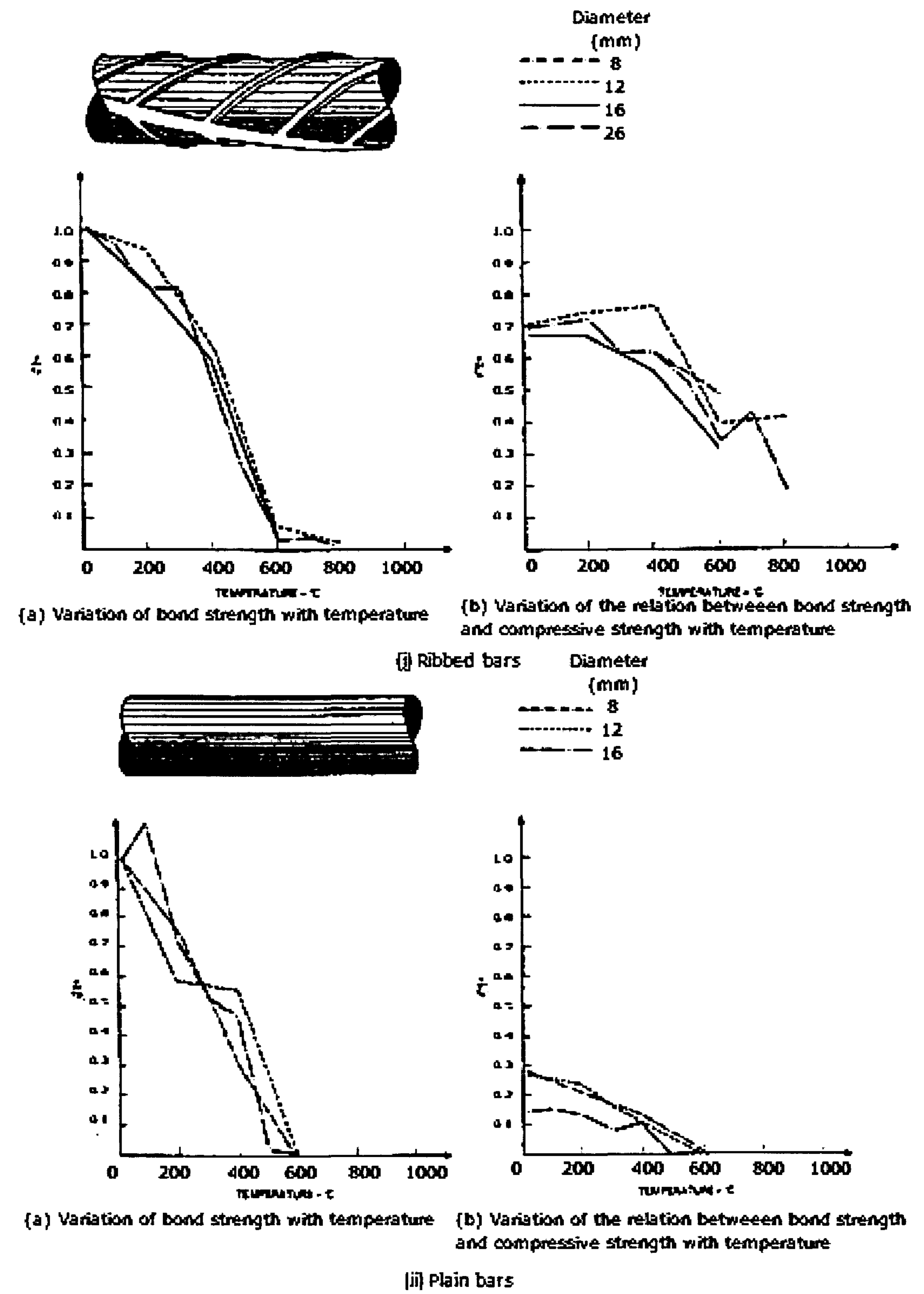


Figure 3.58: Effect of Bar Diameter on Bond Strength after Elevated- Temperature Exposure: (i) ribbed bars, (ii) plain bars [108]

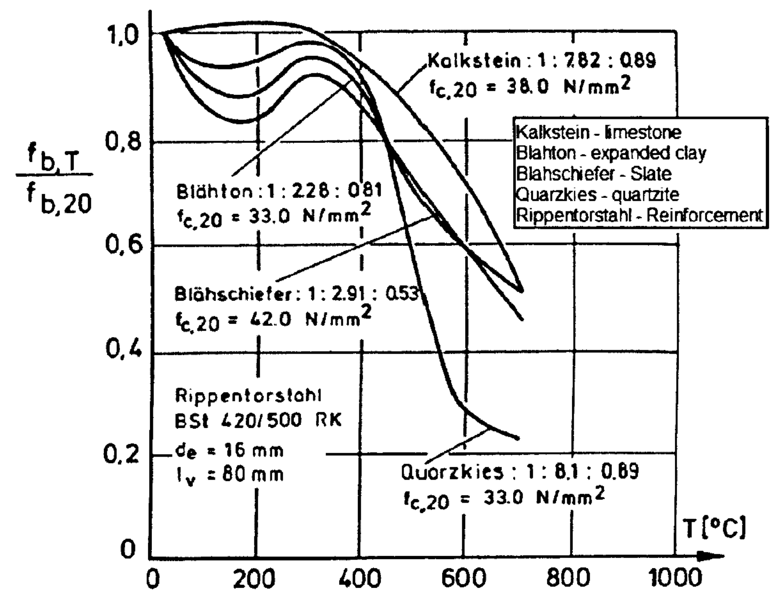


Figure 3.59: Bond between Concrete and Deformed Bars Exposed to High Temperature [110]

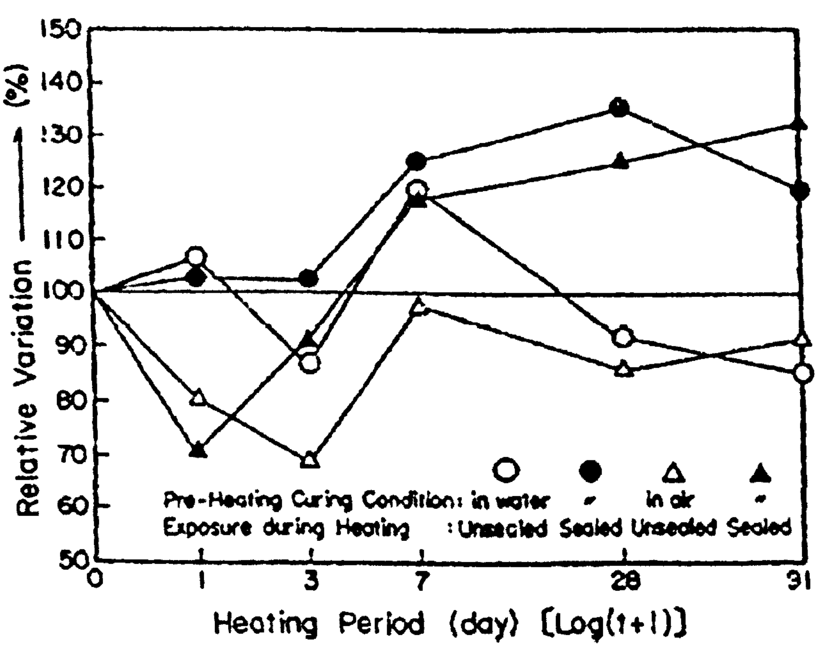


Figure 3.60: Relative Variation in Bond Strength at Start of Pull Out for Hard Sandstone Aggregate Concrete after Various Heating Periods at 175 °C [79]

Conclusions on Steel Reinforcement

With this summary of some of the key aspects around steel reinforcement it should be apparent that the use of steel in concrete at high temperature, both as reinforcement and pre-stressing, does require careful assessment. It is apparent however that it should be possible to design a concrete with steel reinforcement at the temperatures being considered. Some of the key considerations are:

- Special consideration needs to be given to the mechanical properties of the reinforcing steel and prestressing cables, namely the yield strength and modulus of elasticity [106]. This is needed to ensure that the conditions of reinforcing and stressing that are designed for the structure are maintained.

- The thermal properties of reinforcing steel also require careful assessment to ensure matching of properties such as thermal expansion.

- The use of ribbed bars is strongly recommended, probably in the region of 12mm diameter for reinforcement [108]. This has been shown to provide the best response to temperature.

- Aggregate choice, moisture condition, and time at temperature all have an effect on the bond strength [110]. Limestone appears to have the best response to in excess of 450°C, while a sealed condition appears to significantly increase the bond strength with extended periods of heat exposure [79].

The literature study concludes with this summary of the key aspects concerning steel reinforcement. It should be apparent that there are a multitude of factors that require consideration in the design of both the material and the structure.

Chapter 4

Testing and Modeling Techniques and Systems

4.1 Introduction to Testing and Modeling

Testing of concretes at high temperatures can be complicated and due care needs to be taken to ensure that the correct data are collected, as explained by Pihlajavaara [36]. The correct collection and presentation of data, as well as the importance of well thought out testing processes, is a key lesson learned from this project, with some attempts at testing proving to be insufficient against these criteria, as explained later in this Chapter.

One also needs to consider the depth and breadth of literature available on the subject that indicates that many avenues of research have been considered in depth. An excellent example of this are the thermal properties of a concrete, for which there is a significant body of literature that correlates fairly well, allowing for the development of models and functions to predict the material response to temperature.

The development of testing processes and apparatus can also use this body of literature as there are many publications that describe the testing methods used [7, 53]. Care does however need to be taken with this approach, as translation from a brief discussion in literature to a complete testing methodology can lead to problems with testing, as experienced with the sealing methods in this project, described in Section 4.4.

Keeping in mind the ultimate goal of this project was to research a concrete that could withstand temperatures of 225°C for operation and 450°C for accident scenarios, such as a LOCA, Figure 4.1 was developed to summarize the work that needed to be done for any concrete mix design. Ideally at least all mechanical and transport properties should be physically tested for a concrete to be qualified for use in nuclear reactors, however, practically this proves to be difficult and unnecessary while still at the point of testing the mix design philosophy, as carried out in this project.

The property of primary interest for testing, strength, was focused on to

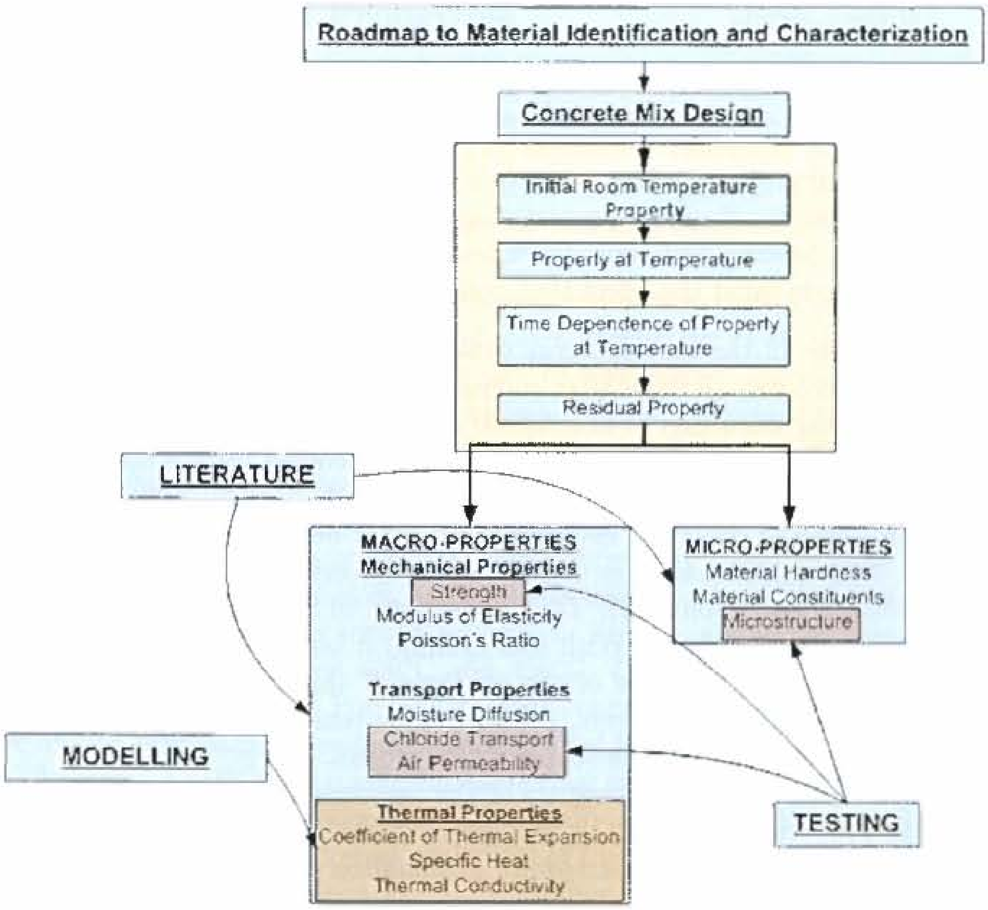


Figure 4.1: Road map to the characterization of high temperature concrete

gain an understanding of the response of the property to temperature. It was also used to validate the concepts gained from literature. A secondary focus of testing, largely relating to the transport properties of the concrete, was also carried out. These properties are useful in the context of understanding the effect of temperature on the durability of concrete structures and give an indication of changes to the microstructure of the concrete (porosity, interconnectedness of pores, microcracking).

Figure 4.1 indicates the appropriate areas where literature, testing or modeling were to be used to analyze the concrete response to temperature. Using these three in tandem ultimately would allow the cost and time effective analysis and development of the material.

The key stages of heating that need to be assessed for any property being considered are:

- Initial room temperature property - The unheated property of the concrete.

- Property at temperature - The response of the property to first heating of the concrete.

- Time dependence of property at temperature - The changes that occur to the property with length of exposure to high temperatures.

- Residual property - The property once the concrete has been cooled from temperature. Residual properties can also be used to assess the response to first heating and time dependence of the property of interest, while keeping in mind the effect that cooling would have on these results.

Herein lies one of the first concepts drawn from literature. Concrete testing for this project was all done after cooling, i.e. were residual properties. This was for varying durations of heating, to address the property at temperature and time dependency of the property. Although cooled testing does not give the same results as a concrete tested hot, trends derived from literature suggest that unsealed concretes experience a drop of between 10% and 20% with cooling, while sealed concretes experience a recovery of strength of about the same amount with cooling [7]. This is discussed in Section 3.2.2.1, supported by Figure 3.14 on page 48. With this in mind it became appropriate to only consider the cooled response of the concrete at this stage. With confirmed concrete mix design parameters, the testing at temperature would become a necessity, but was beyond the scope of this project.

A brief summary from literature of the response that can be expected for all of the properties of interest, is now given. There are two assumptions about the state of the concrete that require explanation with a view to defining a constant state through which properties can be defined. These assumptions are:

- The moisture state on testing of a concrete is either sealed or unsealed. Although there is a continuum of states between these two, effectively defining the response of a concrete in these states should define the envelope to the response of concrete.

- Specifically the response of the concrete will be considered without pre-stress. This is because, apart from the effect on creep, pre-stress generally provides a beneficial effect with all properties [7]. Strength retention and modulus of elasticity have clearly been shown to be positively affected by the application of pre-stress. It is also noteworthy that pre-stress will likely have a positive effect on the retention of transport properties, as the development of micro-cracks will be reduced.

Interestingly ACI 349 [3] places a stipulation that the response of a concrete exposed to temperatures higher than the limits imposed by the code has to be proven to be sufficient in both a stressed and an unstressed state, further supporting the consideration of unstressed concrete.

Literature relating to the properties of interest are now summarized, with focus on temperatures of 225°C and 450°C.

4.1.1 Mechanical Properties

Strength Concretes can give a wide range of strength response to high temperatures [52], dependent on both intrinsic factors such as material constituents and on the environmental conditions of exposure. There can be an improvement in strength up to 250°C after which there is generally a deterioration with higher temperatures. The causes of this improvement of strength were given particular focus.

For concretes with fly ash replacement ratios in excess of 50% that have been exposed to temperatures around 225°C, Seeberger et al. [17] and Kropp et al. [44] have illustrated that there can be a significant increase in strength in sealed states, when compared to normal Portland cement concretes. This strength gain can be anywhere in the region of 20% to in excess of 50%. There has been no data identified on what happens to a concrete with these mix proportions at temperatures in excess of about 250°C in a sealed state. Xu et al. [16] and Poon et al. [55] have sufficiently demonstrated that for unsealed concretes with high fly ash contents and short term transient heating environments, a concrete should be able to achieve about the same as the unheated strength between 400°C and 450°C. This response was better than the response of a normal Portland cement concrete, which suggests that the use of high pozzolanic extender contents is ideal for high temperature concrete.

Aggregates with a low coefficient of thermal expansion are useful in limiting the development of microcracking, specifically amorphous igneous rocks [7]. Limestone, which has the lowest coefficient of thermal expansion of all common aggregates, appears to encourage hydrothermal reactions relating to calcium oxides in sealed concretes [17], causing a significant reduction in strength.

The use of fibres in the context of strength would suggest steel fibres improve the strength retention and ductility of concrete, especially once the concrete is developing microcracking above 250°C [59].

The time dependency of strength is difficult to determine as it is intrinsically related to the mix design used, and specifically related to hydrothermal reactions in the paste and aggregate-paste expansion [39, 67]. While some literature has presented concretes that have shown a marked reduction of strength [45, 67], a concrete may be designed to gain strength with temperature exposure in the region of 225°C [17]. Kropp et al. [44] have demonstrated cement pastes experience a strength gain in excess of 100% with high fly ash content in sealed environments. This strength gain is effectively complete within 20 and 40 hours of temperature exposure. The primary distinctions to make in this regard are reducing the effect of deleterious hydrothermal reactions in the paste, the thermal stability of the aggregate and the aggregate-paste interaction.

Practically, it appears that using high quantities of fly ash reduce deleterious hydrothermal reactions in concrete, while the use of aggregate with very low thermal expansion properties, such as amorphous igneous rock will minimize the differential thermal expansions of aggregate and paste.

Modulus of Elasticity Modulus of elasticity also has a broad response to high temperatures [52], but generally deteriorates with temperature, with no improvement as demonstrated with compressive strength. Around 225°C the modulus could be between 80% and 30% of the original value, while at 450°C it could be between 50% and less than 20%. This illustrates the importance of understanding the response of this property to temperature in the context of designing the reactor cavity structure.

The use of siliceous or amorphous igneous aggregates gives the best response to high temperatures [38, 76], especially when compared to calcareous aggregates. The use of extenders appears to cause a reduction in modulus at temperature when compared to plain Portland cement concretes [49].

Sealed environments cause a large reduction at temperatures in the region of 225°C and on cooling when compared to unsealed concretes [39, 66]. Sealed environments demonstrate a reduction at temperature of up to 60% of its unheated value when heated above 93°C [39]. This could recover when cooled, except at higher temperatures in the region of 232°C where the modulus still demonstrates a marked reduction in the region of 50%. Unsealed concretes show more similarities between at-temperature and cooled results, being in the region of 80% at 232°C[39].

The length of exposure at temperature appears to have a deleterious effect on both sealed and unsealed concretes at 232°C [67], probably relating to hydrothermal reactions that caused a similar effect on the strength of the concrete. Suzuki et al. have shown a slight increase in modulus with length of exposure at 110°C for sealed concretes, correlating well with a significant improvement in strength [68]. This correlation does not however extend to unsealed concretes that demonstrated a reduction in modulus, while the strengths improved over time. Suzuki et al. reported that changes in the modulus are effectively complete after 90 days up to temperatures of 110°C, while Nasser and Chakraborty [67] demonstrated a continued deterioration up to 180 days for temperatures up to 232°C.

Poisson's Ratio Literature suggests that the Poisson's ratio is not significantly affected in a sealed state [63], while an unsealed concrete can expect a gradual reduction of the Poisson's ratio value with temperature [78]. Time dependency suggests that Poisson's values generally recover over time at temperature [80].

4.1.2 Transport Properties

The conclusions from literature relating to the effect that temperature has on the transport properties of a concrete are as follows. That the concrete is moulded against a steel liner on the hot face of the structure implies a sealed state where excess moisture in the concrete, and moisture from the dehydration of the cement paste, cannot escape [85, 73]. This creates high pore pressures, in the region of 0.6 MPa, in the concrete that drive moisture away from the hot face towards the exposed cold face of the structure over a long period of time [47].

The ability for the water to migrate away from the hot face of the structure is governed by the porosity and permeability of the concrete. This in turn is governed by the constituents of the concrete, with low water:cement ratios significantly reducing porosity, while the use of extenders slightly increases porosity at a given water:cement ratio [16]. High aggregate contents in a concrete do however increase the permeability of a concrete through interconnectedness of the interfacial transition zones. The addition of polypropylene fibres that melt at 170°C can be used to reduce the pressures developed in the concrete and increase the ability of the water to migrate from the highest temperature regions of the concrete by creating large, interconnected capillaries [60].

The use of extenders provides a significant improvement in the resistance of the concrete to chloride ion diffusion. Although the relative deterioration with temperature, and subsequent increase in diffusivity, is greater for concretes with high extender quantities, the actual value still significantly lower than a concrete with only Portland cement [16].

Considering that air permeability is directly affected by the presence of micro-cracks and increased porosity of a concrete, it is reasonable to suggest that with a sufficiently low water:cement ratio, the porosity growth at the temperatures of interest can be counteracted, reducing the permeability of a concrete [16]. Bazant and Thonguthai suggest that there is an increase in permeability of around two orders of magnitude above 100°C, most likely due to smoothing of pore surfaces [82]. Microcracking in a sealed environment with high levels of fly ash could lend to autogeneous healing of the concrete through further pozzolanic reactions and exposure of unreacted Portland cement, in turn reducing the permeability and porosity.

4.1.3 Thermal Properties

In terms of thermal properties, there are three properties that need consideration, coefficient of thermal expansion, thermal conductivity (K) and specific heat capacity (C_p). A fourth property, thermal diffusivity (D), is a measure of the rate at which temperature changes can occur, and is calculated from thermal conductivity and heat capacity by $D = K/C_p\rho$.

Considering the coefficient of thermal expansion, the factors of primary significance are the type of aggregate chosen and the amount of aggregate used in this concrete. This will directly affect the expansion properties of the concrete, and likely have a significant influence on the amount of microcracking that will occur in an accident scenario. Basalt and limestone offer the lowest expansion properties in terms of conventional aggregates, with limestone being ruled out because of the possibility of increased deleterious hydrothermal reactions [7, 17]. Up to approximately 200°C the binder paste and aggregate expand at similar rates, while above this temperature the paste begins to contract and the aggregate continues to expand, with the aggregate characteristics dominating the concrete characteristics [7].

Concrete generally demonstrates a net contraction or expansion after heating [91]. This is strongly related to the type of aggregate used. Subsequent cycles of heating see the concrete following an expansion path similar to the cooling path of the first cycle [94].

At temperatures below 150°C the specific heat is strongly related to the water content of the concrete. Above this temperature the response is the same as oven dried concrete, which is generally governed by the aggregate [7].

Thermal conductivity is governed by the crystalline nature and silica content of the aggregate used [96]. Normal weight concretes either demonstrate a gradual decrease between 100°C and 300°C or are stable at these temperatures, and are stable above 300°C. Thermal diffusivity, as a function of specific heat capacity and thermal conductivity, generally reduces with temperature [7].

4.2 Mix Designs

Using the literature study and the previous summary of expected properties the following deductions have been made with regard to the concrete material constituents and quantities:

1. Normal Portland cement of CEM type 1 42.5 or 52.5 is suitable as a primary cementing compound in the concrete [22]. Although clearly there are many different reactions that take place, it should be possible to achieve a material within the limits required for the design of a structure using Portland cement as opposed to any other material. The use of a CEM 1 52.5 may be justified to ensure the concrete achieves suitable mechanical properties by 28 days.

2. The Portland cement content in the concrete should be limited to as low a value as possible while still giving acceptable mechanical properties, as it is apparent that the primary constituent that changes properties with exposure to temperature is Portland cement [7].

3. The addition of a large quantity of fly ash (FA) or ground granulated blast furnace slag (GGBS) is necessary to combat the chemical transformation that CSH gel undergoes in a sealed state [17, 49, 44]. Using condensed silica fume can lead to excessive pore pressures due to the refinement of the pore structure in a concrete, and should not be used as the primary extender in the binder [56]. The choice between FA and GGBS appears to be relatively unimportant in the context that both provide a beneficial effect, when included in large quantities, at high temperatures [55]. The FA to total cementitious compounds ratio (FA:C) should not

be less than 0.5 [17, 16]. A corresponding value for GGBS has not been identified.

4. The water:cement ratio and water content play a small role in the context of unsealed concretes [16]. There is limited data available on what the effect water content and water:cement ratio has on sealed concretes. However with high FA:C ratios in excess of 0.5 and a low content of Portland cement, it is likely that a low water:cement ratio will have to be used to attain acceptable mechanical properties.

5. Coarse aggregate requires careful selection, with the first priority being selecting a natural aggregate as opposed to a manufactured and more expensive substitute. An amorphous aggregate like basalt is ideal [7], while granite can possibly provide acceptable properties. Aggregates with high contents of silica, such as quartzite, have very high thermal expansion properties which are not ideal, while limestone aggregates increase the availability of calcium oxides to encourage the chemical transformation of the CSH gel [17]. Using local natural aggregates from the Western Cape region suggests the use of granite [12].

6. Fine aggregates require similar careful selection, with avoidance of limestone and excessively high silica contents. Selection of fine aggregates also needs to be on the basis of a good grading to ensure maximum packing considering the desire for low cement content [17]. With this in mind, there were two primary candidates for fine aggregate in the Cape Town region, Philippi dune sand (that has about 30% shell content that is lime rich) and klipheuwel sand, with Klipheuwel providing better grading properties.

7. The addition of steel fibres may be justified in terms of limiting the damage experienced by the concrete at accident temperatures (450°C). This would be in the form of acting as micro-crack arrestors [59]. Steel fibres only provide significant benefits in high strain environments at and beyond the maximum failure stress of the concrete, and as such can be removed from consideration at this point.

8. Similarly, the studies carried out in this project were not related to pore pressure development and moisture management of the concrete. As such polypropylene fibres, which could be used to manage the development of pore pressures in the concrete, were not considered in this project. It has been clearly shown that the addition of these fibres has little impact on the strength properties of a concrete when compared to one without fibre addition [60].

So, in summary, considering the conclusions reached above, the primary concrete constituents that were used in this project were:

- CEM 1 42.5
- Fly ash (high content ≥ 0.5)
- Condensed silica fume may be used as a secondary extender
- Igneous coarse aggregate - Cape granite, 6mm grading (as limited by sample size (Section 4.3))
- Siliceous fine aggregate - Klipheuwel sand
- Superplasticizer to improve workability of mixes with low water contents

Confirmation of the concepts gained from literature was required, specifically the improvement of strengths with very high extender quantities and that granite was a suitable aggregate.

With this in mind, two concrete mix designs were selected for testing, with the main difference between the two being the binder content, in that one contained a normal binder content and the other a low binder content. These were drawn directly from literature with minor adjustments, to facilitate a direct comparison with literature that was readily available.

Furthermore, two mortar mix designs were developed using the concrete mix designs, with the same proportioning of constituents but the coarse aggregate phase removed, in an attempt to isolate the changes that were happening to the microstructure of the binder phase.

At this stage it becomes appropriate to briefly discuss a terminology issue around calling a concrete 'conventional' or 'low cement'. The strict guidelines for refractory concretes as given by Bazant and Kaplan [7] are 12% to 25% calcium aluminate cement for conventional concretes, 6% to 9% for low cement concretes and 1% to 2% for ultra low cement concretes. With these definitions in mind (and ignoring the differentiation between refractory and Portland cement concretes), both of the mix designs suggested here fall between these ranges when either considering Portland cement content or total binder content. As such a differentiation that is less rigorous has been applied here, calling the concrete with the higher Portland cement content 'conventional' and the concrete with the lower Portland cement content 'low cement'. This differentiation was useful in practically identifying the concretes.

4.2.1 Conventional Concrete Mix Design

The first mix design considered was that of Xu et al. [16], with a 55% replacement of Portland cement with fly ash, as shown in Table 4.1 on the following page. This concrete contained 9.5% Portland cement and 21% total binder content, by mass. The corresponding mortar mix design is also presented, having removed the coarse aggregate and, keeping the same ratios, scaling the values to $1m^3$.

Table 4.1: Conventional concrete and mortar mix design (per m^3)

	W/B	FA Ratio (%)	Cementitious Materials (kg/m^3)			Sand (kg)	Coarse Aggregate (kg)	Super-plasticizer (L)
			OPC	FA	Total			
Concrete	0.3	55	225	275	500	634	1086	10.5
Mortar	0.3	55	380	465	845	1071	-	17.7

Xu et al. reported that the concrete mix provided an unheated 90 day cube compressive strength of approximately 80 MPa, an increase when heated in unsealed conditions up to 250 °C of approximately 15%, and 450 °C strength approximately the same as the unheated strength.

The mix designs presented in Table 4.1 are for $1m^3$of concrete or mortar. In the laboratory much smaller volumes of material were manufactured, with Table 4.2 presenting the same concrete and mortar mix designs scaled for different volumes. Set 1 is suitable for a full moulding of 40 compressive specimens (with dimensions and mould presented in Section 4.3), and set 2 being suitable for four 100mm cubes with which one can manufacture one set of durability index samples. In the testing phase these scaled mixes were adjusted according to what was required, an example being the need to manufacture 7 sets of durability index samples for various temperature exposure conditions requiring 28 100mm cubes.

4.2.2 Low Cement Concrete Mix Design

The second mix design that was employed was similar to that of Ghosh and Nasser [49]. This mix design had a 60% Portland cement replacement by fly ash, and 10% by condensed silica fume, as presented in Table 4.3. A mortar mix based on this concrete mix is also presented in this Table.

Most significantly this concrete had a very low Portland cement content of 4.6% by mass of concrete, with a total binder content of 14% by mass, in order to determine the effect that very low contents of Portland cement had on the concrete.

The mix design was adapted from Ghosh and Nasser as the mix determined from literature was found to have poor workability. As such, more superplasticizer and a higher content of water were used to improve the workability of the mix.

As with conventional concrete, a summary of the low cement mix designs, scaled to a 40 sample set of moulds for compressive strength or a set of four 100mm cubes is presented in Table 4.4.

Table 4.2: Conventional concrete and mortar mix designs for specific volumes

		Sample Volume (L)	Mix Volume (L)	Cementitious Materials (kg)		Sand (kg)	Coarse Aggregate (kg)	Water (kg)	Super-Plasticizer (L)
				OPC	FA				
Concrete	Set 1 - 40 Compressive Specimens*	1.70	3.00	0.68	0.83	1.90	3.26	0.45	0.03
	Set 2 - 4 100mm Cubes**	2.00	2.20	0.50	0.61	1.39	2.39	0.33	0.02
Mortar	Set 1 40 Compressive Specimens*	1.70	3.00	1.14	1.39	3.21	-	0.76	0.05
	Set 2 - 4 100mm Cubes**	2.00	2.20	0.84	1.02	2.36	-	0.56	0.04

* - As only one mould of 40 samples was available, this mix had to have a large volume of excess concrete to enable manufacture.

** - In practice more than 1 set of 100mm cubes would be manufactured, allowing for greater excess volume of concrete (maintaining 10% extra volume manufactured)

Table 4.3: Low cement concrete mix design (per m^3)

	W/B	FA Ratio (%)	Cementitious Materials (kg/m^3)				Sand (kg)	Coarse Aggregate (kg)	Super-plasticizer (L)
			OPC	FA	CSF	Total			
Concrete	0.42	60	117	234	39	390	878	1072	10.6
Mortar	0.42	60	196	391	65	652	1468	-	17.7

4.3 Specimens

Testing in this project largely considered two sets of properties, compressive strength, and durability index tests. Testing of these properties required specimens of different dimensions, and are each discussed in turn in this section, along with special mould designs, manufacturing and sample preparation methods.

Compressive strength specimens Conventional compressive strength specimens such as $100mm$ cubes or $\varnothing 100mm \times 200mm$ cylinders could not be used in this project for a variety of reasons. One set of $\varnothing 80mm \times 160mm$ cylinders were prepared and tested at room temperature to draw a correlation between the special specimens and conventional specimens. The special specimens were primarily limited in dimensions by three factors:

- Limited space in the available heating furnaces.
- The sealing method used to create a sealed environment for the sample.
- The maximum force allowable on the selected testing machine (100kN).

The third factor proved to be the limiting issue. Noting that high strength concretes were being considered, a maximum expected stress from the samples in the region of 100MPa was selected. This resulted in a maximum diameter of 35mm as shown below. To allow for an adequate safety margin a maximum sample diameter of 30mm was used.

$\sigma = \frac{F}{A}$ where $A = \pi\frac{\varnothing^2}{4}$

Therefore, rearranging:

$\varnothing_{max} = \sqrt{\frac{4F}{\sigma\pi}} = \sqrt{\frac{4\times100\times10^3}{100\times10^6\times\pi}} = 35.7mm$

Thus, rounding down:

$\varnothing = 30mm$

Table 4.4: Low cement concrete and mortar mix designs for specific volumes

		Sample Volume (L)	Mix Volume (L)	Cementitious Materials (kg)			Sand (kg)	Coarse Aggregate (kg)	Water (kg)	Super-Plasticizer (L)
				OPC	FA	CSF				
Concrete	Set 1 - 40 Compressive Specimens*	1.70	3.00	0.35	0.70	0.12	2.63	3.22	0.49	0.03
	Set 2 - 4 100mm Cubes**	2.00	2.20	0.26	0.51	0.09	1.93	2.36	0.36	0.02
Mortar	Set 1 40 Compressive Specimens*	1.70	3.00	0.59	1.17	0.20	4.40	-	0.81	0.05
	Set 2 - 4 100mm Cubes**	2.00	2.20	0.43	0.86	0.14	3.23	-	0.60	0.04

* - As only one mould of 40 samples was available, this mix had to have a large volume of excess concrete to enable manufacture.

** - In practice more than 1 set of 100mm cubes would be manufactured, allowing for greater excess volume of concrete (maintaining 10% extra volume manufactured)

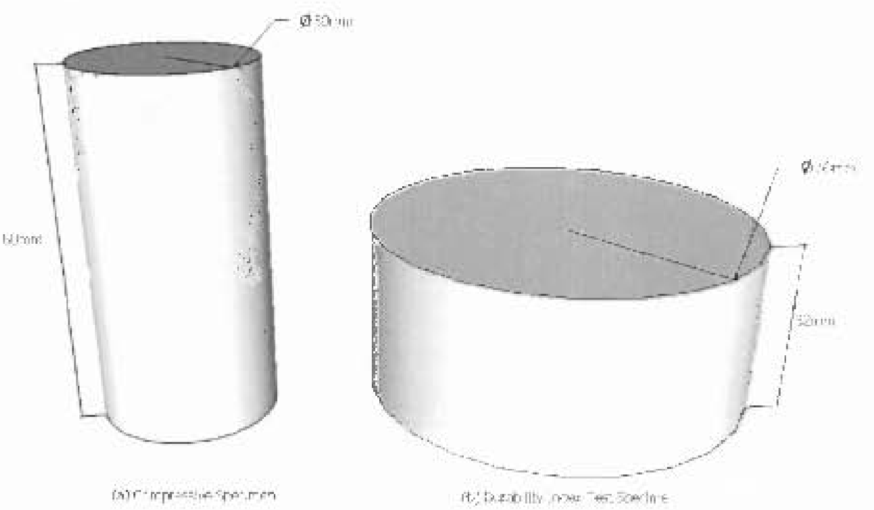


Figure 4.2: (a) compressive strength and (b) durability index specimen dimensions

Using civil engineering standard specimen dimensions, the length of the sample was determined to be 60mm (i.e. $2 \times \emptyset$). This sample size placed a limitation on the maximum coarse aggregate size that could be used, following the rule presented in Fulton's Concrete Technology that the maximum aggregate size should be 4 times smaller than the smallest dimension of the sample [12]. Thus the sample size placed a limitation of 6mm aggregate on the concrete ($6 \times 4 = 24mm < 30mm$). A representation of the compressive specimen is given in Figure 4.2 (a).

Durability index specimens The standard dimensions for durability index test specimens are a thickness of 30mm to 32mm and a diameter of 68mm to 70mm. These specimens are cut from conventional castings of any dimension, although in this project all samples were cut from 100mm cubes. Each cube provided two specimens, while each set of durability index data required eight specimens, requiring four cubes per durability index test. A representation of durability index sample dimensions is given in Figure 4.2 (b).

4.3.1 Moulds

Compressive Strength Specimens The unconventional dimensions of the compressive strength specimens required moulds to be manufactured to enable the manufacture of these specimens. Two attempts were made at manufacturing moulds.

The first attempt involved using PVC piping of outer diameter 32mm bonded to a base of perspex, as can be seen in Figure 4.3 (a). The drawings for this mould are in Appendix B. Large quantities of moulds were prepared

a) Mould

b) Samples with excessive void content

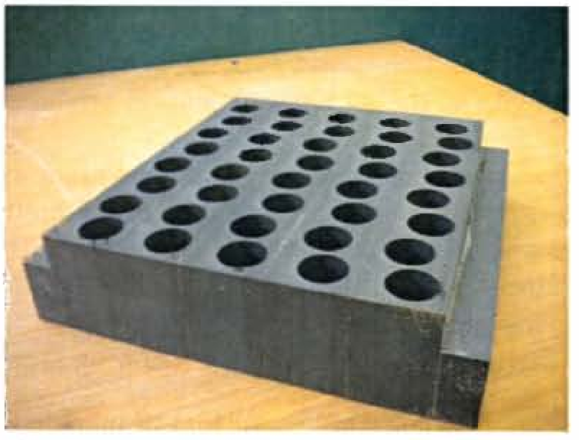
Figure 4.3: Mould attempt 1: (a) mould and (b) samples with excessive void content

and bonded to bases of plywood, with the right number of specimens required for a specific set of samples on a particular base.

This design proved to have several problems. The first was around using PVC piping, in that the piping used had varying internal dimensions due to two different grades of pipe being used, giving a sample diameter of between 27.2mm and 28.8mm. The moulds were also found to be too unstable and lacking in rigidity to allow for proper compaction of specimens on a vibrating table, with the moulds shaking loose from the plywood base. This caused the specimens to have large void sizes and contents as shown in Figure 4.3 (b).

The second attempt at manufacturing moulds was carried out after receiving advice from supervisors and workshop staff, and was manufactured in the civil engineering workshops of UCT. This mould consisted of a block of PVC from which 40 holes of diameter 30mm and depth 60mm were machined. The block of PVC was manufactured using five 300mm long by 75mm wide slices of PVC sheet with a thickness 50mm, bonded together with PVC glue. There was no PVC sheet available with a thickness greater than 50mm, requiring this more complicated approach to enable the manufacture of samples with the desired dimensions. A step was bonded onto either side of the mould to allow for attachment to a vibrating table using clamps. 4mm holes were also drilled into the base of each large hole to allow for the demoulding of samples using compressed air.

This mould proved to be significantly more rigid and easy to manufacture samples with, and facilitated good vibration of the samples. An image of this mould is given in Figure 4.4, along with a picture of an improved specimen, while drawings of the mould are given in Appendix B.



(a) Final compressive specimen mould

(b) Sample of improved quality

Figure 4.4: (a) Final mould and (b) improved specimen quality for compressive specimens

Durability Index Specimens The durability index specimens were moulded using conventional 100mm cubes, from which the specimens were cut.

4.3.2 Casting

Casting of the concretes was carried out in batches according to the different phases of the project. There were three different phases:

- Preliminary phase: This phase consisted of the manufacture of sets of samples for conventional concrete and mortar, and low cement concrete and mortar. This phase was used to determine the validity of concepts from literature and the direction of testing. Compressive specimens for this phase were manufactured using the first mould design, while durability index specimens were manufactured using 100mm cubes. A set of three large specimens were manufactured for conventional concrete to assess the response of the concrete using conventional moulds of Ø$80mm \times 160mm$ against the smaller specimens.

- Second phase: This phase consisted of the in depth study of conventional concrete exposed to various different thermal environments. Compressive specimens were manufactured using the improved mould design, while a set of durability index specimens was manufactured to assess the concrete response at 28 days, in line with conventional practice.

- Third phase: This phase consisted of the manufacture of conventional concrete samples to assess the room temperature characteristics of the concrete, namely the strength development over 28 days, and the shrinkage of the concrete.

As the third phase of the project was also based on conventional concrete, these results have been included in the section considering the in depth testing of conventional concrete. A summary of the number of samples produced is given in Table 4.5.

It is worth keeping in mind that in the first phase of the project many samples had to be discarded due to excessive void content, considerably limiting the number of samples that were available for testing. In phase two and three a full set of 40 samples were produced, even if this was not required, to allow for excess in case further testing was required.

Casting of the concretes was carried out according to the following process:

1. Oil and prepare moulds. Plug blowholes in the bottom of moulds with tissue paper.
2. Proportion all constituents separately.
3. Place the fine and coarse aggregate into the mixer, and start the mixer.
4. Place the extender and Portland cement into the mixer.
5. Ensure that all constituents are being mixed well. Allow mixing to occur for about 1 minute.
6. Place the water into the mixture. Ensure an even distribution of water, and allow for mixing for about 30 seconds.
7. Place the superplasticizer in the mixer, ensuring all constituents are being mixed thoroughly.
8. Allow mixing to continue for about 1 minute.
9. Stop the mixing machine, load moulds half full of concrete.
10. Vibrate moulds for 30 seconds.
11. Top up moulds until full.
12. Vibrate moulds for a further 30 seconds.
13. Place moulds under black plastic and allow to set.

The concretes were checked approximately every 12 hours after moulding for readiness for demoulding. The compressive specimens for the first mould design were demoulded by breaking off the perspex base of the mould and bending open the PVC using the slit cut into the mould.

The specimens from the second mould design and 100mm cubes were demoulded by removing the tissue in the bottom hole of the mould and using compressed air to force the specimen out of the mould. The compressive strength samples proved to come out of the mould at speed, so tissue and

Table 4.5: Summary of number of samples produced

	Compressive Specimens			**Durability**
	1st Mould Design (Ø30mm x 60mm)	**2nd Mould Design** (Ø30mm x 60mm)	**Large Mould** (Ø80mm x 160mm)	**Cubes** (100mm x 100mm)
Phase 1				
Conventional Concrete	102	-	3	28
Conventional Mortar	60	-	-	-
Low Cement Concrete	102	-	-	28
Low Cement Mortar	60	-	-	-
Phase 2				
Conventional Concrete	-	80*	-	3
Phase 3				
Conventional Concrete	-	40	3	-
*Two sets of samples were manufactured, two days apart.				

black plastic were used to catch the specimens without causing damage. The samples were then wiped down with tissue to remove any excess oil from the mould, and allowed to cure.

4.3.3 Curing

It was discovered that the concrete did not generally set after one day, but had to be left in the mould for usually two days, but occasionally for three days before being demoulded. This was likely due to the high quantities of superplasticizer and klipheuwel sand, which are known to delay setting of a concrete. This was to allow the demoulding of samples without causing excessive damage to the material. If a concrete proved to take longer than 2 days to achieve a suitable level of cure to allow demoulding, the mould was placed in a water bath until demoulding the following day.

The demoulded samples were placed in a water bath at a temperature of 21°C for the entire duration of curing. Concretes were cured for either 28, 70 or 90 days in this environment before testing.

It was discovered at one stage that the temperature control element had blown, and it is believed the concretes may have spent some time being cured at a temperature lower than 21°C. This loss of curing was difficult to rigorously quantify (as the temperature history of the bath while the element was blown was unknown), however Neville has discussed the issue of concrete maturity [11].

Maturity of concrete is measured in °C-hours with a common reference value for maturity being after 28 days cured at 18°C, giving 19800°C-hours. Concrete generally has a limiting curing temperature of between -10°C and -12°C, in that the concrete will not cure below this temperature. Thus when calculating the maturity of the concrete, one has to take the value from this origin and not 0°C. Calculation of maturity is as shown below:

Curing temperature = 18°C

Origin temperature = -11°C

Temperature difference = curing temp. - origin temp. = 29°C

Time of curing = 28 days = 672 hours

Therefore concrete maturity = temperature difference $\times$time of curing (hours)

$= 29 \times 672$

$= 19488^{\circ}C - hours$

This value is very similar to the value of 19800°C-hours suggested by Neville [11].

For a concrete cured at 21°C for 90 days (the maximum curing cycle), a maturity of 69000°C-hours will be achieved. Assuming the blown element occurred for the whole period of cure, and the bath was at a temperature of 15°C for this duration, a maturity of 56000°C-hours was achieved. This allows a difference in cure of 13000°C-hours.

2. The samples were numbered and underwent the heating cycle.
3. Once cool, the samples were placed into a desiccator.
4. The samples were then capped with Pratley's Quickset putty in the testing rig. Care was taken to ensure the samples were placed in the machine in a defined position and orientation.
   (a) The samples were marked to indicate orientation by scribing a middle line at the base of the sample and two lines 90° (along the axis of the sample) either side of the middle line.
   (b) The centre of the testing rig was identified with a marker. The testing rig had the centre scribed on it already.
   (c) Pratley quickset was mixed together.
   (d) Two small balls of putty were placed on the ends of the sample.
   (e) The sample was placed and closed into a plastic bag to reduce the amount of dirt created in the crushing process.
   (f) The sample was placed on the center of the testing rig, with care taken to ensure the middle line was facing directly forwards.
   (g) The testing machine platens were closed slowly to compress and squash the putty over the end surfaces of the sample. Care was taken to not load the sample above 500 N.
   (h) Once the putty had spread over the whole surface and could be seen around the edges of the sample, the platens were separated, the sample removed and placed aside to allow the putty to cure.
5. Once the putty had set (Pratley's Quickset has a 6 hour cure time) the samples were loaded into the machine and crushed according to Section 4.5.1. Care was taken to ensure the samples were placed in the same position and orientation as when capped.

This methodology facilitated significantly improved results for the rest of the testing.

4.3.5 Durability Index Sample Preparation

All of the samples for the durability index tests were prepared according to the Durability Index Testing Procedure Manual [29]. As these samples had to be cut from 100 mm cubes, with two samples per cube, the process that was undertaken is outlined below:

1. Cubes were removed from the curing tank approximately 8 days before the durability index testing was to occur, and grouped into sets of four (as eight samples were required for one durability index test).

(a) Coring machine (b) Cutting machine

Figure 4.5: (a) Coring machine and (b) cutting machine

2. Cores of diameter approximately 68 mm were made using the coring machine shown in Figure 4.5 (a).

3. The cores were faced using the cutting machine shown in Figure 4.5 (b). Approximately 5 mm was taken off each face.

4. The outside faces of the cores were identified with a marker.

5. Slices of thickness between 30 mm and 32mm were cut from the marked cores using the cutting machine. The two outside faces were ensured to be on a sample, with a middle piece of about 20mm thickness left over.

6. If the samples were to be tested at room temperature, they were placed into a drying oven at 50°C for approximately 7 days. Samples for heat exposure were placed in the heating environment directly.

At this stage the samples are ready for testing.

4.4 Environmental Exposure

The environment of temperature exposure needed to be carefully managed and documented to enable a comprehensive understanding of the response of the concrete. This environment is strongly related to the environment the PBMR would place on the concrete as discussed in Section 3.1.2. The translation of the heating environment of the PBMR into an environment of testing is outlined in this Section.

4.4.1 Thermal Environment

In terms of the thermal environment that the concrete is exposed to, two primary temperatures were defined by PBMR:

- 225°C operating temperatures for the operational lifetime of the structure (40 years) [10].
- 450°C accident temperatures for 30 days [10].

These temperatures translate into three different scenarios, with a continuum of environments between scenario two and three possible:

1. Plant operates for its lifetime (40 years) at 225°C and is then decommissioned.
2. Plant experiences an excursion/LOCA on first heating. The LOCA takes the concrete to 450°C for approximately 30 days, with a gradual reduction of temperature from 450°C.
3. Plant operates for its lifetime and experiences an excursion/LOCA at 40 years.

With these three scenarios in mind thermal modeling of a wall section was undertaken to fully understand the environment the PBMR would place the concrete under.

Modeling of the Thermal Environment

Basic modeling was carried out during the project, in terms of the thermal properties of the concrete, to develop an idea of the heat distribution through the structure during operation and in the case of a loss of coolant accident (LOCA). From this heat distribution qualitative statements based on literature can be drawn in terms of the strength properties of the concrete. This model was implemented using Dassault Systémes ABAQUS finite element program.

The thermal property models that were applied were accessed from the work of Kugeler [33]. These models are fairly comprehensive in a statistical format, utilizing several sources of data from literature.

These thermal properties were applied to a 30° quadrant of a cylinder, inner radius 5m, outer radius 7m. This is broadly representative of the expected structure of the PBMR, and is a direct representation of the HTR-Modul reactor cavity structure upon which the PBMR is based.

A surface film condition to represent external air temperatures of 25°C was applied to the outer surface of the section, while the hot face had a boundary condition of the respective temperature of interest applied to it. An image illustrating the section once it has reached steady state operating temperatures is given in Figure 4.6.

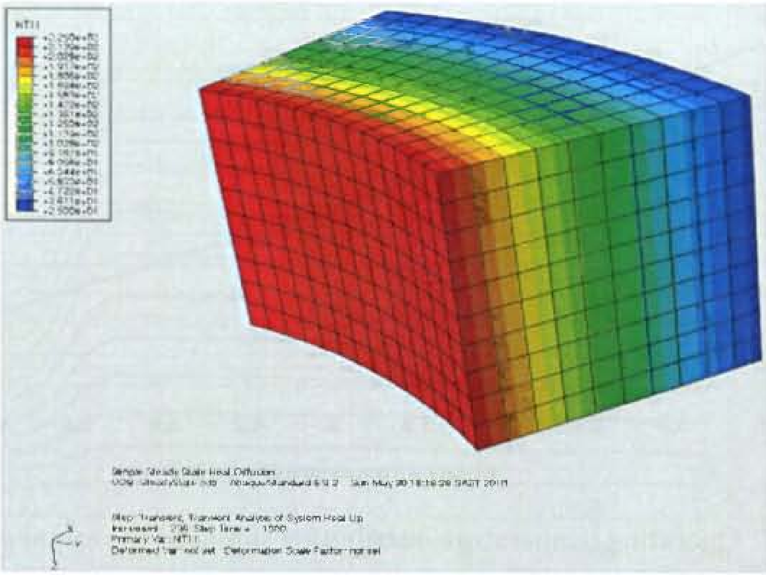


Figure 4.6: Operating temperature distribution in concrete section

This temperature distribution is given in Figure 4.7 in a graphical form. The outside face of the concrete wall achieved a temperature of 29°C. The pertinent illustrative point from this graph is that the temperature in the wall during normal operation would only be at 225°C at the hot face of the concrete, and would drop almost linearly through the concrete. This means that the properties between room temperature and 225°C are of primary interest. Assuming a linear interpolation of property values between these two points is not reasonable as this transcends the 100°C boiling temperature for water, resulting in different property responses above and below this point.

Considering the work of Chapman and England [47], and Ichikawa and England [48], it is reasonable to assume that with a temperature distribution as shown above the concrete would experience a gradual migration of moisture away from the hot face of the structure. Chapman and England [47] have suggested that within the first 50 days of temperature exposure there will still be some level of moisture available within 0.2m of a face heated to 200°C. This effectively suggests a sealed state with high moisture content for at least some degree of time. The concrete would tend towards an unsealed state in this area, with moisture content and pore pressures reducing over time.

The temperature distribution also carries implications in terms of a LOCA. Generally it can be postulated that such an accident would only occur sometime during the lifetime of the reactor and not on first heating. This implies that the concrete would have spent a considerable time (up to 40 years) with exposure at 225°C, undergoing hydrothermal reactions over a short period of temperature exposure then slowly tending towards an unsealed and lower pore pressure state before experiencing the rise in temperature. Thus the concrete would be closer to a steady state unsealed condition that would be less reactive

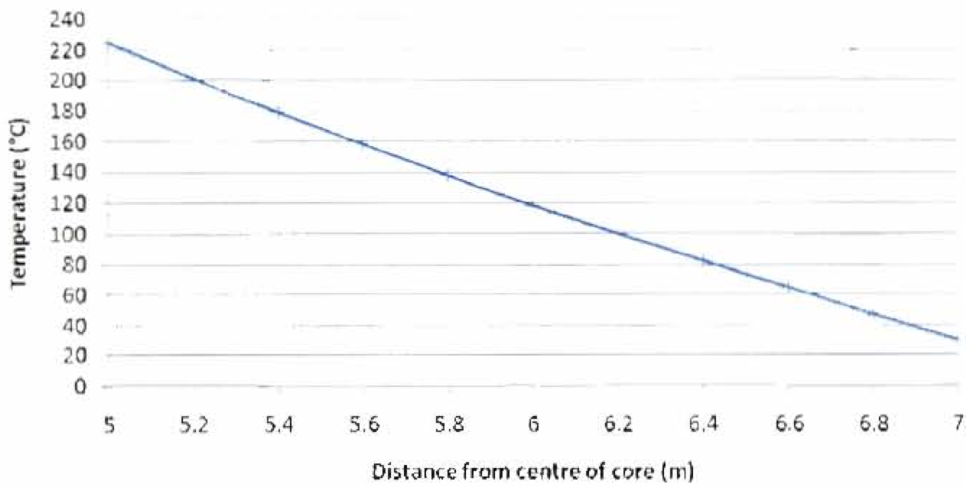


Figure 4.7: Operating temperature distribution through the reactor cavity wall

to the increase in temperature (in both a positive and negative way).

A transient model representing a LOCA was also implemented. This was using data from the HTR Modul out of the the Kugeler report [33], namely 200 hours to reach maximum temperature then a gradual cool down over a further 1000 hours. A plot of the temperature distribution for the nodal points is given in Figure 4.8.

This history is interesting in that it suggests that only about $\frac{1}{4}$ of the concrete wall is exposed to temperatures considerably in excess of 300°C (the section from 5.0m to 5.6m). This suggests that most of the structure can be expected to conform more closely to the 225°C response of the concrete than the 450°C response.

Testing Thermal Environment

With a well developed understanding of the PBMR thermal environment as explained, the following testing thermal environments were defined:

- 225°C for varying durations (as explained in Section 4.4.2).
- 450°C for varying durations.
- 225°C for a period, then a rise to 450°C.
- Thermal cycling to 225°C.
- Thermal cycling to 225°C, with the last thermal cycle to 450°C.

A definite focus was needed on the response to 225°C due to this being in the region of the maximum temperature that most of the structure will be exposed to. A heating rate of 10°C per hour was employed, to model the conditions expected with the PBMR while allowing for a rate higher than expected.

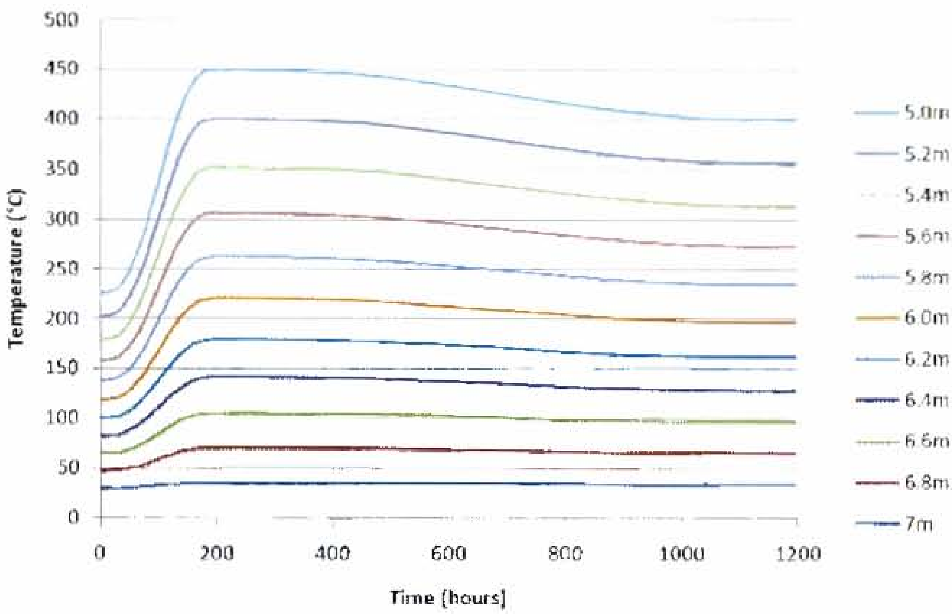


Figure 4.8: Nodal temperature history of section of reactor cavity structure during a LOCA

4.4.2 Duration

The duration of heating was crucial to determining the ultimate response of the concrete to high temperatures. It is however unreasonable to carry out tests of up to the lifetime of the structure (40 years for operation and 40 years for cool down) due to the practical implications involved in doing so. Significantly shorter tests that demonstrate a trend were employed with a view to verifying the concepts developed from literature.

A heating rate of 10°C per hour was employed, requiring 22.5 hours to reach 225°C and 45 hours to reach 450°C. The specimens were kept at temperature for the durations outlined below (with 1 day = 24 hours), and then cooled at the same rate of 10°C per hour.

Tests were carried out according to the durations outlined below:

- Single temperature tests:
  - 225°C - 1 day, 5 days, 7 days, 14 days.
  - 450°C - 1 day, 5 days.
- Multiple temperature and thermal cycling tests:
  - 225°C to 450°C - 5 days at 225°C and 3 days at 450°C.
  - 225°C - 14 days at 225°C, cooled and two cycles of 1 day to 225°C.
  - 225°C to 450°C - 14 days at 225°C, cooled, one cycle of one day to 225°C and one cycle of 1 day to 450°C.

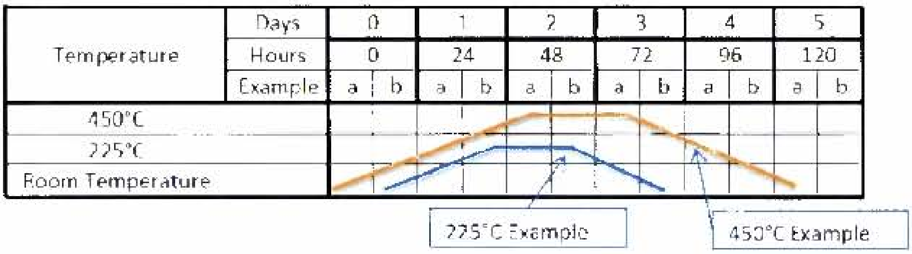


Figure 4.9: Example test schedules (a) 450°C for 1 day and (b) 225°C for 1 day

One thermal cycle involved heating the samples to temperature at a rate of 10 °C/hr, leaving them at the temperature for the allotted time and cooling them back down to ambient. This process was repeated for each cycle. Two examples, one of a heating schedule for a sample heated for 1 day to 225°C and a second of a sample heated for 1 day at 450°C are given in Figure 4.9.

As can be seen, the total test time for the 225°C amounted to:

$22.5 + 24 + 22.5 = 69 hours$ (Ramp up + at temperature + cool down = total test time)

Likewise, the 450°C example had a total test time of 114 hours.

4.4.3 Moisture State

Two moisture states were investigated, sealed and unsealed.

Unsealed samples were weighed, numbered with a pencil and placed in the kiln. Using a pencil allowed the markings to stay on the samples through the heat exposure, enabling easy identification of the samples on removal from the kiln. Permanent marker proved to not withstand high temperature exposure.

Two attempts were made on achieving a sealed state with concrete. The first was an attempt for an easy sealing method for 225°C using aluminium foil and a high temperature gasket silicone sealant. Several iterations were undertaken, with the aluminium foil generally rupturing. These samples failed to have characteristics any different from those of unsealed specimens (mass loss was the same as unsealed samples, and tested properties were basically the same as the unsealed samples). When one considers that these samples may very well reach pore pressure in the region of 0.5 MPa [47], the failure of this sealing method is understandable.

The second method of sealing samples was similar to one used in literature by Nasser and associates [53, 54]. This involved TIG welding caps onto steel pipe, with the samples inside the pipe, as shown in Figure 4.10 (b), with the drawings for the design in Appendix B. The primary difference was that in literature the caps were welded on by brazing. The containers were placed in a bath of water to try and keep the container, and the samples within, cool. A hole was drilled in the lid of the container to allow excess pressure to

(a) Welding of containers (b) Sealed container

Figure 4.10: (a) Sealing of samples in steel containers and (b) sealed container

escape from the container while welding the cap, with the hole being sealed by welding after the cap had been welded on. These containers held a set of three samples each, effectively comprising a unit that could be exposed to a specific temperature environment.

Although this sealing method appeared to provide a significant property change in terms of strength when compared to unsealed samples, the containers lost mass during heating (as discovered by weighing the sealed container before and after temperature exposure, results are shown in Appendix A). As well as this, once the samples were removed from the container by cutting the cap off with a hacksaw, it was found that mass loss for the samples was very similar to that of the unsealed samples. This implies that moisture was escaping from the containers, most likely through porosity or microvoids in the welds. This issue was not resolved by the end of the project and as such all data presented relating to sealed concretes had this issue. As already mentioned, these samples did demonstrate a significantly different property change from the unsealed samples, indicating that the loss of moisture and pressure may have been gradual, allowing a certain period of time at temperature in a very moist environment for this change to occur.

4.5 Testing

Testing of concrete took two main directions, namely compressive strength and permeability relating to the South African durability index tests. Although attempts were made to test modulus of elasticity using the compressive strength specimens, it was determined that the output from the tests did not account for compliance of the testing machine and rig, and as such could not be used to directly determine the modulus of the concrete.

4.5.1 Compressive Strength

The compressive strength of the samples was determined using a Zwick universal testing machine with a compressive test rig attached. Once the curing of the capped samples had been completed, after 6 hours, the samples were placed into the compressive rig in the same position and orientation as the capping had occurred in. Care was taken to ensure that the plastic bag used to keep the machine tidy when the samples failed did not fold over or crease between the sample and machine platens, which would have caused stress concentrations in the sample.

The tests were carried out with displacement rate control, with a constant rate set at 0.42mm/min for all testing. This rate allowed a maximum stressing rate in the region of 10 to 15 MPa/minute for unheated samples, although this rate varied depending on the temperature exposure the sample had experienced.

4.5.2 Durability Index Tests

The South African durability index tests assess the permeability of the concrete with water, gas and chlorides. The results from these tests allow the statistical prediction of the lifetime of a structure. One of the primary concerns the tests account for is corrosion of steel reinforcement, using the data relating to permeability of the structure to predict how long carbonation and chloride diffusion fronts will take to reach the reinforcement steel. This allows the designer to set a minimum depth of the reinforcement in line with the lifetime requirements of the structure. It should be noted here that one should refer to the durability index testing procedure manual [29] for a complete summary of the procedure applied as it is outside of the scope of this masters to present this theory here.

Oxygen Permeability

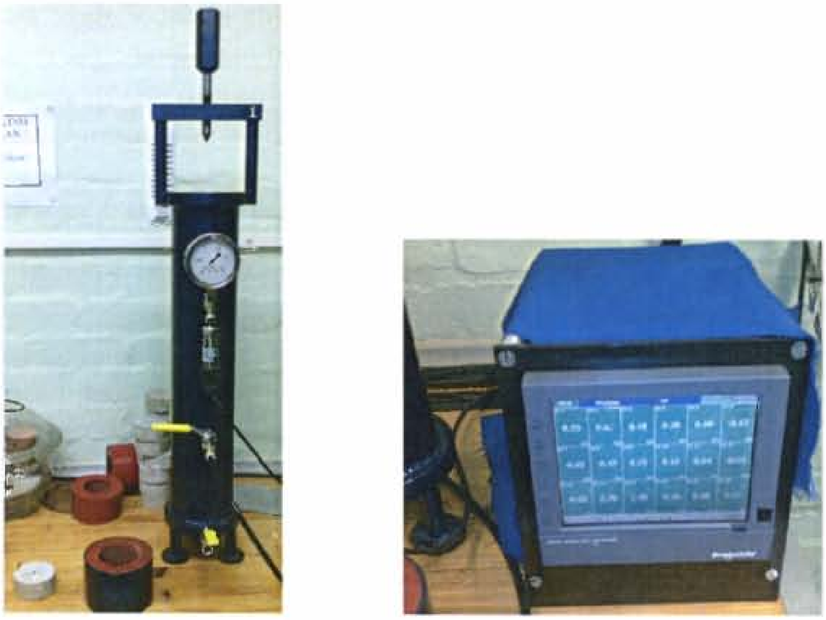
Oxygen permeability tests are used to determine the gas diffusivity of a concrete, which is directly related to the ability for carbon dioxides to reach steel reinforcement and cause corrosion. The methodology of carrying out the test is outlined below. For a more comprehensive document describing these tests and the calculation of the properties of interest from the results, refer to the Durability Index Testing Procedure Manual [29]. An image of the testing apparatus is given in Figure 4.11 (a).

1. Four samples that had either been oven dried for 7 days at 50°C or exposed to a temperature regime were used.
2. The samples were loaded into the top cylinder caps as shown in Figure 4.11 (a).
3. The cylinder caps were placed on top of the cylinders and loosely secured.
4. The oxygen line was charged, and each cylinder had some pressure let into it.
5. The cylinder cap was released briefly and secured again, in order to flush out normal air.
6. The bottom release valve was briefly released to flush normal air out of the system.
7. The cylinder caps were tightly secured to the cylinders.
8. The cylinders were charged with approximately 100 KPa of oxygen, with 100 KPa being the minimum pressure.
9. All valves were checked to be closed, and each cylinder checked for leaks.
10. The data recording system was checked to be operating, as shown in Figure 4.11 (b).
11. The tests were allowed to run for either 6 hours or until the pressure dropped to 50 KPa.
12. The samples were removed from the cylinders and the data collected from the recording system.

The data garnered from these tests were then processed according to the mathematical formulae presented in the durability index testing procedure manual [29]. This calculation is an application of the D'arcy coefficient of permeabililty equation using the slope of linear regression calculated from the results of testing. The oxygen permeability index rating is calculated by taking the log of the average of the calculated coefficients of permeability. Thus, the output data presented is the coefficient of permeability and related oxygen permeability index (OPI) rating.

Chloride Diffusivity

The permeability of the concrete to chloride ions is determined by the rapid chloride diffusion test for the durability index. This test involves applying a potential difference across a sample that has been saturated in a sodium chloride (NaCl) solution, and measuring the current. This gives an indication of the ability of a concrete to resist the transport of chloride ions. The test is outlined below:

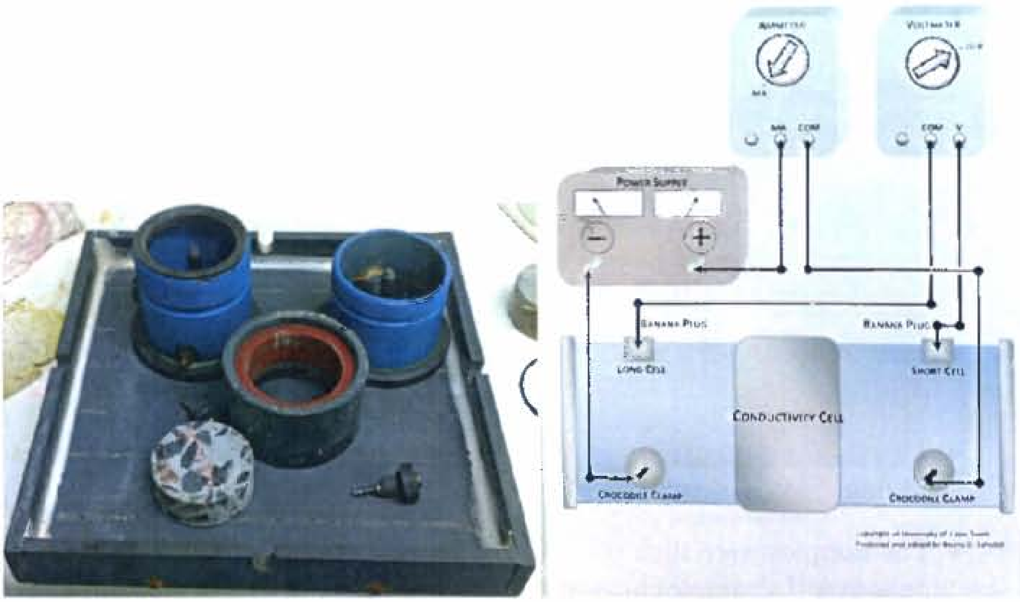


(a) OPI Chamber, cap and sample

(b) Data logger

Figure 4.11: Oxygen permeability test apparatus: (a) cylinder, cylinder cap with sample and (b) data recording system

1. Four samples that were either oven dried or had been exposed to temperature were selected.
2. These samples were weighed.
3. The samples were placed in a vacuum chamber, and a vacuum was drawn on the samples.
4. After three hours under vacuum a 5 mol solution of NaCl was drawn into the chamber, and the vacuum redrawn.
5. After 1 hour the vacuum was released and the samples left overnight to soak in the NaCl solution.
6. The next day, each sample was removed as it was needed for testing.
7. The testing apparatus was loaded with NaCl solution.
8. The sample was placed into the testing apparatus. The apparatus and sample are shown in Figure 4.12 (a).
9. The testing apparatus was assembled.
10. The testing circuit shown in Figure 4.12 (b) was assembled and a potential difference applied across the sample.



(a) Conductivity cell and sample (b) Circuit diagram

Figure 4.12: Chloride diffusivity testing: (a) Sample and testing apparatus and (b) testing circuit

11. The current in the circuit was measured and recorded.
12. The sample was removed from the apparatus, dabbed dry with paper towels and weighed.
13. Another sample was tested from point 8 onwards.

In this testing great care had to be taken to ensure the circuit had good connections, as many of the connecting wires had corrosion on them. The results of the testing were applied into two equations as presented in the durability index testing procedure manual [29]. The equation of chloride conductivity (mS/cm) as described in the durability testing procedure manual is simply the equation for specific conductance. Porosity (%) is calculated by the difference between the mass of the dry and saturated samples of concrete.

Water Sorptivity

The water sorptivity of the sample is a measure of the rate at which water is drawn into the sample through capillary action. The testing methodology was as follows:

- The four samples from the OPI tests were used.

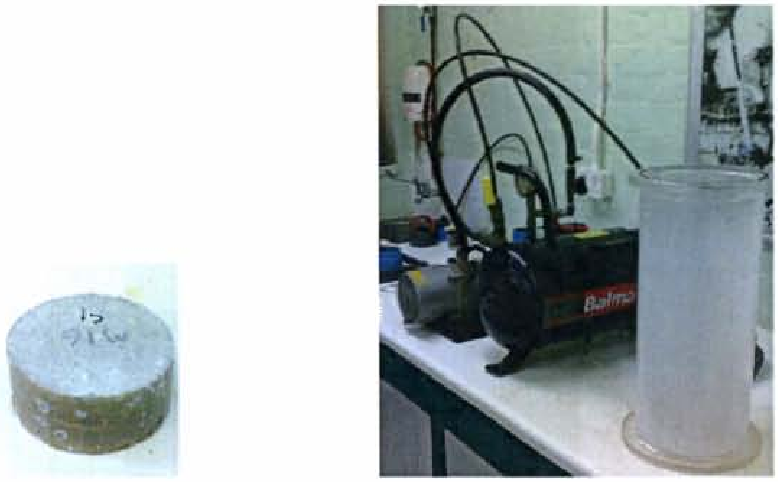
- Each sample had its circumferential surface sealed with brown plastic tape, with special care taken to ensure the tape was in line with the base of the sample (the outside face of the sample), see Figure 4.13 (a).
- A tray had four sheets of paper towel placed in it, and a 5 mol solution of calcium hydroxide ($Ca(OH)_2$) placed into the tray to the level of the paper towel. Care was taken to ensure the paper towels were saturated.
- The samples were weighed and recorded.
- The samples were placed in the tray, with the base of the sample on the paper towel.
- The weight gain of the sample was measured at regular intervals up to 25 min.
- The samples were then placed in a vacuum chamber, and a vacuum was pulled on the samples for three hours. An image of the vacuum apparatus is given in Figure 4.13 (b).
- The solution of $Ca(OH)_2$ was drawn into the vacuum chamber, and the vacuum reapplied.
- After 1 hour of soaking in the solution under vacuum it was released and the samples allowed to soak overnight.
- The following day, the samples were removed from the chamber, dabbed dry and weighed.

This data was applied into a series of equations presented in the durability index testing procedure manual [29] to give readings of sorptivity ($mm/\sqrt{hour}$) and porosity (%).

4.5.3 Shrinkage Testing

Shrinkage testing was carried out on the concrete to assess the effect of drying shrinkage on the concrete, with a view to assessing the shrinkage properties of the concrete. The use of very small coarse aggregate (6 mm) could suggest this concrete would have very high shrinkage tending towards the characteristics of mortar. This needed to be verified, with the method of testing outlined below.

- Three concrete cylinders of dimensions ($\varnothing 100mm \times 200mm$) were moulded.
- The samples were demoulded after 2 days, and placed into the curing bath.
- 3 days after moulding the samples were removed from the bath and allowed to have excess moisture on the samples evaporate.



(a) Sorptivity sample with taping (b) Vacuum chamber

Figure 4.13: Sorptivity test apparatus and methodology: (a) taping of specimens and (b) test in progress

- The samples were scribed with a centre line. An image of a sample is in Figure 4.14.
- Two measuring points were attached with epoxy paste on each sample, on opposite sides of the sample, on the centre line, approximately 1/3 of the way up the sample.
- Two more measuring points were attached once the first two had set, approximately 100mm from the previous measuring points. The location of the measuring point was corrected to the exact distance needed using the shrinkage measuring tool.
- Once the epoxy paste had set, the samples were placed in a moderate humidity room and the distance between measuring points was measured using the shrinkage measuring tool at regular intervals up to 60 days.

The net shrinkage, in μstrain, of the samples was calculated using the measurements taken.

4.5.4 Testing Matrix

It should be apparent that a wide range of testing was undertaken in this project, of which a comprehensive list of the tests and number of tests undertaken are given in Table 4.6 for shrinkage and durability tests and Tables 4.7 and 4.8 for compressive strength (single temperature tests and multiple temperature tests respectively). For each test identified in the Table, three compressive specimens were tested for strength tests, three specimens for a

Figure 4.14: Shrinkage sample with points mounted

shrinkage test, and four durability index specimens were tested for durability index tests.

This table appropriately summarizes all of the testing that was carried out during the project. A point worth noting is that only conventional concrete was dealt with after the first batch of testing that was carried out using samples manufactured with the first mould design. This was due to several factors:

- The first stage of testing illustrated that low cement concrete and mortar had an unacceptable response with exposure to 450°C with both strength and more specifically the durability index tests, as will be described in the results section.
- This allowed specific focus to be given to conventional concrete to ensure an appropriate number of environments were assessed accordingly.
- The limited number of castings that could be produced from the improved mould placed limitations on the number of samples that could be produced in one batch (recall that the concrete took at least 2 days from casting before demoulding).

Table 4.7: Testing Matrix - Compressive Strength Tests* (a) - Single Temperature Tests

Test	Temperature Exposure	Curing Age (Days)	Exposure Duration	Conventional Mortar				Conventional Concrete				Low Cement Mortar				Low Cement Concrete			
Compressive Strength Single Temperature Tests				Mould Design 1		Mould Design 2		Mould Design 1		Mould Design 2		Mould Design 1		Mould Design 2		Mould Design 1		Mould Design 2	
Moisture State[a]				US	S	US	S	US	S	US	S	US	S	US	S	US	S	US	S
	Room Temp.	7		.	.	.	.	.	.	1	.	.	.	.	.	.	.	.	.
		14		.	.	.	.	.	.	1	.	.	.	.	.	.	.	.	.
		28		1	.	.	.	1	.	2	.	1	.	.	.	1	.	.	.
		70		.	.	.	.	.	.	1	.	.	.	.	.	.	.	.	.
		90		1	.	.	.	1	.	1	.	1	.	.	.	1	.	.	.
	225ºC	28	1 day	.[b]	.	.	.	.[b]	.	.	.	.[b]	.	.	.	.[b]	.	.	.
		70	1 day	.	.	.	.	.	.	1	.	.	.	.	.	.	.	.	.
		90	1 day	1	.	.	.	1	.	1	.	1	.	.	.	1	.	.	.
		90	5 days	1	.[c]	.	.	1	.[c]	.	.	1	.[c]	.	.	1	.[c]	.	.
		70	7 days	.	.[c]	.	.	.	.[c]	1	1	.	.[c]	.	.	.	.[c]	.	.
		70	14 days	.	.	.	.	.	.	1[d]	1[d]	.	.	.	.	.	.	.	.
	450ºC	90	1 day	1	.	.	.	1	1	.	.	1	1	.	.	1	1	.	.
		90	5 days	1	.	.	.	1	1	.	.	1	1	.	.	1	1	.	.

*Note - each value in the table represents 1 test with 3 samples

a - Moisture state: US - Unsealed, S - Sealed

b - 28 day temperature tests exhibited excessive variation and were discounted

c - Sealed tests attempted at 225ºC using aluminium foil and silicon sealant, all sealing failed

d - Thermal cycling tests continued after steady state temperature exposure of 14 days (i.e. 1[st] cycle is single temperature test)

Table 4.8: Testing Matrix - Compressive Strength Tests* (b) - Multiple Temperature Tests

Test	Temperature Exposure	Curing Age (Days)	Exposure Duration	Conventional Mortar				Conventional Concrete				Low Cement Mortar				Low Cement Concrete			
Compressive Strength				Mould Design 1		Mould Design 2		Mould Design 1		Mould Design 2		Mould Design 1		Mould Design 2		Mould Design 1		Mould Design 2	
Moisture State[a]				US	S	US	S	US	S	US	S	US	S	US	S	US	S	US	S
Multiple Temperature Tests																			
	225ºC to 450ºC	90	5 days (225ºC) and 1 day (450ºC)	.	.	.	.	.	.	1	1	.	.	.	.	.	.	.	.
		90	5 days (225ºC) and 2 days (450ºC)	.	.	.	.	.	.	1	1	.	.	.	.	.	.	.	.
		90	5 days (225ºC) and 5 days (450ºC)	.	.	.	.	.	.	1	1	.	.	.	.	.	.	.	.
Thermal Cycling																			
	225ºC[e]	70	1^{st}cycle - 14 days at 225ºC	.	.	.	.	.	.	1[d]	1[d]	.	.	.	.	.	.	.	.
		70	2^{nd}cycle - 1 day at 225ºC	.	.	.	.	.	.	1	1	.	.	.	.	.	.	.	.
		70	3^{rd}cycle - 1 day at 225ºC	.	.	.	.	.	.	1	1	.	.	.	.	.	.	.	.
	450ºC[e]	70	3^{rd}cycle - 1 day at 450ºC	.	.	.	.	.	.	1	1	.	.	.	.	.	.	.	.

*Note - each value in the table represents 1 test with 3 samples

d - Thermal cycling tests continued after steady state temperature exposure of 14 days (i.e. 1^{st}cycle is single temperature test)

e - 450ºC third temperature test after two cycles to 225ºC

4.6 Microstructural Scanning Electron Microscope Studies

In order to gain an understanding of the effect that temperature was having on the microstructure of the concrete several samples of concrete exposed to either 225°C or 450°C were used for microstructural studies using the scanning electron microscope unit at UCT. The samples were shards of concrete from previously crushed compressive strength specimens. Three temperature regimes were considered:

- 225°C for 1 day and 7 days, in both sealed and unsealed states.
- 450°C for 1 day in an unsealed environment.

The methodology used in testing the samples is as follows:

- The crushed samples were in plastic bags as mentioned previously. A bag was selected and opened.
- An appropriate piece of concrete was selected, ideally having a relatively flat surface, and a piece of aggregate in the piece.
- The sample was bonded to a SEM viewing disc using double sided tape, and given an easily identifiable code on the viewing disc with a fine felt tip pen.
- The disc was placed in a dessicator and taken to the scanning electron microscope unit of UCT.
- The sample was more firmly bonded to the disc using a mixture of carbon and glue.
- The glue was allowed to set.
- The disc was then placed in a vacuum chamber that coated the sample in carbon dust to prevent the sample from charging up in the microscope.
- After being left under vacuum overnight the sample was transferred to a dessicator, taken to the scanning electron microscope and loaded into the microscope.

This method allowed the samples to be viewed in the microscope while not requiring excessive vacuum drawing times for the microscope and preventing excessive charging of the sample in the microscope. Excessive charging leads to very bright spots on the microscope images, reducing fine detail of the images. Images were taken of points of interest, namely aggregate-paste interfaces, microcracks and formations of new calcium silicate hydrate (CSH) gel.

The SEM work was not a comprehensive study of the microstructure of the concrete, but was rather used to complement the compressive testing results. The studies were used to further develop an understanding of the response of concrete to temperature, and as such are presented in the discussion Chapter.

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Chapter 5

Results of Testing

This chapter presents data from the testing that has been carried out. The compressive strength results are presented first, beginning with the preliminary stage of tests. These tests were used to determine how fruitful the approach taken towards testing was and take some key lessons on the response of the concretes and mortars, resulting in a decision to focus on conventional concrete. This allowed more in depth testing using specimens of better quality, as presented in Section 5.1.2. The durability index data is presented next, with oxygen permeability, chloride diffusivity and water sorptivity results for one or five days of temperature exposure in an unsealed environment. SEM studies are included in Chapter 6 as a complement to the discussion.

5.1 Compressive Strength

As discussed in Chapter 4, the compressive strength of specimens was tested on the Zwick universal testing machine after capping the samples with Pratley's Quickset putty to ensure the samples had plane ends. The testing phase consisted of three different series, with the first using the first mould design and testing two concretes and two mortars. The second and third testing series used the improved mould design and considered conventional concrete in much greater depth, including strength development over 28 days and various heating regimes at either 70 or 90 days of curing. Testing series two and three were combined into Section 5.1.2, the in depth assessment of conventional concrete. It is worth reiterating here that each data point presented in this section represents the average of three specimens, and the trend lines illustrated in the Figures are based on these averages. Most of the data here is presented as a percentage of the unheated strength, and error bars are placed in the Figures to illustrate the range of results for a given test.

5.1.1 Preliminary Tests

The first stage of tests was used to assess the different concrete and mortar responses to temperature while drawing direct comparisons between each, and furthermore to determine the direction to progress with testing. The points focused on with this testing included:

- The effect that different aggregate contents in the concrete had, namely what was the impact of higher contents of aggregate (and subsequently lower binder contents).

- The impact the inclusion of coarse aggregate had on the response of the concrete when compared to the mortar, keeping in mind the different thermal expansion properties of the binder and aggregate phases, and the likelihood of microcrack development.

With the motivation behind the testing appropriately outlined, four issues became apparent from the testing.

1. The tests were carried out using samples manufactured with the first mould design, which resulted in samples with excessive void content, non-plane end surfaces and some variability of sample dimensions. The non-plane surfaces and variability of sample dimensions were counteracted in the 90 day results with greater care in the sample preparation, but not the 28 day tests.

2. Sealing of samples proved to be difficult, with attempts to seal samples exposed to 225°C using aluminium foil and gasket sealant completely failing, and samples sealed in steel containers exposed to 450°C also losing mass, implying a loss of moisture. However the samples exposed to 450°C had sufficiently different properties from the unsealed specimens to require consideration.

3. The orientation of the steel container (either vertical or horizontal) in the furnace exposed to 450°C for 1 day may have caused excessive variation in the 90 day results. It is possible that this caused the bottom side of the sample to be lying in liquid water with the upper part of the sample in a gaseous mixture of water and air, while the container was being heated to temperature (note that the critical point of water, above which it is a super critical fluid, is 374°C). This could have encouraged differential strength and stress-strain characteristics to develop over the section of the sample, allowing for an increased shearing effect to occur in the sample during crushing.

4. Another issue that became apparent in hindsight from this testing was that the unheated samples were not tested in a saturated state, but were rather tested in a partially dried state. This was because samples

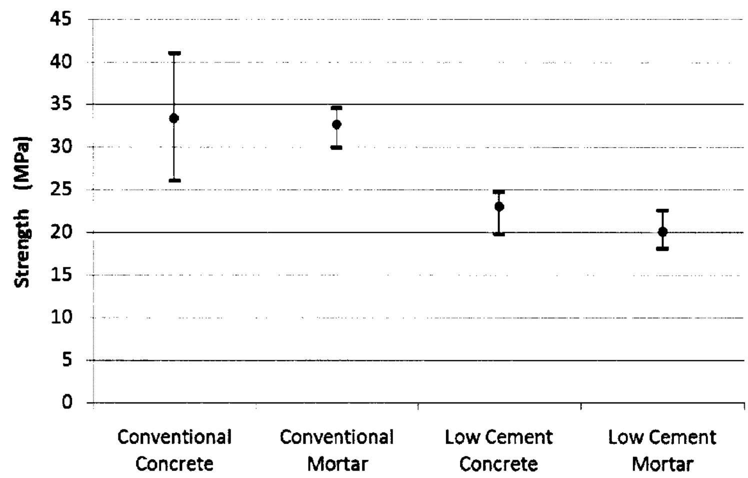


Figure 5.1: 28 day unheated compressive strengths of all concretes and mortars (preliminary tests - see point 1 Section 5.1.1)

were selected from the curing tank and placed to one side while the heated samples were exposed to their respective environments, allowing the samples to dry during this period (between 1 and 3 days). This will have caused higher strengths to be attained, possibly in the region of 10% to 20% above the fully saturated values [12]. This issue was accounted for in subsequent testing series with samples removed from the curing tank on the day of crushing, and closed into plastic bags shortly after being removed from the tank and capped.

These issues placed a certain limitation on the quality of the data generated, demonstrating large variability and sometimes contradictory trends. Keeping in mind that a purely qualitative assessment of the responses of different concretes and mortars was being taken with a view to improving the subsequent methodology, broad conclusions could be made on the responses and to further motivate testing in a specific direction.

28 Day Unheated Results

The first set of data worth considering is that of the unheated 28 day strengths of the concretes and mortars. This is presented in Figure 5.1. Conventional concrete and mortar both demonstrated strengths of 33 MPa while the low cement concrete and mortar demonstrated strengths of 23 MPa and 20 MPa respectively. These results are significantly lower than the reported results that the concretes were based on [16, 49], which is understandable considering differences in aggregate grading, size and fineness modulus. The fundamental motivation behind the testing does however stay the same, in that the constituent proportioning (fly ash: cementitious compounds) is the same.

The high variability of the sample strengths is clearly apparent, with the results for conventional concrete being particularly notable with a range of over 15 MPa for a strength of 33 MPa, giving a maximum to minimum range of approximately 50%. Some tests were carried out with exposing the concrete to temperature, however, due to the inherent inconsistency of the tests (between 30% and 50%), the results were removed from consideration.

The unheated strengths of the concrete support the different water:cement ratios used in the concrete (0.3 for conventional concrete and 0.4 for the low cement concrete).

90 Day Results

The 90 day test results showed a significant improvement in quality, largely because of greater care being taken in preparation, capping and crushing of the samples. This enabled the successful testing of concretes exposed to either 1 day or 5 days at 225°C or 450°C. These durations of testing were used to give a reasonable indication of the response of the concrete to first heating (1 day) and the time dependency of the response (5 days).

As has already been mentioned, attempts at sealing concrete at 225°C using aluminium foil and high temperature gasket sealant failed, requiring they be removed from consideration at this point. The use of steel containers provided a notable property change at 450°C, suggesting that this was a more effective method of sealing specimens, however it was discovered that the containers lost mass on heating. This was on average 24 grams per container (holding 3 specimens), while unsealed samples lost 6 grams on heating. This suggests that the containers still lost moisture, in fact more mass per sample than an unsealed sample, probably due to excess moisture inside the container. With this stated, as already mentioned, the property change demonstrated by these samples was sufficiently different from the unsealed samples to warrant consideration.

Low cement content mortar and concrete are considered first, followed by conventional mortar and concrete. Conclusions and trends that can be observed from this data, along with probable causes, are also discussed.

Low Cement Content Mortar Three lines of testing were considered for low cement mortar, namely:

- 225°C unsealed tests at 1 and 5 days.
- 450°C unsealed tests at 1 and 5 days.
- 450°C sealed tests at 1 and 5 days.

The low cement content mortar had an unheated strength of $f_c = 32\,MPa$ with an average range from minimum to maximum of 23% for the testing series. The results are presented in Figure 5.2 on the next page.

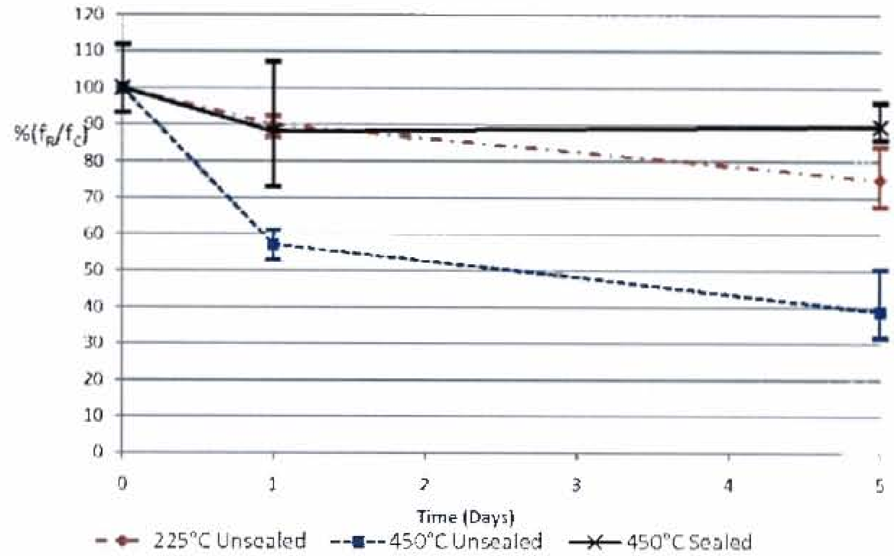


Figure 5.2: 90 day low cement mortar results, $f_c = 32\,MPa$

The average range of the results were affected by the large spread of the 1 day sealed results at 450°C, with a range in excess of 30%, possibly due to the orientation of the steel container (as the container was heated in a horizontal orientation) as mentioned previously.

There are several trends that can be drawn from the response of the mortar to temperature exposure. At 225°C in an unsealed state, there is a reduction of about 10% in strength after 1 day of exposure, and a 25% reduction with 5 days of exposure. This suggests a gradually deteriorating response of the material to this environment as is expected with high fly ash contents [44], due to high shrinkage and dehydration of the binder phase. This is further supported by the low cement concrete results presented shortly.

With exposure to 450°C in an unsealed state, the deterioration is further encouraged. A reduction of 43% after 1 day of exposure and 61% after 5 days was demonstrated. This is in agreement with the theory that changes to the binder phase relating to shrinkage and dehydration are deleterious to the material response to temperature.

The results for sealed mortar specimens exposed to 450°C are particularly interesting, noting that this environment is more characteristic of the PBMR than the unsealed results. These showed a much lower deterioration when compared to the unsealed mortar showing only an 11% reduction after 1 day, staying roughly at this level (10%) after 5 days. Following Kropp et al. [44], deleterious hydrothermal reactions would have been counteracted by the high fly ash content coupled with a pozzolanic reaction forming new CSH. That the concrete was exposed to 450°C and the results show a deterioration, suggests that this temperature damages the binder phase, but that the presence of fly ash stabilizes the extent of the damage. This is in line with the conclusions reached from literature that suggest high extender contents in sealed environments provide either a similar or better response over the unsealed response to temperature [17].

Low Cement Content Concrete As with the low cement mortar, three lines of testing were considered for the low cement concrete:

- 225°C unsealed tests at 1 and 5 days.
- 450°C unsealed tests at 1 and 5 days.
- 450°C sealed tests at 1 and 5 days.

The low cement concrete had an unheated strength of $f_c = 38\,MPa$ with an average range of 22% for all the tests, with the results shown in Figure 5.3.

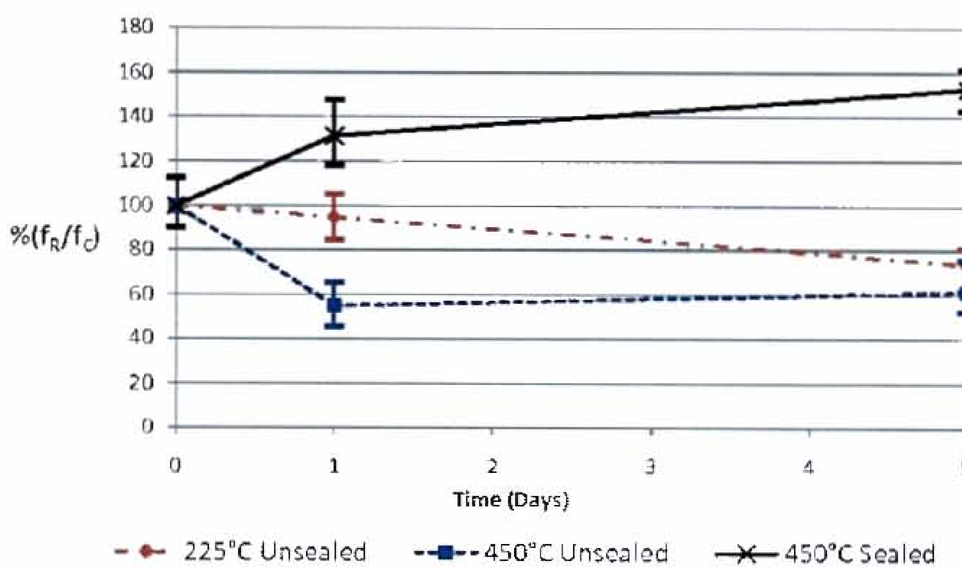


Figure 5.3: Low cement concrete strength results, $f_c = 38\,MPa$

The possibility of the orientation (lying horizontally or vertically) of a sample being heated in a sealed environment affecting the results is supported, at least to some extent, here. The 450°C 1 day sealed results had a range of 29% while being heated lying horizontally, while the 5 day results demonstrated a range of 23% while being heated vertically.

The response of the concrete to 225°C in an unsealed environment was very similar to that of the mortar, giving 94% after 1 day, and 75% after 5 days. This suggests that the 6mm coarse aggregate had a minimal impact in an unsealed concrete at these temperatures. Noting that the thermal expansion of paste and aggregate are probably quite close at this temperature [7], it is reasonable to conclude that the response of the binder dominates the response of the concrete at this temperature.

When the concrete is exposed to 450°C in an unsealed environment, it also demonstrates similarity to the response of the mortar for 1 day of heating, giving 55% of the unheated strength. The response to 5 days appears to have stabilized at the 1 day response to temperature, within the range of the results. At this temperature it is likely that differential shrinkage/expansion between the aggregate and paste dominate the response of the concrete, especially considering the high fly ash content [44], causing microcracking in the concrete. This would be effectively complete once the sample is at temperature, and would show limited time dependency.

The most interesting results are those of the sealed response to 450°C. These demonstrated a marked increase with temperature exposure, showing a 30% improvement with 1 day of exposure and a 50% improvement with 5 days of exposure. It is important to keep in mind the results of Seeberger et al. [17] and Kropp et al. [44] in this case (although their results are for 250°C), who demonstrated an improvement in strength in hydrothermal conditions due to pozzolanic reactions forming new gel-like phases. The high aggregate content of the low cement content concrete would likely have caused microcracking at 450°C, which may have exposed unused fly ash and Portland cement. This would have allowed the formation of new CSH via pozzolanic and normal cementing reactions due to the moist environment. The limiting case to this hypothesis is the extent of microcracking and the amount of unhydrated Portland cement and fly ash available, as Kropp et al. [44] showed that the relative CH content of paste drops to zero in about 20 hours in an equivalent concrete heated to 180°C. Provided the microcracking exposes unhydrated Portland cement, normal cementing reactions will form new CH for pozzolanic reactions beyond this time frame.

Conventional Mortar Due to limited availability of sealing containers and samples of sufficient quality, only two lines of testing were carried out for conventional mortar:

- 225°C unsealed tests for 1 or 5 days.
- 450°C unsealed tests for 1 or 5 days.

The conventional mortar achieved an unheated compressive strength of $f_c = 65\,MPa$ with an average range for the testing set of 9%, as presented in Figure 5.4.

The conventional mortar demonstrated a reduction of 14% after 1 day at 225°C in an unsealed state, and 29% after 5 days of exposure. This is roughly in agreement with the response of the low cement mortar, which is understandable, as the main differentiator between the two mortars was that low cement mortar had condensed silica fume and a higher content of sand.

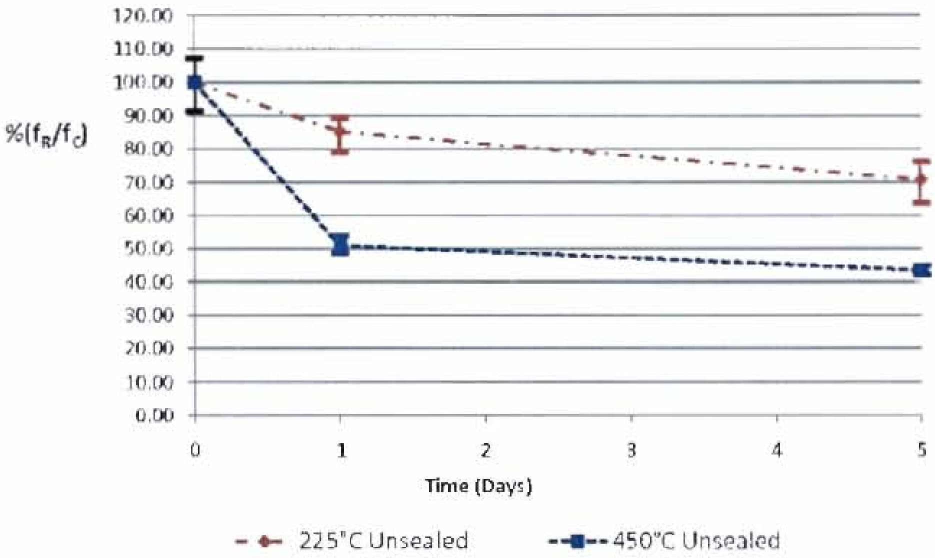


Figure 5.4: Conventional mortar strength results, $f_c = 65\,MPa$

The response of the mortar to 450°C in an unsealed state further supports the similarities of the response with low cement mortar, with a 49% reduction after 1 day of exposure, and a 56% reduction after 5 days of exposure.

Conventional Concrete Conventional concrete was tested according to the same three lines as low cement concrete and mortar, namely:

- 225°C unsealed tests for 1 or 5 days.
- 450°C unsealed tests for 1 or 5 days.
- 450°C sealed tests for 1 or 5 days.

The conventional concrete achieved an unheated compressive strength of $f_c = 56\,MPa$ with an average range for the testing set of 18%, with the results presented in Figure 5.5.

The orientation of the sealed samples at 450°C after 1 day of exposure appears to not have had a significant role here. However the particularly low values of this set of samples, roughly the same as the unsealed samples, suggests the sealing of the container may have failed completely, tending the samples towards an unsealed response that would have had a smaller range between maxima and minima.

The 225°C unsealed tests illustrated an average of 17% reduction after 1 day of heating, reducing to 9% after 5 days of exposure, with the error bars suggesting there was little change after 1 day. Following that the thermal expansions of the aggregate and cement paste are probably quite close at this

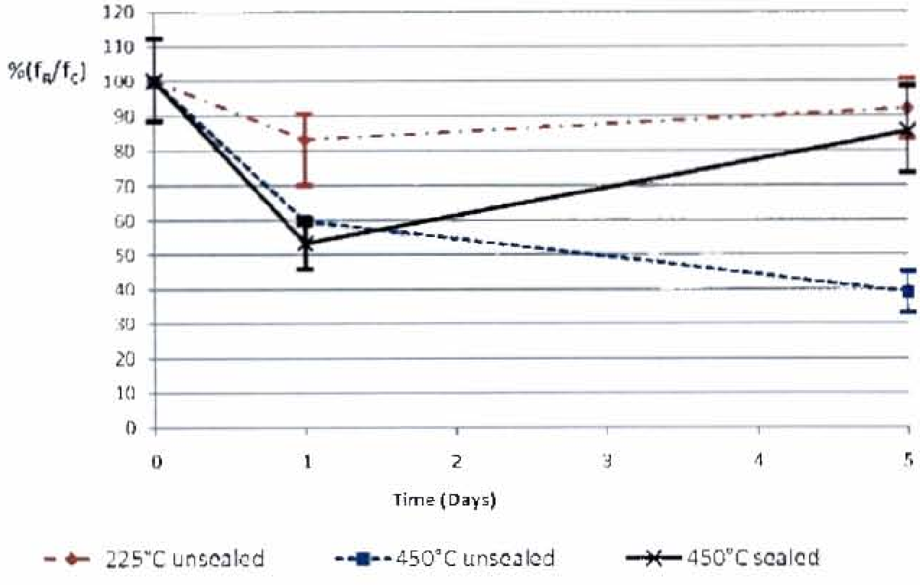


Figure 5.5: Conventional concrete strength results, $F_c = 56\,MPa$

temperature, it is likely that the strength of the concrete is governed by the strength of the binder. There is a however a difference between the 5 day response of the concrete and mortar that is difficult to explain.

The 450°C unsealed response demonstrated a loss of 40% after 1 day of exposure and 60% after 5 days of exposure, giving a similar response to unsealed conventional mortar. This suggests that the binder response is still governing the response of the concrete at this temperature. This then suggests that there is less microcracking developing than in the low cement content concrete, due to the lower aggregate content (and subsequently higher binder content) of conventional concrete.

Interestingly the sealed 450°C response demonstrates a reduction of 56% after 1 day, recovering to a reduction of 14% after 5 days. These values are much lower than the results of the low cement concrete which demonstrated strength gains of 30% and 50% respectively with these tests. Following the hypothesis that the strength gains in low cement concrete are due to the development of microcracking allowing further beneficial hydrothermal reactions, it follows that the lower aggregate content of conventional concrete will lead to less microcracking, and subsequently less strength gain.

Clearly, determining the response of a concrete to high temperatures is a very complicated endeavour, requiring consideration of many factors. Explaining this response from a microstructural perspective can provide some insights, while adding further complexity.

Large conventional concrete specimens Three large (Ø$80mm \times 160mm$) conventional concrete specimens were tested to assess the difference between the small and large specimen strength response. These were tested in the Amsler compressive strength machine in the civil engineering department of the University of Cape Town. The results are presented in Table 5.1. These samples had a compressive strength of 60 MPa.

Table 5.1: Compressive strength of large concrete specimens

	Units	Sample 1	Sample 2	Sample 3
Mass	kg	2	2	2
Diameter	mm	80	80	80
Length	mm	147	152	152
Load	kN	330	242	326
Strength	MPa	66	48	65
Average	MPa			60

Recall that the small conventional concrete samples had an average compressive strength of 56 MPa, showing that the use of the samples with smaller dimensions did not have a substantial effect on the strength of the concrete. There was however still a large range in the results from the specimens of 30%.

Deductions From Preliminary Testing

Several deductions were made based on the results obtained from the preliminary testing, as outlined below:

- Managing the sealing of the concrete was of paramount importance. The use of aluminium foil and sealant was ineffective, and greater care needed to be taken to ensure sealing with steel containers was effective.

- The inclusion of 6mm granite aggregate into the mortar had a limited effect in terms of the unsealed response of the concrete to high temperatures, especially at 225°C. At 450°C the concrete appears to have developed microcracking, dependent on the aggregate content, however, the binder still appears to govern the response of the concrete.

- The inclusion of coarse aggregate in sealed concretes exposed to 450°C demonstrates either a lower reduction of strength, or even an improvement in strength with duration of exposure. This appears to be related to the development of microcracking in the concrete facilitating further beneficial hydrothermal reactions.

- Interestingly the use of higher aggregate contents and lower binder contents in a concrete suggests a greater improvement of strength in sealed concretes exposed to 450°C. This is most likely due to more extensive development of microcracking in concretes with a greater aggregate content, exposing unreacted Portland cement and fly ash that then reacts to autogeneously heal the concrete and even improve the strength. This extensive microcracking is supported by the durability index tests presented in Section 5.2.

With these deductions in mind, it was decided to further investigate conventional concrete. This decision was based largely on the durability index results, presented in Section 5.2, that supported the theory of increased microcrack development in low cement concrete. The development of microcracking in a concrete is an undesirable property when considering other properties such as modulus of elasticity, creep and all transport properties. Although the possibility of autogeneous healing could enable the recovery of these properties over time at temperature, this could have implications for the dimensional stability of the structure. Similarly, although autogeneous healing may provide significantly improved strengths, and indeed probably occurs in the conventional concrete to a lesser extent, it is difficult to justify sacrificing other properties (such as modulus or creep) for this.

The testing that solely considered conventional concrete is now presented.

5.1.2 In Depth Conventional Concrete Testing

This Section is concerned with the in depth strength testing that was undertaken for conventional concrete. The sole consideration of conventional concrete was justified by enabling a more comprehensive testing of various exposure environments such as thermal cycling.

Several differences in the sample manufacturing, curing and testing methodologies were implemented in this phase of the testing. Most notable was the use of an improved mould design, allowing significantly improved sample quality. With this said, issues that became apparent in this testing phase included:

- The unheated strengths of this set of concretes proved to be considerably lower than the preliminary phase of testing, suggesting a difference in the moulding and curing environments. Although it was difficult to isolate the exact causes of these low strengths, it may be attributed to manufacturing inconsistencies that may have lead to a different water content in the concrete. It was discovered that the curing tank temperature was not controlled as the heating element for the bath had blown at some stage in the curing cycle, probably causing significantly lower temperatures in the tank. Further discussion on the possible causes of these low strengths is given with the 70 day results.

- All sealed tests were undertaken with the steel containers used in the preliminary stage of testing. Although due care was taken to prepare the containers to ensure effective welding, the containers still proved to lose mass on heating, 25 grams on average. This unfortunately suggests that the containers did not seal effectively, allowing the escape of moisture. With this said, as with the preliminary stage of tests, there was a significant difference between the sealed and unsealed responses of the concretes, warranting consideration of the results.

Strength Development, Durability Index and Shrinkage Results

The first set of data presented is related to the unheated properties of the concrete, with a view to assessing the suitability of a concrete with similar proportions for application in the PBMR. Table 5.2 presents a summary of the 28 day properties of the concrete relating to strength and the durability index tests (although the effect of temperature on the durability index tests is discussed in Section 5.2, it is appropriate to include these here in order to effectively suggest the commonly accepted properties of the unheated concrete).

Table 5.2: 28 day results for various properties of conventional concrete

Property		Value
28 day compressive strength		29.7 MPa (variance 7 MPa)
Durability Tests		
Oxygen Permeability Test	Permeability Coefficient	$1.8*10^{-11}$m/s
	OPI Value	10.7
Chloride Conductivity Test	Chloride Conductivity	0.21 mS/cm
	Porosity	5.7%
Sorptivity Test	Sorptivity	7.3 mm/hr$^{1/2}$
	Porosity	6%

When one considers the 28 day strength of the concrete, a strength of 29.7 MPa was achieved. This was considerably lower than the 40 MPa design strength, but in order to maintain consistency with the testing process this was determined to be acceptable. At this stage the project was attempting to isolate the effect that temperature had on the strength of the concrete, as opposed to designing a concrete to the suggested requirements. With an appropriate understanding of the effect of temperature, the design of a concrete giving the appropriate properties would be considerably simpler.

In terms of the durability index tests, a permeability coefficient of $1.8 \times 10^{-11} m/s$ affords an oxygen permeability index of 10.7, which is an acceptable value for the concrete, being near the higher end of the range of OPI values. A chloride conductivity of $0.21 mS/cm$ is a very low value, indicating that the concrete had a very low chloride diffusivity, while a sorptivity of $7.3 mm/\sqrt{hr}$ is also considered to be acceptable. A porosity of between 5.7% and 6% is

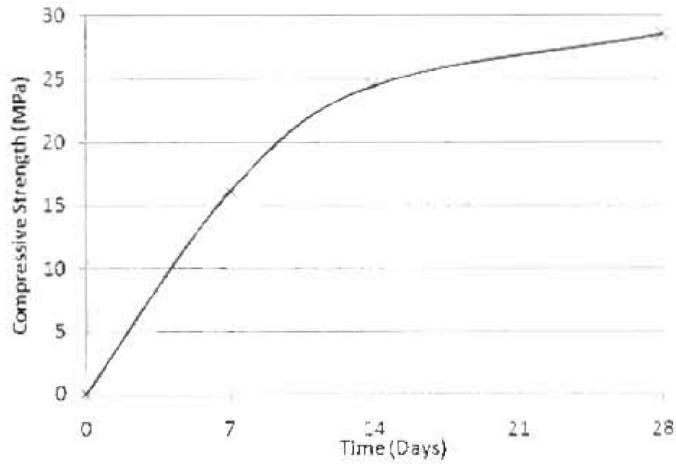


Figure 5.6: Strength development up to 28 days

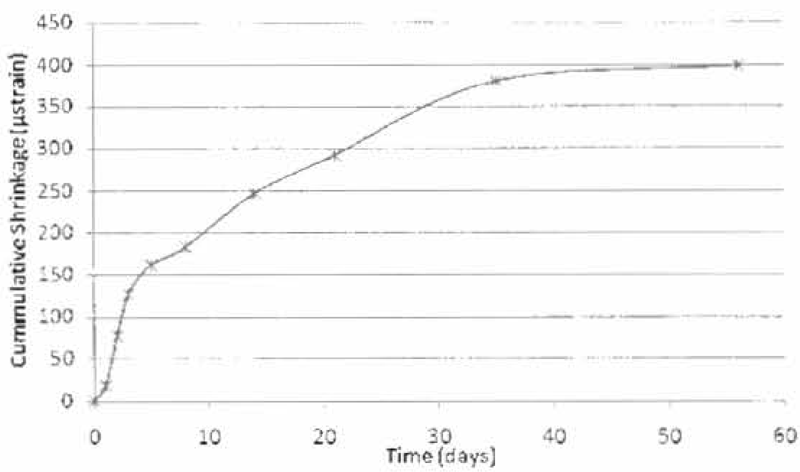


Figure 5.7: Shrinkage up to 60 days

relatively low. The strength development of the concrete is presented in Figure 5.6.

This strength development is in line with the expectations of a concrete with a very high fly ash content, suggesting that there is an improvement of strength happening after 28 days due to the slow nature of the pozzolanic reaction from fly ash. For this reason, when developing the final mix designs for the PBMR consideration should be given to using CEM 52.5.

The development of shrinkage was determined using $\varnothing 100mm \times 200mm$ cylinders, as described in Chapter 4, and is shown in Figure 5.7. This data clearly shows that the concrete tended towards an asymptotic shrinkage value in the region of 400μstrain. This value is rather high in terms of a concrete mix design, however when one considers that 6mm aggregate was used in the manufacturing of the samples, the high shrinkage is understandable.

Two ages of concrete were tested to determine the response to high temperatures, namely 70 days and 90 days. This was to allow a broader range of heating environments to be tested with the limited apparatus available, but also gave an indication of the effect that age of concrete may have on the response to temperature.

70 Day Results

The testing carried out after 70 days of cure are presented in this Section. This consists of two different tests, with the second a continuation of the first. A single temperature test at 225°C was carried out for 1, 7 or 14 days. Extra samples that had been heated for 14 days were cooled and then subjected to thermal cycles either of twice to 225°C, or once to 225°C and once to 450°C.

As such these results are split into single temperature tests that consider the results collected up to 14 days, and thermal cycling tests that consider the results from 14 days onwards.

Single Temperature Results The single temperature tests are for sealed and unsealed concretes exposed to 225°C for 1, 7 and 14 days at temperature, keeping in mind the heating and cooling rate of 10°C/h. These results are presented in Figure 5.8 on the following page.

Considering Figure 5.8 (a), a remarkable improvement in strength of a sealed concrete exposed to 225°C for up to 14 days is demonstrated. After 1 day the strength is 60% higher than the unheated strength, and is 133% higher than the unheated strength after 7 days, staying roughly at this value after 14 days. This is in reasonable agreement with Kropp et al. [44] who demonstrated a 100% strength gain of a cement paste with a similar fly ash replacement ratio. The results suggest the formation of new gel-like phases.

The unsealed concretes interestingly demonstrate a 24% to 53% increase in strength after heating. This is markedly different from the response of the concrete in the preliminary stage tests which demonstrated a 9% to 17% reduction in strength with exposure to 225°C. Interestingly, these two values appear to be converging in terms of actual value, i.e. the first stage strengths were between 49 and 52 MPa, while the tests presented here were between 40 and 49 MPa.

With this said it should be noted that qualitatively a significant improvement, of the order of 130%, in strength of a concrete in a sealed state has been demonstrated, which was in line with the concepts gained from literature [17, 44].

Thermal Cycling Results After the concretes had been exposed to 14 days of 225°C, three thermal cycles were undertaken to assess the impact of thermal cycling on the concrete, as shown in Figure 5.9. The cycles consisted of either two cycles to 225°C or 1 cycle to 225°C and 1 cycle to 450°C.

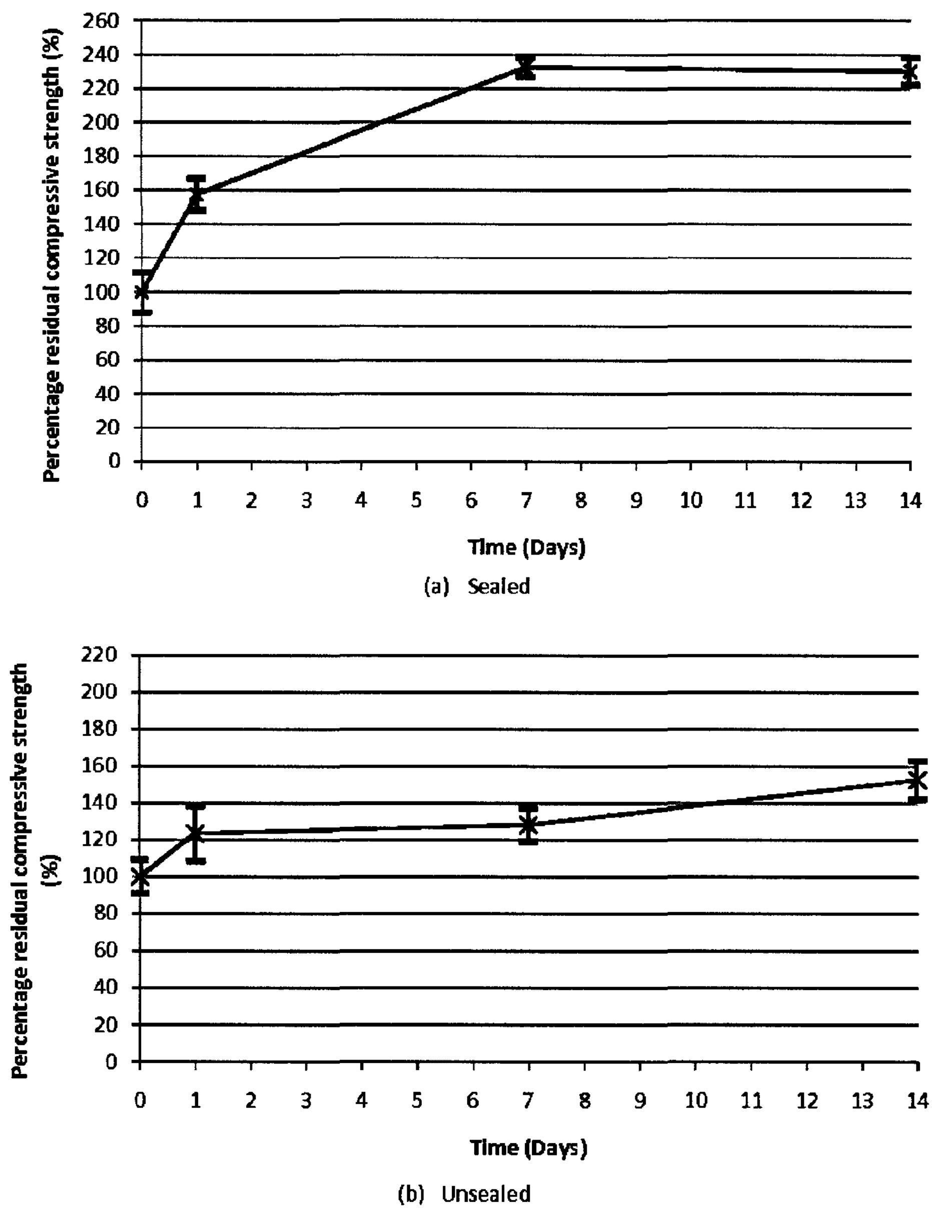


Figure 5.8: Compressive strength results for (a) Sealed and (b) Unsealed conventional concrete, $Fc = 32\,MPa$

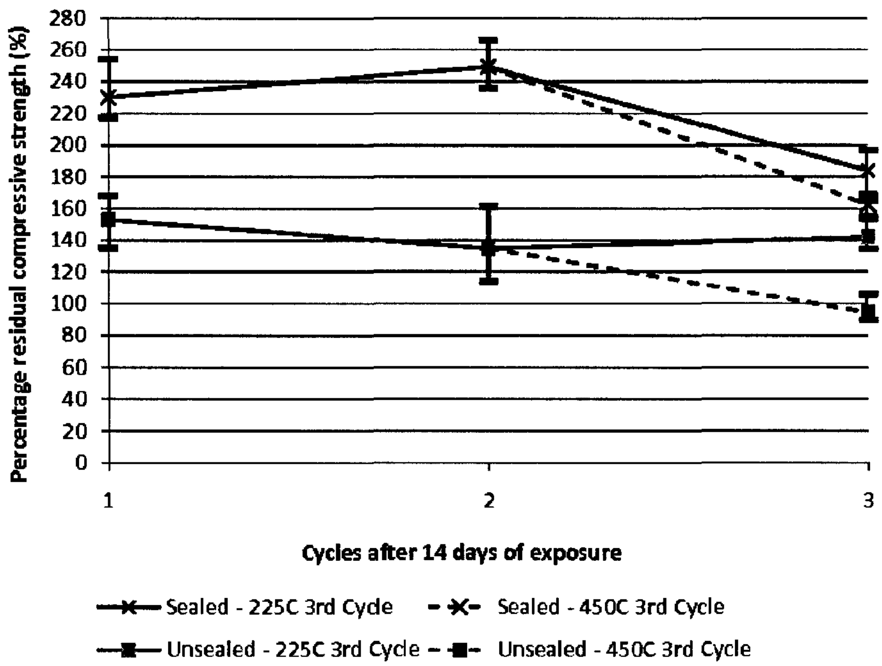


Figure 5.9: Thermal cycling results

When one considers the unsealed response of the concrete (the square markers), it is apparent that there is no significant effect with thermal cycles to 225°C. After the third cycle to 225°C the concrete demonstrated roughly the same strength as after 1 cycle. When this concrete is taken to 450°C on the third cycle (the dashed line with square markers), a decrease in strength to 94% of the unheated strength is demonstrated. This is a reasonable decrease, in line with expectations.

Considering the sealed response (the crossed markers), it is apparent that for the first two cycles there is a limited effect of thermal cycling, most likely relating to the inherent variability of concrete strengths. The third cycle response is particularly interesting. Considering the 225°C third cycle response (the solid line with crossed markers) there is a clear deterioration of strength. This is uncharacteristic with the other tests (the unsealed response and the first two cycles of the sealed concrete) and suggests that the container the samples were sealed in may have failed, allowing the escape of moisture comparatively more quickly. This would have caused the concrete to not achieve the first cycle strength of about 230%.

The sealed response to 450°C (dashed line with crossed markers) demonstrated a decrease to 162% of the unheated strength, from between 230% and 250% after 225°C. This is in line with the expected response of the concrete, in that exposure to 450°C will exhibit a decrease from the 225°C response.

90 Day Results

The tests carried out after 90 days of curing were used to assess the impact of different ages of concrete, and the effect of exposure for up to 5 days at 225°C followed by 3 days at 450°C. Recall that the heating rate was 10°C/hr, requiring an additional day as the concrete was heated from 225°C to 450°C (22.5 hours). This day has been included in the graph presented under the 450°C response, as it was in the middle of the test. This data is presented in Figure 5.10 on the next page.

Considering Figure 5.10 (a) the sealed concretes demonstrated a strength increase of 100% over the unheated concrete for the first 5 days of heating (at 225°C). This was about 30% lower than the strengths achieved after 70 days of cure, suggesting that the concrete was less responsive to temperature exposure after a longer period of cure. After 5 days of heating at 225°C the concrete was heated to 450°C at the heating rate of 10°C/hr, followed by 3 days at this temperature. This demonstrated a marked decrease of 50% from the 225°C strengths, followed by a slow recovery to 170% of the unheated strength of the concrete. This supports the hypothesis of microcracks developing in the concrete at this temperature, exposing unreacted Portland cement and fly ash, followed by further hydrothermal formation of gel-like phases.

The unsealed results demonstrated an improvement in strength with exposure to 225°C of around 50%, stabilizing after the first data point of 2 days of heat exposure. This is about the same as the 70 day results, if not higher than some of the data points, suggesting that the age of the concrete had a limited effect on the unsealed concrete, at these ages. On further heating to 450°C the unsealed concrete experienced a reduction in strength, to 106% of the unheated strength, but then also demonstrated a recovery to 123% of the unheated strength with duration at 450°C.

With the strength test results appropriately considered, it now becomes necessary to consider the durability index testing that was carried out.

5.2 Durability Index Testing

Durability index testing was carried out with the preliminary phase of testing to help identify the fundamental differences in the responses of the conventional and low cement concretes to high temperatures. These tests provided some very interesting insights into the response of concretes with high fly ash contents to extended periods of heating.

Recall that with the durability index tests all tests were done in an unsealed state, at temperatures of 225°C and 450°C, for either 1 or 5 days.

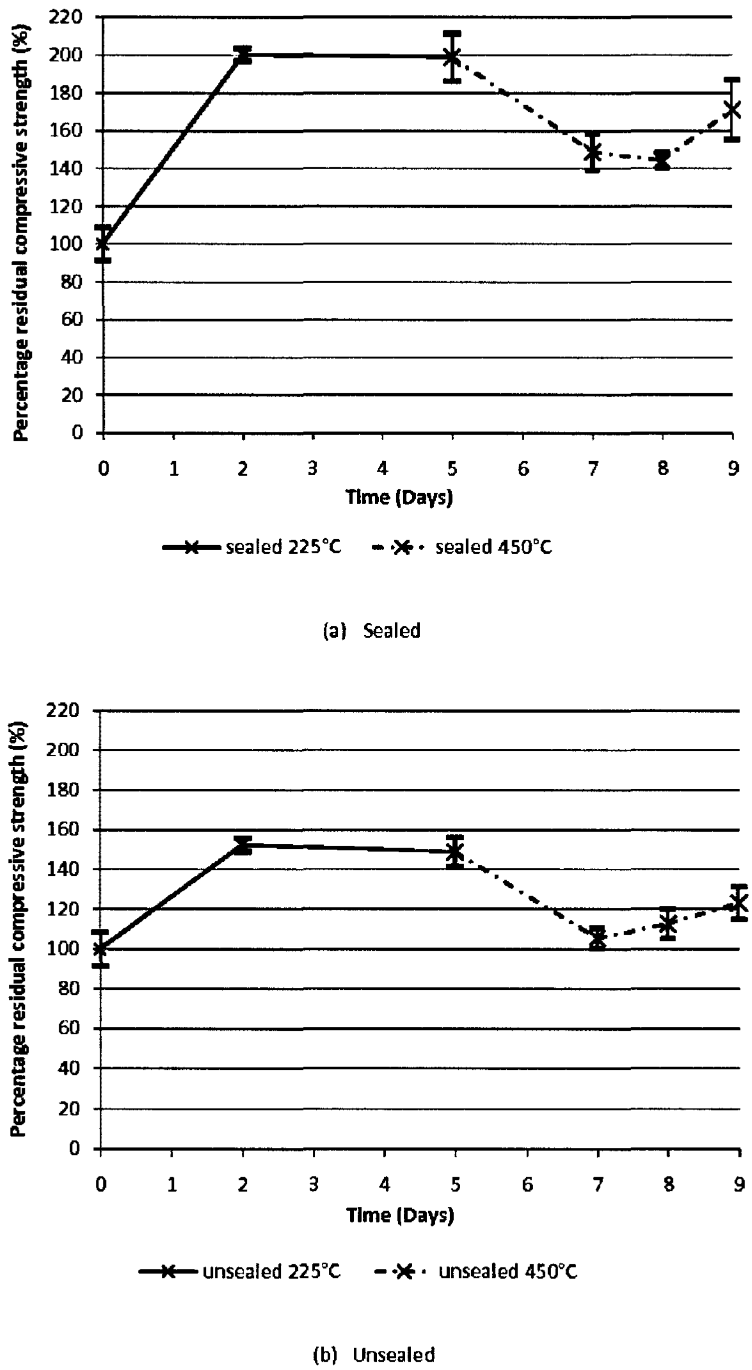


Figure 5.10: 90 day compressive strengths: (a) sealed and (b) unsealed concrete, $F_c = 31\,MPa$

5.2.1 Oxygen Permeability

The permeability of the concrete to gases is of particular interest here because of a requirement stating that the permeability shall be such that the leakage rate shall not be higher than 5% volume/day at 172.5 kPa (g) [10]. There are two ways of presenting oxygen permeability data, namely presenting the permeability coefficient values and the corresponding oxygen permeability index (OPI) values. It should be noted that the OPI value is an inverted log scale value of the permeability coefficient. As such, when one considers the graphs presented in this Section, the permeability coefficient values rise (giving an indication of the increase in permeability), while the OPI values drop. The permeability coefficient values are presented on a log scale here as well.

Both the permeability coefficient and OPI values have been presented to enable assessment of the response of the concrete in terms of the permeability according to the design requirements, and according to the conventionally applied durability index. In effect, the OPI value is a more accessible way of determining the permeability of a concrete with respect to durability.

Keeping in mind the importance of the structural integrity of the PBMR, it should be noted that as high OPI value as possible was desired, especially considering temperature exposure has a deleterious effect on the permeability of the material.

Low cement concrete The oxygen permeability results for low cement concrete are presented in Figure 5.11, with (a) showing the permeability coefficients of the concrete on a log scale, and (b) showing the oxygen permeability index.

From Figure 5.11 (a) it is apparent that there is an increase in permeability by about an order of magnitude with exposure to 225°C, and a further increase by another order of magnitude with exposure to 450°C. It appears that the permeability increases slightly with length of exposure.

The significant increase in permeability is possibly due to the development of microcracking in the interfacial transition zone and the high content of aggregate in the concrete. Higher aggregate contents indicate that the aggregate would be more closely packed, allowing greater interconnection of the ITZ's. The presence of fly ash and silica fume would lead to a denser ITZ, which is beneficial at room temperatures. However a denser ITZ would allow less differential thermal expansion on heating between the aggregate and binder phase before developing microcracking. This would then lead to more extensive microcracking in a heated concrete than one with a less dense ITZ.

The unheated OPI value of 10.9 was ideal, and the reduction to approximately 10 with 225°C can be acceptable if the time dependency of the property is correctly understood. However, with exposure to 450°C, the concrete demonstrates a marked reduction in OPI value to below 9, which is generally considered to be undesirable, allowing the carbonation front to progress at a very high rate. However when one considers the concrete will be heated in

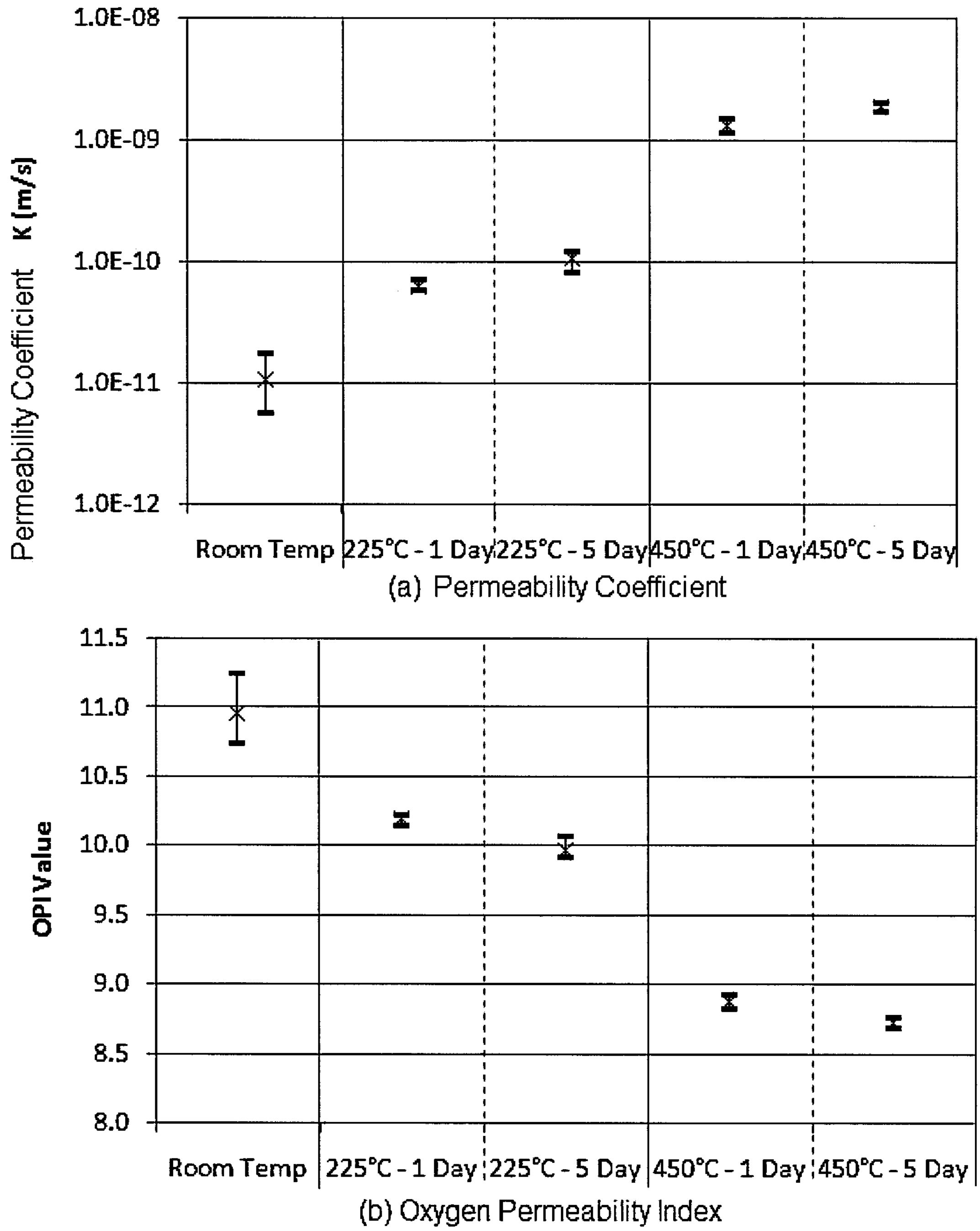


Figure 5.11: (a) Diffusivity and (b) oxygen permeability index results of low cement content concrete

this state it is likely that moisture will migrate away from this area and tend the material towards a dried state. A dried concrete undergoes very little carbonation.

Conventional concrete The results from the oxygen permeability tests of conventional concrete are shown in Figure 5.12, with (a) showing the permeability coefficient and (b) showing the OPI value.

This Figure illustrates the same trends as low cement concrete, although there is a significantly lower increase in permeability with temperature. Considering the permeability coefficient, an increase from 3×10^{-11} m/s to 6×10^{-11} m/s when the concrete is taken to 225°C is most likely due to a densification of the solid phase of the binder paste and increase in pore size, allowing greater flow of gases. The more significant increase that occurs when the concrete is taken to 450°C suggests the development of interconnected microcracking in the concrete that significantly increases the rate that a gas can transport through the concrete. This is in agreement with the low cement concrete that had a higher aggregate content, leading to a greater development of microcracking and subsequently greater increase in diffusivity.

The initial unheated OPI value of 10.4 is in-line with expected values, with a moderate decrease to between 10.2 and 10.1 with exposure to 225°C, which is still a high OPI value for this concrete. There is a significant reduction in OPI with heating to 450°C, to between 9.4 and just below 9, however, the concrete will likely dry out due to moisture migration, and as such reducing the rate of carbonation to a small value.

5.2.2 Chloride Conductivity

Chloride conductivity is a measure of the ability of chlorides to transport through a concrete, with units of mS/cm. The conductivity is presented in Figure 5.13 with (a) showing the results for conventional concrete and (b) showing the results for low cement concrete.

Firstly, considering the unheated data, these values in the region of 0.2 mS/cm demonstrate a fundamental aspect of the use of high fly ash contents, in that it provides a very low conductivity when compared to normal Portland cement concretes (that generally achieve in the region of 1 mS/cm [12]).

When one considers the 225°C results it becomes apparent that there is a significant increase on first heating, and then a subsequent decrease over time of exposure. This is more pronounced for the conventional concrete, reaching values of 0.8 mS/cm and reducing to 0.3 mS/cm, and less so for the low cement concrete, increasing to 0.7 mS/cm and reducing to 0.5 mS/cm. This is interesting in that it suggests that the property recovers with length of exposure to temperature.

In terms of the 450°C data a similar case occurs for conventional concrete in that after 1 day of exposure a conductivity of 1.8mS/cm was achieved, and after

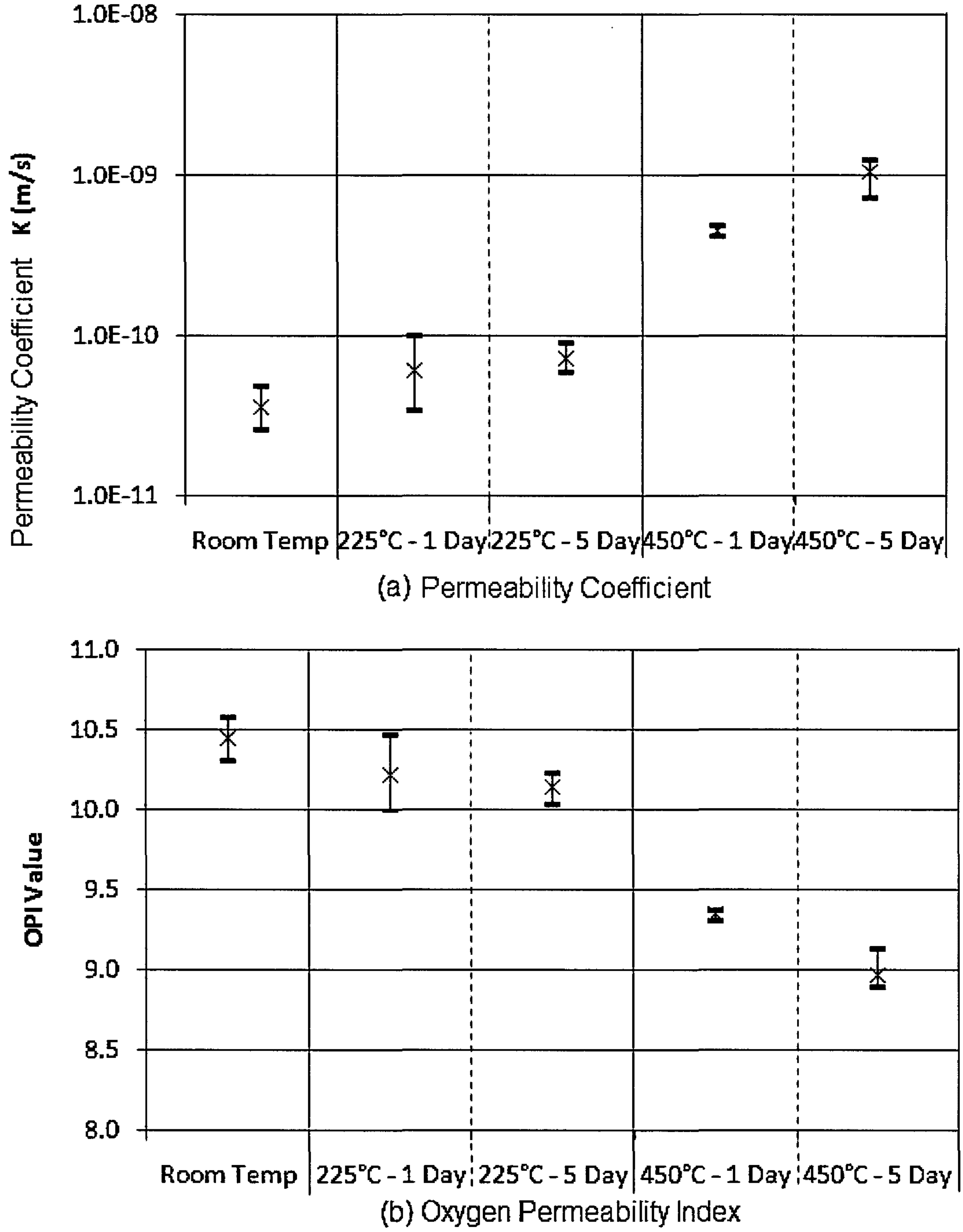


Figure 5.12: (a) Diffusivity and (b) oxygen permeability index results of conventional concrete

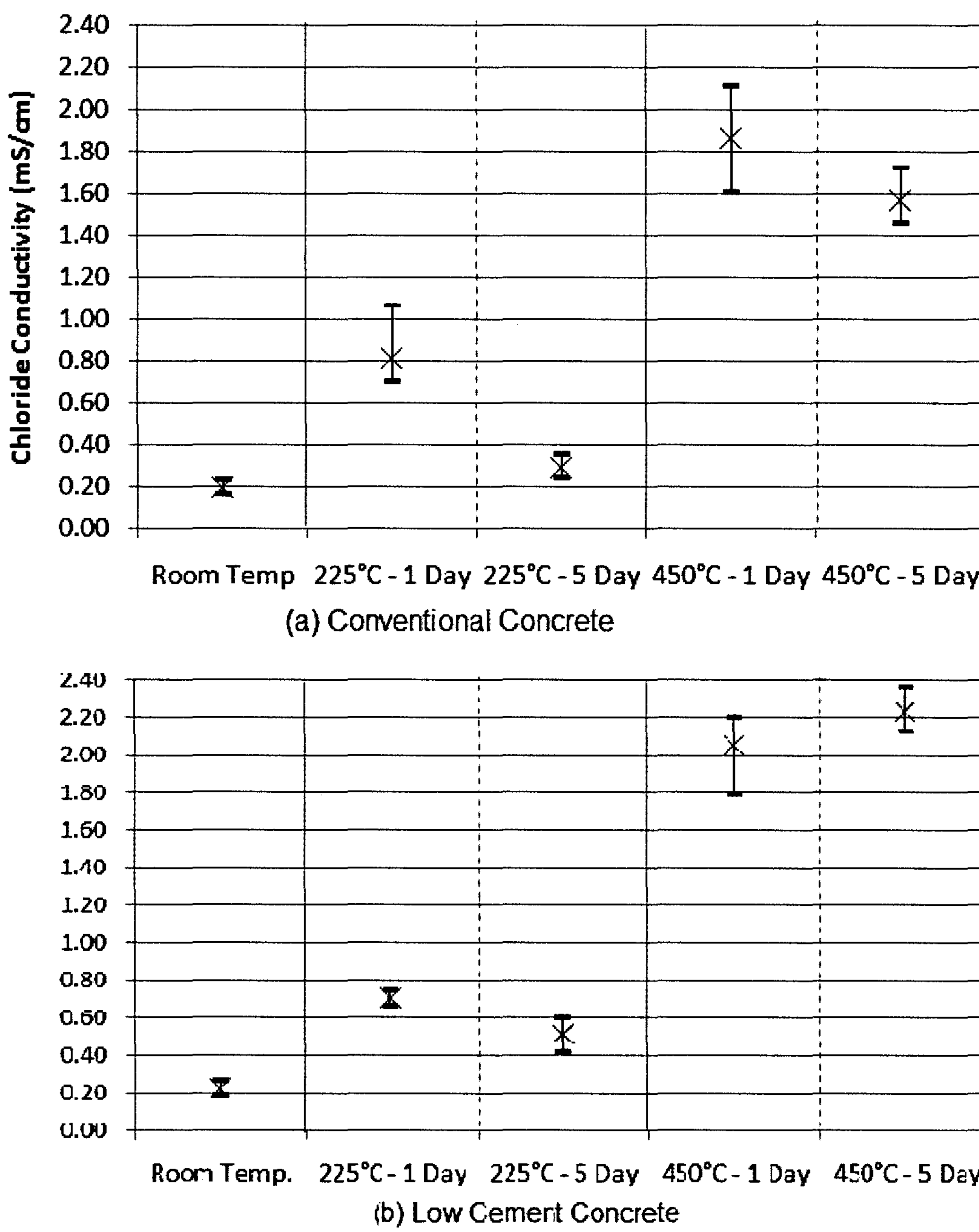


Figure 5.13: Chloride conductivity of (a) conventional and (b) low cement concrete exposed to high temperatures

5 days of exposure a conductivity of 1.55mS/cm was achieved. These values are high in terms of acceptable everyday structures, but considering these are the values relating to an accident they can be deemed to be acceptable.

The low cement concrete interestingly did not demonstrate a similar behaviour of recovery with time at temperature for 450°C, increasing from 2.0 mS/cm after 1 day to 2.2 mS/cm after 5 days. Considering the low rate of recovery at 225°C and the continued increase in conductivity with 450°C, this suggests that a certain 'limiting' temperature has been reached whereby the recovery of the property no longer occurs.

5.2.3 Water Sorptivity

The water sorptivity test is a measure of the ability of a concrete to absorb water that may carry deleterious chemicals. The results for (a) conventional concrete and (b) low cement concrete are shown in Figure 5.14.

The sorptivity data from the concretes shows a similar trend to that of the chloride conductivity when one considers the 225°C data. A slight increase in sorptivity followed by a reduction over time occurs with both conventional concrete, shown in Figure 5.14 (a) and low cement concrete, shown in Figure 5.14 (b). Very low sorptivities were achieved after 5 days of exposure, with conventional concrete being below $2mm/\sqrt{hr}$ and low cement concrete being below $1mm/\sqrt{hr}$, although, by the nature of the test these values were difficult to determine. This does however suggest that the concrete experiences a densification of the solid phase, while not developing microcracking and capillaries large or interconnected enough to accelerate the transport of water through the paste.

The 450°C data does not however correlate very well with the chloride conductivity (except in that there is a significant jump between 225°C and 450°C). The sorptivity of both concretes increases significantly on first exposure, conventional concrete achieving a sorptivity of approximately $11mm/\sqrt{hr}$ and low cement concrete achieving approximately 19mm/hr. This continues increasing with time at temperature, conventional concrete achieving about $16mm/\sqrt{hr}$ and low cement concrete achieving in excess of $21mm/\sqrt{hr}$ after 5 days. This is most likely due to the growth of microcracks in the concrete with time of exposure, as well as dehydration of the cement and densification of the solid phase, creating a significant jump in porosity and interconnected capillaries available for the transfer of water.

5.2.4 Porosity

Porosity is measured in two of the durability index tests, namely the chloride conductivity and water sorptivity tests. This is by weighing samples once dried, and comparing this to the saturated mass of the samples. The results of the sorptivity test porosity are given in Figure 5.15.

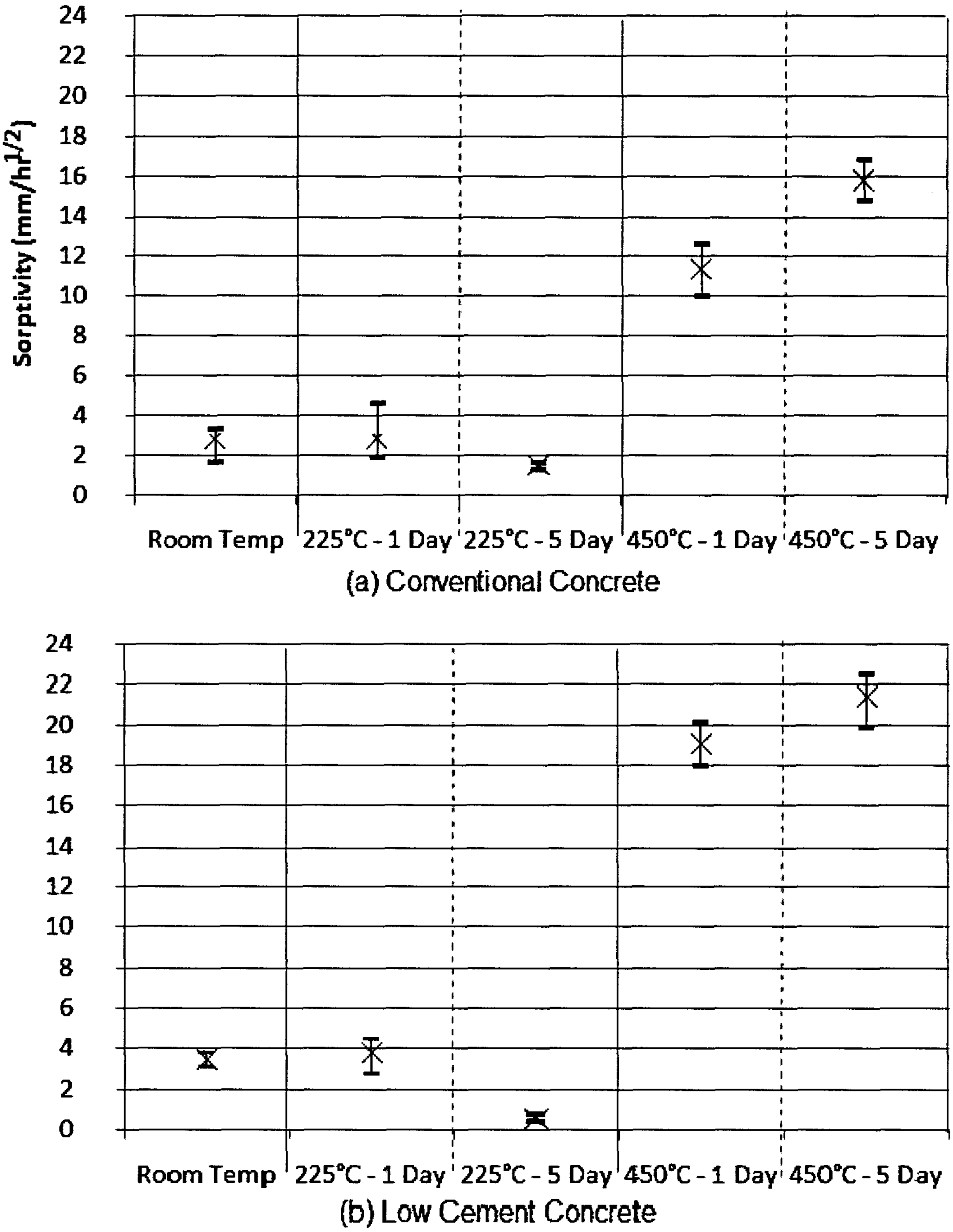


Figure 5.14: Sorptivity of (a) Conventional and (b) Low cement concrete exposed to temperature

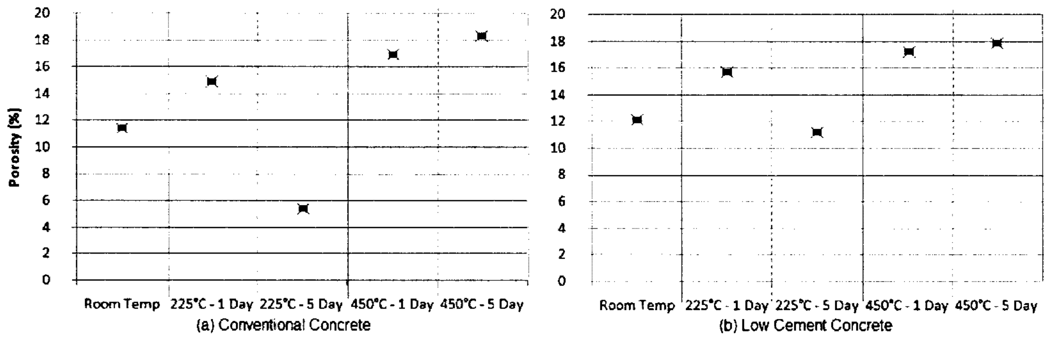


Figure 5.15: Porosity calculated from sorptivity test for (a) conventional and (b) low cement concrete

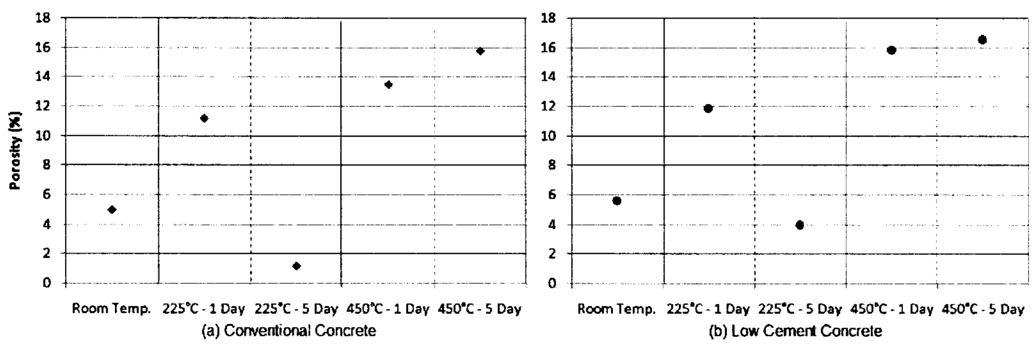


Figure 5.16: Average porosity calculated from chloride conductivity test for (a) conventional and (b) low cement concrete

The results in this Figure are particularly remarkable when one considers the 225°C results. Considering the conventional concrete in Figure 5.15 (a), 1 day of exposure leads to an increase from 11.5% to 15%, which then shows a marked reduction to 5.4% after 5 days of exposure. This is interesting in that this strongly supports the reduction in water sorptivity and chloride conductivity that was demonstrated previously. It is difficult to explain this phenomenon, although one possibility is that the moisture in the concrete, which is a saturated solution of $Ca(OH)_2$, forms calcium hydroxide crystals in the pores of the concrete. This would effectively reduce the porosity of the concrete. The drop in porosity is supported by Figure 5.16, determined from the chloride conductivity tests (which were different samples exposed to the same environment).

Clearly the trend is supported by this data, with length of exposure at 225°C significantly reducing the porosity of the concrete. It should be noted that chloride conductivity tests generally yield a lower reading of porosity than water sorptivity tests.

The low cement concrete results, presented in Figure 5.15 (b) and 5.16

(b) illustrates a less significant decrease in porosity after 5 days at 225°C, supporting the lower recovery of chloride diffusivity at this temperature.

When one considers the porosity at 450°C, it becomes apparent that there is probably a different mechanism driving the porosity, as there is an increase with first heating and a further increase with duration at temperature. This possibly suggests that the dehydration of the binder pastes is creating significantly greater pore spaces, coupled with the development of microcracking. This would support the steady growth of porosity with length of exposure to 450°C.

5.3 Summary of Testing

Here a brief summary of the key aspects determined from the testing are outlined. The results of the testing indicate that the response of a concrete to temperature is a complicated phenomenon that is primarily driven by the binder and aggregate type and content, and interactions between the two. In terms of compressive strength the following characteristics were noted, while keeping in mind the concerns over the quality of the sealed test results:

Compressive strength

- Considering the conventional and low cement content mortars that were tested:
  - On exposure to 225°C in an unsealed state, the mortars experienced a reduction of about 10% after 1 day and 25% after 5 days.
  - On exposure to 450°C in an unsealed state, a reduction of about 40% after 1 day and in excess of 50% after 5 days was demonstrated.
  - The low cement mortar demonstrated a much lower reduction at 450°C in a sealed state, losing about 10% after 1 day and staying at this value to 5 days.
  - The response of the mortar is governed by hydrothermal reactions in a sealed state, and dehydration in an unsealed state.
- Considering the preliminary testing of conventional and low cement content concrete:
  - With exposure to 225°C in an unsealed state, conventional concrete strength demonstrated stability after 1 day of exposure at between 85% and 90%, while low cement concrete demonstrated a continued reduction from 90% to 75% between 1 and 5 days.

  - On exposure to 450°C in an unsealed state, the conventional concrete demonstrated a continued reduction from about 60% to about 40% between 1 and 5 days, while the low cement concrete demonstrated stability around 60% of the unheated strength.
  - With exposure to 450°C in a sealed state, the conventional concrete demonstrated a reduction of greater than 50% after 1 day, recovering to a reduction of around 15% after 5 days. The low cement concrete demonstrated an increase of 30% after 1 day, and 50% after 5 days.
  - The unsealed response of the two concretes to 225°C is most likely governed by dehydration of the binder phase, whereas the response to 450°C appears to be governed by both microcracking and dehydration of the binder phase.
  - The sealed response of the two concretes to 450°C is governed by both microcracking and hydrothermal reactions in the cement paste. Higher aggregate contents appear to cause more extensive microcracking, exposing greater quantities of unhydrated Portland cement and fly ash that subsequently undergo hydrothermal reactions forming gel-like phases in the concrete.

- Considering the in depth testing of conventional concrete:

  - The sealed concrete demonstrated a remarkable improvement in strength with the first 7 days of heating at 225°C, in excess of 100%. The effect of the loss of moisture from the containers was difficult to quantify in this case, however following Kropp et al. [44], only small amounts of water are required to enable hydrothermal reactions to occur.
  - The unsealed concrete in this phase demonstrated an improvement in strength of between 20% and 50% on heating to 225°C, likely due to low unheated strengths of the concrete. The unsealed strengths after exposure to 225°C were similar to that of the preliminary phase of testing.
  - Thermal cycling to 225°C has a limited effect on the unsealed response to temperature.
  - Thermal cycling to 225°C could have a limited effect on the sealed response of the concrete, however some deterioration was demonstrated in the 3rd cycle of testing. The cause of this deterioration was difficult to identify, as the first two cycles demonstrated a similar response.
  - A thermal cycle to 450°C for both sealed and unsealed states caused a deterioration in the strength from the 225°C strength. This was still either at or above the room temperature strength.

  - An increase to 450°C after a period at 225°C for both sealed and unsealed states shows a loss of strength on first exposure to this temperature, followed by a recovery, over time, to some extent.

Although several issues were apparent in the compressive strength testing of the materials, not the least the concern over the effectiveness of the sealing method of the samples, the fundamental trend of a significantly improved response to temperatures in a sealed environment is apparent.

When one considers the transport properties and the tests relating to these, the following conclusions were drawn:

Transport properties

- Oxygen permeability, which is a measure of the permeability of the concrete to gases deteriorates with temperature of exposure. Considering the two concretes tested:
  - Conventional concrete experiences a lower increase of permeability, doubling with exposure to 225°C and increasing by an order of magnitude when exposed to 450°C.
  - Low cement concrete experiences an increase of an order of magnitude with exposure to 225°C, and a further increase of an order of magnitude with exposure to 450°C.
  - These results suggest that higher aggregate contents and subsequent interconnectedness of the ITZ, and a denser ITZ caused by silica fume cause greater microcracking on exposure to temperature.
- Chloride conductivity demonstrates the following characteristics:
  - An increase (i.e. deterioration) with first exposure to 225°C, recovering to some extent with length of exposure for both concretes.
  - Conventional concrete demonstrates a similar response to 450°C, experiencing a significant increase with first exposure but recovering with length of exposure.
  - Low cement concrete demonstrates a significant increase with exposure to 450°C, increasing with length of exposure.
  - These results suggest that low cement concrete reached some limiting temperature after which a recovery with length of exposure did not occur.
- Water sorptivity for both concretes demonstrated a slight increase with exposure to 225°C, followed by a significant drop with length of exposure. On exposure to 450°C both concretes demonstrated a marked and continued increase with initial exposure and length of exposure.

- Porosity demonstrated an increase on first heating to 225°C for both concretes, followed by a substantial drop with length of exposure. Exposure to 450°C caused a significant increase which continued to rise with length of exposure. This response of the porosity strongly supports the water sorptivity results, and shows a reasonable correlation with the chloride conductivity results.

This summary of the testing results and trends completes the testing Section. The results will be discussed in detail in Chapter 6, with a comparison against the requirements outlined for the project.

Chapter 6

Discussion on High Temperature Concrete

This Chapter will discuss the literature and testing results collected during the project and compare them to the requirements of the PBMR heating environment as outlined in Section 3.1.2. This will be complemented with results from the SEM studies to illustrate relevant points, with all images presented at 2000x magnification. All SEM studies were carried out on conventional concrete that had been cured for 70 days and had been prepared according to Section 4.6.

Section 6.1 Material Constituents will focus mainly on lessons from literature and how the mix designs were selected, while Sections 6.2 and 6.3 will focus on the results of the testing and how these relate to both literature and the PBMR environment. Section 6.4 will discuss aspects of the heating environment that had little impact on the material selection, but may prove important in the design of the structure.

Designing a concrete for high temperature service requires consideration of multiple factors to ensure a successful material. Similarly, strictly adhering to design codes places significant limitations on this design, two examples being:

1. The use of high aluminate cements (HAC) has been restricted in South Africa for structural concretes [12]. Thus this material has to be removed from consideration early in the design phase, and its excellent high temperature response cannot be used to benefit the design. Note that HAC's are regularly used in refractory insulating concretes well in excess of 1000°C.

2. ACI 349-01 [3] limits the amount of extender content that can be added to a concrete to standard practice limits such as 30% for fly ash.

With such limitations in the material design it should be recognized that a very strong case needs to be made if the Codes are not to be followed, as Nuclear Regulators would require substantiated evidence to justify this move.

Designing a concrete for high temperature service can not however follow a prescriptive approach due to the numerous factors that play a role in its response. Some of the factors that affect the response of a concrete include:

- Rate of heating
- Time at temperature
- Maximum temperature
- Moisture state

Each of these factors has an effect on other factors; for example a very high rate of heating will affect the maximum temperature the concrete can withstand before experiencing significant damage.

Possibly the most important factor in the context of the PBMR is the moisture state of the concrete, in that the hot face of the concrete will be moulded against a steel liner which will prevent moisture from escaping from the concrete (a sealed state). As has been shown from literature and in the testing, this can produce a remarkable difference in response of the concrete when compared to an unsealed concrete. This difference can be accounted for in the selection of the material constituents.

6.1 Material Constituents

The requirements of the project were to determine the material constituents of a mix design for application in the reactor cavity structure of the PBMR. As such, the effect that different material constituents have on various aspects of the concrete at temperature is discussed below.

6.1.1 Chemical and Physical Changes

The first point that needs to be made with chemical and physical changes relates to the different moisture states of the concrete. An unsealed state is representative of concrete where water has the ability to escape freely, while sealed concrete is where water is inhibited from escaping from the concrete either by surrounding concrete, or a steel liner as in the case of the PBMR. This definition of different moisture states is also highly dependent on the other aspects of the heating environment, for example in an environment where the heating rate is extremely high such as a fire, concretes are prone to spalling, partly due to the steep thermal gradient and partly due to high pore pressures (a sealed state phenomenon) near the heated face of the concrete [7]. As has already been mentioned, the PBMR is representative of a sealed environment at the hot face of the concrete.

For completeness sake a discussion surrounding both unsealed and sealed states is carried out throughout this discussion, to draw comparisons and to give a better picture of the overall response of concrete to high temperatures.

In unsealed states the primary changes relating to a concrete are the dehydration of the binder phase, causing the paste to shrink and thermal expansion of the aggregate [7]. This differential shrinkage/expansion between the binder phase and the aggregate leads to the development of microcracking [39]. It appears that the cement paste and aggregate both expand up to between 200°C and 250°C, after which the paste begins to contract and the aggregate continues to expand, generally at an accelerated rate.

This accelerated expansion above 250°C of the aggregate is related to the silica content of the aggregate. Aggregate can be broadly split up into quartzitic, igneous crystalline, igneous amorphous and sedimentary carbonate groups, with thermal expansion generally related to the silica content and size of silica crystals. As such, quartzitic aggregate, having the highest silica content in large crystals experiences the greatest expansion, while sedimentary carbonate (limestone) and igneous amorphous (basalt) aggregates experience the lowest thermal expansions.

In sealed states there are several effects to consider:

- On first heating high pore pressures will be experienced near the hot face of the concrete. Chapman et al. [47] suggest this could be in the region of 0.6 MPa for a temperature of 200°C. These pore pressures will encourage the development of microcracking.

- New binder phases are formed in a hydrothermal environment. These reactions appear to be dependent on temperature, mainly above 150°C and include:

  - For neat Portland cement pastes the phases that are formed are lime rich, crystalline and are fairly coarse particles [39]. These reactions appear to be related to the amount of free calcium oxides that are available in the concrete. At 250°C the predominant phase is $\alpha - C_2SH$ [44], while there is still evidence of CH in the binder. The phases that are formed are [39, 44]:

    1. Hydrogarnets (HG) - $C_3(A,F)SH_4$
    2. Hydroxylellestadite (E) - $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$
    3. αdicalcium silicate hydrate $(\alpha - C_2SH)$ - $C_2SH_{0.3-0.1}$

  - For Portland cement pastes with high quantities of a siliceous additive (such as fly ash or ground quartz) the formation of fine gel-like dominates, dependent on the amount of siliceous additive. Evidence of CH disappears from these concretes, most likely being consumed in pozzolanic reactions. The phases that are formed are [44]:

    1. Hydrogarnets (HG) - $C_3(A,F)SH_4$

2. 11Å tobermorite

- Keeping in mind that deleterious reactions in the binder phase appear to occur in the presence of free lime (CaO), limestone has been noted to encourage these transformations [17].
- Differential thermal expansion between the paste and aggregate is also expected, as the paste will likely dehydrate to some extent (due to the activation energy of chemically bound water).

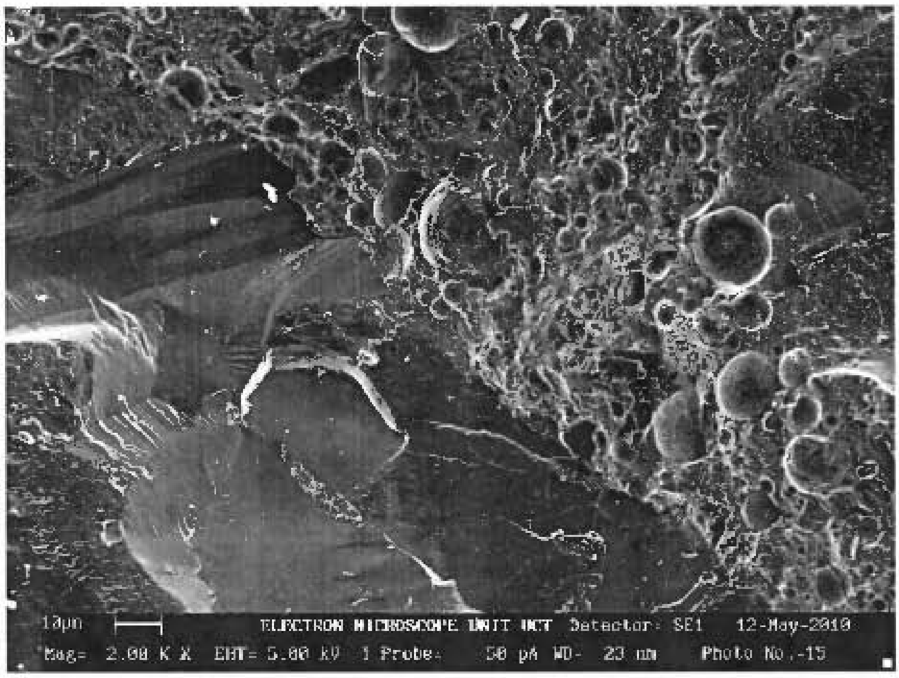


Figure 6.1: SEM picture of conventional concrete with no exposure to high temperatures

Figure 6.1 is of conventional concrete (with mix design as described in Chapter 4) that has not been exposed to any high temperatures and is an excellent representation of the microstructure of the concrete before heating. There are several notable points to consider in this image. First, consider the high quantity of unreacted fly ash there is in the binder paste, as shown by the spheres. This is due to the high quantity of fly ash replacement (60%), as required for a sealed environment. It is also worthwhile noting how dense the microstructure of the cement paste is, which is unsurprising in the context of it being a 90 day old concrete made with a water to cement ratio of 0.3, but this dense structure is at odds with the low compressive strength achieved with the concrete. In the bottom left hand side of the image is a piece of aggregate, which was granite. Selection of aggregate was largely governed by locality, while being mindful of the goal of an igneous amorphous rock, with granite being available in the Cape Town region.

6.1.2 Mechanical Properties

The mechanical properties of interest are strength, modulus of elasticity and Poisson's ratio. Creep is another very important property, but has not been considered in depth in this project. Strength and modulus of elasticity appear to be primarily dependent on the material constituents selected for the concrete, while Poisson's ratio appears to be governed by the moisture state of the concrete.

Strength The strength response of a concrete to high temperatures is different considering either the sealed or unsealed response. In terms of the unsealed response of a concrete, this is primarily governed by the dehydration of the binder phase and the development of microcracking through the differential thermal expansion of the paste and aggregate. In this case the goal is to minimize the shrinkage of the binder phase and expansion of the aggregate phase. There are varying data in this regard with it being shown that siliceous aggregates generally provide a similar or better response over limestone and quartzite up to approximately 450°C [57, 58]. Kropp et al. [44] state that the amount of extender addition needs to be limited for unsealed environments as this leads to excessive shrinkage of the binder phase. However Xu et al. [16] and Poon et al. [55] have shown for short term heating with high heating rates the use of high quantities of extender (40% fly ash or 40% ground granulated blast furnace slag) offers a beneficial response over ordinary Portland cement concretes.

Figure 6.2 is an image of conventional concrete that has been exposed to 1 day of 225°C in an unsealed condition. It is worth noting that there is still clear evidence of fly ash particles present with little spheres throughout the cement paste. The cement paste is also still very dense like that of the room temperature cement, however a slight increase in pore and void size may be evident. This is supported by the following two images, where Figure 6.3 a) illustrates the dense nature of the cement paste and some micro-cracking around an aggregate particle, while Figure 6.3 b) illustrates an anomalous region of new CSH gel formation (the region in the centre of the image). New CSH is characterized by a fibrous and 'needle' like formation. Although areas of new CSH formation were very few and far between, these do support the sometimes impressive gain in strength that the unsealed concretes demonstrated after exposure to 225°C (up to 50% improvement in strength). This is possibly due to the slow heating rate allowing an increased rate of reaction in voids in the concrete before the moisture evaporated from the paste.

The selection of mix constituents was however more based on the expected strength response from a sealed environment, as this is more representative of the PBMR environment. For this environment deleterious hydrothermal reactions relating to calcium oxides forming more crystalline phases govern the strength response of neat Portland cement, causing a significant reduction relating to the maximum temperature reached [39, 49]. The addition of high

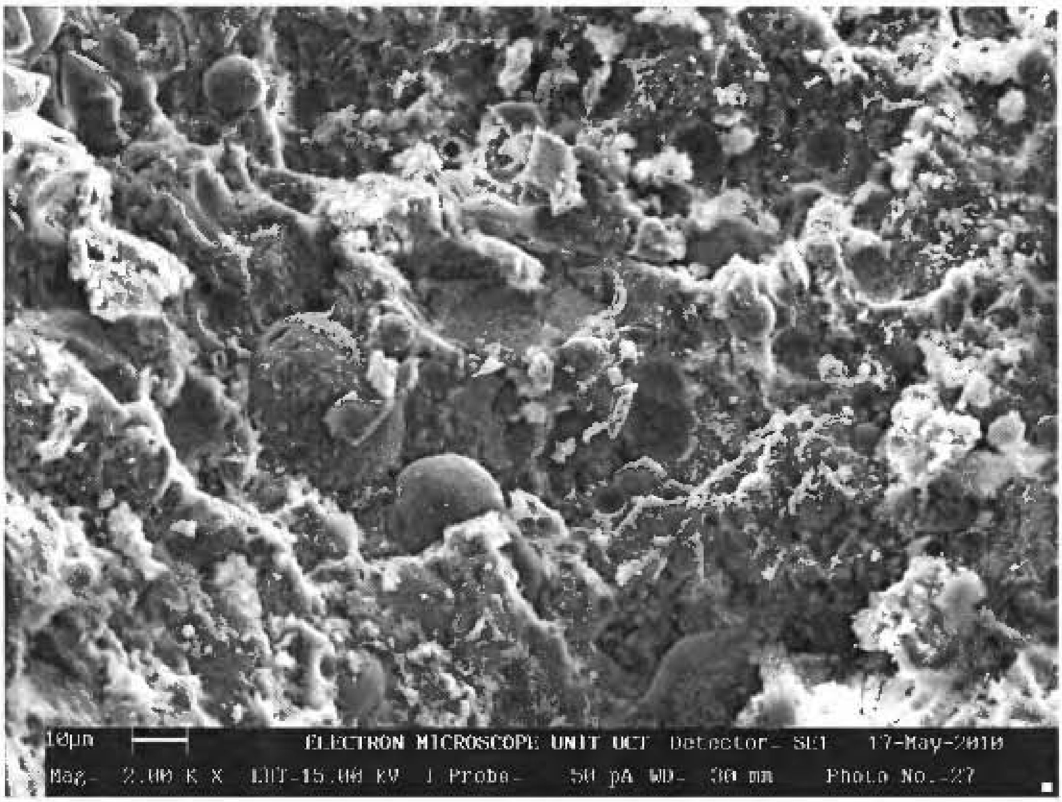
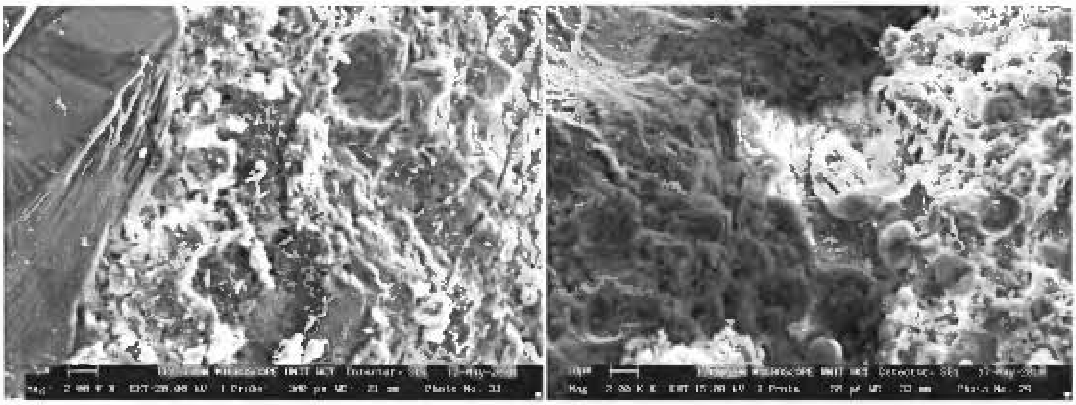


Figure 6.2: SEM picture of conventional concrete exposed to 1 day of 225°C in an unsealed condition



a) interfacial transition zone

b) anomalous region of CSH formation

Figure 6.3: SEM pictures of an unsealed concrete after 225°C exposure – a) interface between aggregate and cement; b) anomaly of cement formation in a void

quantities of extenders such as fly ash reduce these deleterious reactions and form new gel-like phases that, dependent on the amount of extender, can either limit the reduction of strength, or even cause an increase in strength [44]. Ghosh and Nasser [49] have shown a 15% improvement in strength after extended periods of heating and confining stress for a concrete with 60% fly ash, 10% silica fume and 30% Portland cement. Similarly, Seeberger et al. [17] have demonstrated an improvement of 25% after 28 days of heating of a concrete with 60% fly ash.

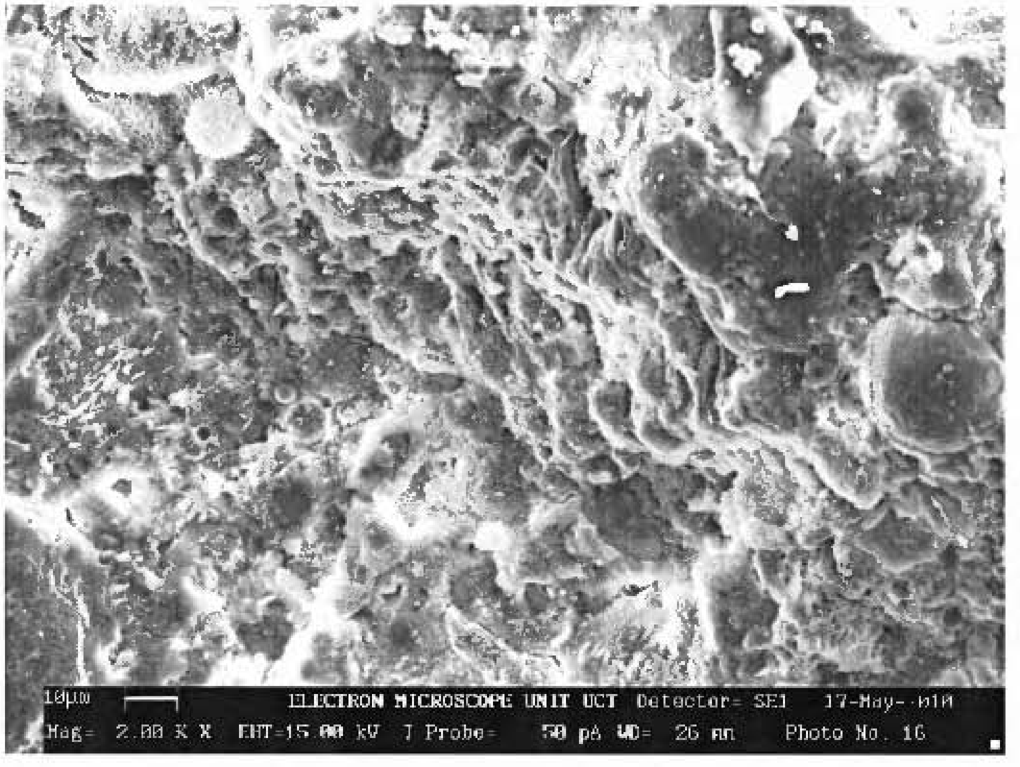


Figure 6.4: SEM picture of conventional concrete exposed to 225°C for 1 day in a sealed condition

Figure 6.4 is an image of a sample exposed to 225°C for 1 day in a sealed environment. This image is fairly characteristic of sealed concrete after 1 day of exposure. There is extensive evidence of CSH gel formation, particularly in regions of cracking and voids, with notable regions being the top left hand corner of the image and the lower middle region of the image. The cement paste is still clearly dense and well structured. The formation of new CSH gel in areas of cracking or voids and the continued dense nature of the cement paste strongly supports the significant increase in strength that the concrete experiences, and is in agreement with Kropp et al. [44].

The flexural and tensile strength of concrete exposed to temperatures has been briefly investigated in Section 3.2.2.2. The following conclusions were drawn for heated concrete:

1. Tensile strength generally reduces with exposure to temperature [7].

2. Siliceous aggregates (i.e. amorphous igneous aggregates) appear to retain properties better than limestone aggregates, although this is highly dependent on the other mix constituents of a concrete [7, 39].

3. Sealed concretes possibly experience a greater reduction of strength, due to hydrothermal reactions [39]. No literature was identified that investigated the tensile strength of concrete with high quantities of extenders in hydrothermal conditions.

4. It has been suggested that there is a progressive deterioration of strength with duration of heating, although this is probably related to hydrothermal reactions in sealed concrete and dehydration of the cement paste in unsealed concrete.

Modulus of Elasticity The modulus of elasticity of a concrete is related to the modulus of the binder phase and the aggregate, with higher contents of the stiffer phase (aggregate) giving the concrete a higher modulus. Literature suggests that modulus generally experiences a significant deterioration with exposure to temperature in both unsealed and sealed states.

Considering unsealed states, the aggregate plays a vital role, with siliceous aggregates being most beneficial up to 500°C, and limestone aggregates being more beneficial above this temperature [74]. The response below 500°C is largely dependent on the higher modulus of siliceous aggregate, which above this temperature undergoes the transformation of quartz from α-quartz to β-quartz, expanding and damaging the concrete [7]. Lankard et al. [39] presented data on gravel concretes up to 250°C, suggesting that the modulus at temperature and after cooling is similar, and deteriorates from about 90% at 75°C to 80% at 250°C.

The data presented by Lankard et al. [39] is also particularly useful when considering sealed concretes. This mix design demonstrated a loss of compressive strengths after exposure to 260°C due to hydrothermal reactions in the binder phase, which correlate well with a significant reduction in modulus at this temperature. Interestingly this reduction (between 50% and 70% of the unheated modulus) appears to occur from about 90°C for a heated concrete, however the modulus recovers for heating temperatures below 140°C. This suggests that below 140°C a reduction in modulus is not dependent on chemical changes of the binder phase, but rather physical changes such as moisture in pores evaporating. Above this temperature the modulus is governed by both physical changes at temperature and hydrothermal reactions of the binder phase, which is in agreement with the finding of Kropp et al. [44] who suggest hydrothermal reactions occur predominantly above 150°C.

Considering literature relating to concretes with high fly ash contents, Savva et al. [57] demonstrated for unsealed concretes that fly ash contents of 30% may experience a greater reduction in modulus than lower fly ash contents. This is probably due to increased shrinkage caused by the modified binder phase [44].

In sealed states limited literature is available, with the work of Ghosh and Nasser [49] being representative of a hydrothermal environment under a confining pressure. The data suggests that there is a greater reduction of modulus with higher fly ash contents, while the same concrete demonstrated an improved strength over one with lower fly ash contents. This appears to be counter-intuitive, and requires further investigation both in testing and literature.

Poisson's Ratio The Poisson's ratio appears to be more dependent on the moisture state of concrete than the specific mix constituents. In unsealed environments the ratio drops with initial temperature exposure [78], while it can be expected to recover over duration of exposure [80]. In sealed environments the ratio experiences little change, however may increase with duration of exposure [63, 81].

6.1.3 Transport Properties

The transport properties of the concrete have implications with regard to the pore pressures experienced near the hot face of the concrete and subsequent moisture migration, as well as the ability for the structure to resist aggressive environments such as coastal environments.

Pore Pressures Pore pressures in heated concrete are caused by the evaporation of pore water. This occurs in both sealed and unsealed concretes, however, the ability for this pressure and subsequent moisture to escape is the basis of the difference between the states. Bazant and Thonguthai [82, 85] suggest that although moisture migration is dependent on moisture content and temperature, it is primarily governed by pore pressures. As such the pore structure is of particular importance to the transport properties of the concrete.

Chapman and England [47] have suggested that pore pressures of 0.6 MPa can be experienced at the hot face of a sealed concrete specimen exposed to 200°C, and that this pressure is still in the region of 0.15 MPa after 531 days.

Moisture Migration As has already been mentioned, pore pressures are the governing factor behind moisture migration. It follows that a more dense concrete with limited interconnectedness between pores and ITZ's will take longer than a concrete with a more porous structure. Chapman and England [47] suggest that there is still some water left 0.2m from the hot surface of a sealed concrete after 531 days, and that there are still pore pressures at this stage, suggesting that moisture migration will continue. The presence of moisture near the hot face of the concrete after 50 days suggest there is ample time for hydrothermal reactions (deleterious or beneficial) to take place. After a certain point of time the concrete would reach an effectively dried state, after which the response should stabilize to the newly formed properties.

Porosity The porosity and interconnectedness of the porosity are fundamental to the pore pressures and moisture migration in the structure. In this regard the use of extenders such as fly ash or silica fume slightly increase the porosity, while reducing the average pore diameter of unheated concrete [12, 16].

Xu et al. [16] analyzed several concretes with two water:cement ratios (0.3 and 0.5) and either 0%, 25% or 55% fly ash replacement in an unsealed short term heating environment. Their findings suggest that high replacement of fly ash (55%) shows a steady increase up to 450°C, from about 20% to 27%. At 250°C a porosity of about 22% was achieved.

Testing results provide an interesting insight into the changes of porosity with temperature and length of exposure. For a concrete similar to that of Xu. et al., having a 55% fly ash replacement and water:cement ratio of 0.3 an increase in porosity of about 6% was observed on unsealed heating to 225°C for 1 day. This value then dropped to about 5% below the original value after 5 days of exposure (i.e. reduced by about 11% from the 1 day exposure value), indicating that further temperature exposure to temperatures of 225°C reduce porosity. The cause of this is difficult to explain, however may be related to the formation of $Ca(OH)_2$ crystals in the pores of the drying concrete.

In terms of sealed concretes, the porosity of a concrete is determined by hydrothermal reactions. It has been suggested by Kropp et al. [44] that deleterious hydrothermal reactions in neat Portland cement paste lead to the formation of coarse, poorly connected, crystalline particles with an increase in pore radii from 20nm to between 100 and 1000nm on heating to 200°C. This is coupled with a significant decrease in specific surface area, to less than 1/10 of the original area.

Kropp et al. [44] also investigated binder pastes with either ground quartz or fly ash replacement. It is indicated that there is a limited increase in pore radii, and a significant increase in specific surface area of 70% for ground quartz and 300% for fly ash. This is due to the formation of new gel-like phases due to pozzolanic reactions.

The formation of hydrogarnets and 11Å tobermorite in binder phases with fly ash replacement will likely have a significant effect on the interconnectedness of pores, thereby reducing the ability for moisture migration.

Gas and Media Transport Considering the hot face of the concrete is sealed, the risk of the ingress of deleterious chemicals here is negligible. Similarly, over time the concrete will tend towards a dried state due to moisture migration, further limiting the risk of carbonation. Investigations were however carried out to identify the effect that temperature has on the transport properties of unsealed concrete, with a view to identifying certain characteristics of the material (for example the development of microcracking).

Bazant and Thonguthai [82] suggest that the permeability of an unsealed concrete increases by an order of magnitude above 100°C. This is broadly in agreement with the results from testing at 225°C, where a doubling of the oxygen permeability was observed for conventional concrete, while low cement content concrete increased by an order of magnitude. These results do appear to increase over time. The difference between the response of the two concretes can be attributed to different aggregate contents. Low cement concrete, having a higher aggregate content would have experienced greater microcracking, especially in the ITZ that would be denser considering condensed silica fume was used. At 450°C both concretes exhibit an increase of an order of magnitude over the 225°C results, indicating that microcracking is becoming the dominant cause of oxygen permeability.

The OPI values for both concretes are between 10 and 10.2 after 225°C and 9 and 9.4 after 450°C. These results are still acceptable in the context of durability of the structure considering extended periods of heating will lead to drying out of the concrete, which would substantially reduce the ability for carbonation.

The requirement to consider the permeability in terms of the leakage rate for the PBMR[10] would be un-representative with the values obtained, as these are for an unsealed concrete while the concrete in the structure would be sealed. It is entirely possible that, with the hydrothermal reactions forming new gel-like phases, the OPI values would increase (i.e. permeability would reduce further).

Very interesting results were observed with the extended exposure to 225°C (5 days) of the chloride conductivity and sorptivity samples, where a drop was observed over the values originally attained at 225°C (1 day of exposure). This recovery over length of exposure is difficult to explain, but may be due to densification of the solid phase of the concrete while not developing microcracking to an extent which might accelerate the transport of water through the paste. This is in agreement with the porosity results from the testing.

The 450°C results for chloride conductivity of conventional concrete demonstrate a similar recovery over time, while low cement concrete demonstrates an increase with time of exposure. This suggests a 'limiting' temperature has been reached for low cement concrete, whereby microcracking and the development of interconnected capillaries become the dominant case.

This implies that a high aggregate content may not be most beneficial for a concrete exposed to temperatures, in that the development of microcracking will be exacerbated due to the close packing of the aggregate.

Thermal Properties The thermal properties of concrete exposed to high temperatures were considered solely from literature. This body of literature appears to be fairly comprehensive and correlates reasonably well. The thermal properties considered were coefficient of thermal expansion, specific heat, thermal conductivity and diffusivity.

Coefficient of Thermal Expansion The coefficient of thermal expansion of a concrete is directly related to the type of aggregate used. With conventional aggregates (that have a significantly higher modulus than the binder phase), these properties dominate over the expansion properties of the binder phase [7]. Lightweight aggregates are affected by the thermal expansion properties of the binder considerably more, due to the lower modulus of these aggregates.

The binder phase of a concrete generally experiences an expansion up to between 150°C and 300°C, followed by a contraction above these temperatures [87, 88, 89]. Aggregate generally expands with temperature, where the rate is dependent on the silica content and crystalline nature of the aggregate. This differential thermal expansion between the aggregate and paste above about 250°C leads to microcracking in the concrete. This is part of the reasoning behind selecting amorphous igneous aggregate (the other part relates to hydrothermal reactions caused by limestone aggregate). Generally this aggregate demonstrates the lowest coefficient of thermal expansion.

As concrete is made with water, and in unsealed concretes this water is allowed to evaporate, a concrete generally demonstrates different expansion paths with first heating and cooling [92]. There is also generally a net expansion or contraction of the concrete after cooling, which has been referred to as dimensional instability [7]. Sullivan [94] suggests that subsequent heating of the concrete follows a similar expansion path to that of the cooling path of the first heating cycle.

Specific Heat Capacity The specific heat capacity of concrete up to 150°C is dependent on moisture content [7] as evaporable water expelled. The high specific heat of water of $4.16Jkg^{-1}K^{-1}$governs this response. Above this temperature the specific heats rise linearly with temperature, most likely due to the release of chemically bound water [7].

Thermal Conductivity The thermal expansion properties of a concrete appear to be related to the crystalline nature of an aggregate [101]. Harmanthy [43] demonstrates the enveloping values of thermal conductivity, with quartzite (representing the crystalline bounding values) dropping gradually to a similar value for anorthosite up to about 800°C and stabilizing thereafter, while anorthosite (representing the amorphous bounding values) appears to be reasonably stable with temperature.

Thermal Diffusivity The thermal diffusivity of a concrete is a function of the specific heat capacity, thermal conductivity and density of a concrete [7]. These values generally drop with temperature, with an envelope relating to the crystalline nature of the aggregate also applying. As such amorphous aggregates represent the lower bound, while highly crystalline aggregates represent the upper bound.

6.2 Heating Environment

The heating environment of the PBMR fundamentally determines the response of a concrete. As such the results from testing are discussed here, compared with the requirements and conditions of the PBMR environment and correlated with relevant literature.

6.2.1 Heating Rate

Khoury [34] has considered the effect of the heating rate on the response of a concrete, and has suggested that below 2°C/min the heating rate has a moderate effect on the response of a concrete, while above 5°C/min the heating rate has a large influence with the risk of explosive spalling. This set of conditions adequately support the need to focus on relevant literature - the response of a concrete exposed to fire will be significantly different to that of one exposed to a more gradual heating rate.

Kugeler et al. [33] have suggested that the maximum heating rate expected from the HTR Modul (during a LOCA), upon which the PBMR is based, is approximately 7°C/hr. Following this, the heating rate for testing was set at 10°C/hr.

This heating rate appears to have had little effect on the results of testing. Considering the in-depth strength results for conventional concrete, the results correlate reasonably well with those of Xu et al. [16] who used a heating rate of 1°C/min (i.e. an improvement in strength around 225-250°C and roughly the same strength as unheated after exposure to 450°C). This correlation suggests that the heating rate had a limited effect on both of these sets of results.

6.2.2 Final Temperature

The limits stipulated in the project Scope of Research Work [10] were 225°C and 450°C, which will occur in a sealed state.

The results indicate strength of a sealed concrete experiences a large increase with exposure to 225°C, in excess of 100%. This is in agreement with the results for binder samples tested by Kropp et al. [44], that achieved a strength of 100%, while a concrete with similar mix proportions demonstrated a 25% increase. The difference between the binder and concrete response, and that the results from this project correlate more with the results of the binder, may be related to the size of aggregate used in the samples. 6mm aggregate was used in the testing phase due to the conditions outlined in Section 4.3, which is small compared to sizes used in general construction, and indeed the

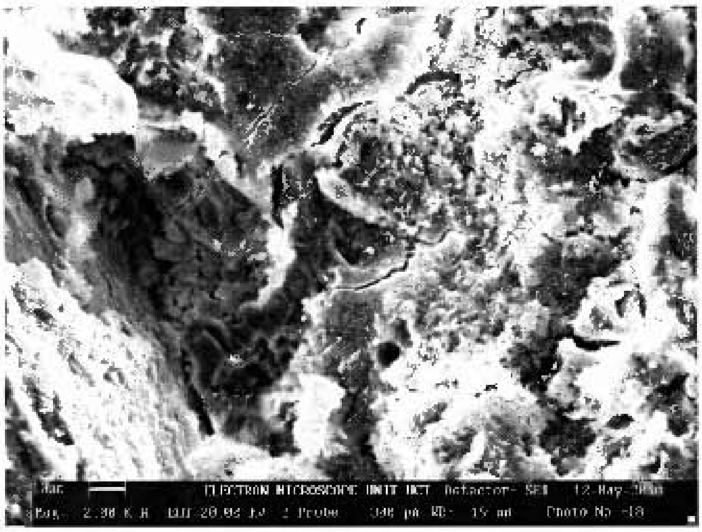


Figure 6.5: SEM picture of unsealed concrete exposed to 450°C

32mm aggregate used by Kropp et al. [44]. With this said, the concept that high fly ash contents provide a beneficial response to temperature in the region of 225°C has been proven.

When the concrete is exposed to subsequent heating to 450°C, there is a reduction in strength from that achieved at 225°C. This suggests that the strength of the concrete is no longer governed by hydrothermal reactions in the cement paste, but rather the development of microcracking through differential thermal expansion between the binder and aggregate. Interestingly this microcracking may lead to further hydrothermal reactions by exposing unreacted Portland cement and fly ash that further react to allow the recovery of strengths to some extent.

The unsealed strengths of a concrete either show a lower improvement in strength or even a decrease in strength when exposed to 225°C, dependent on the initial conditions of the sample (moisture state, cure state, variations in sample manufacture). When these samples are exposed to 450°C there is a significant loss in strength, which demonstrates the development of microcracking in the sample.

Figure 6.5 is of an unsealed concrete exposed to 450°C. This image is strongly characteristic of the concrete at this temperature as there is extensive micro-cracking apparent. Considering the upper middle region of the image, the cement paste appears to be quite grainy and powdery, with little interconnection between the grains. This paste appears to be more granular and has less interconnection between grains when compared to samples exposed to 225°C. There is also no evidence of fly ash in the cement paste in the form of the spheres observed in the previous images. This image strongly correlates with the reduction of strength that these concretes experience.

6.2.3 Thermal Cycling

The effect of thermal cycling appears to be limited for unsealed concretes exposed to 225°C, possibly showing a slight reduction. A reduction over thermal cycles is in agreement with literature [63, 64], with Bazant and Kaplan suggesting a gradual deterioration related to the number of thermal cycles after assessing a large body of literature [7]. The results for sealed concretes exposed to 250°C showed an increase over the first cycle of 20% for the second cycle and reduction of about 50% after the third cycle. These results are difficult to interpret, however it is likely that any hydrothermal reactions will be effectively complete after the first cycle, and the response to subsequent cycling will be quite similar to that of an unsealed concrete undergoing subsequent cycles. Following conclusions from literature, a gradual deterioration may be expected.

6.3 Duration of Heating

The duration of heating for the PBMR is enveloped by the following three cases:

1. Plant operates for its lifetime (40 years) at 225°C and is then decommissioned. In this case, the results for sealed concrete exposed to 225°C for varying durations are relevant. It has been shown in the results for the in-depth testing of conventional concrete that a large increase in strength can be expected within the first days of heating to this temperature, and the strength appears to be reasonably stable after this. This is in agreement with Kropp et al. [44] who suggest that the raise in strength is due to hydrothermal reactions with fly ash and $Ca(OH)_2$, and that the $Ca(OH)_2$is effectively consumed within 20 hours of heating to a temperature of 250°C.

2. Plant experiences an excursion/LOCA on first heating. The LOCA takes the concrete to 450°C for approximately 30 days, with a gradual reduction of temperature from 450°C. This is a concerning case, as the 450°C results for sealed conventional concrete from the preliminary tests will have to be considered. These results demonstrated a reduction to 50% of their original value after 1 day, recovering to about 85% of the unheated strength after 5 days. Testing inconsistencies aside (as the sealing system for samples for 1 day may have failed), this suggests that the plant will be at greatest risk directly after reaching 450°C. That there is a drop in strength is understandable, as the development of microcracking will likely happen at this temperature. The recovery over 5 days supports this theory, as exposed unreacted Portland cement and fly ash will react to repair the cracks.

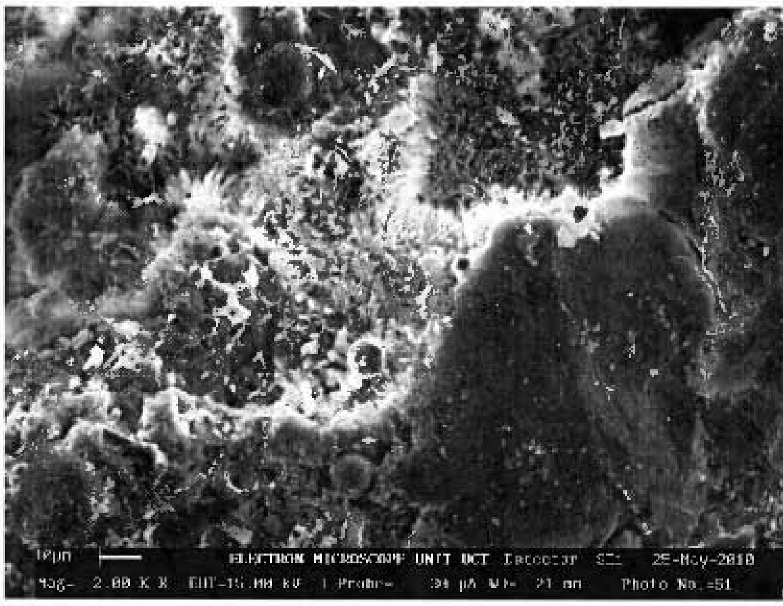


Figure 6.6: SEM picture of conventional concrete after 7 days of exposure to 225°C in a sealed environment

3. Plant operates for its lifetime and experiences an excursion/LOCA at 40 years. This case is particularly interesting as it is solely dependent on extrapolation of results and data from literature. Firstly, it is assumed that hydrothermal reactions are complete and a strength in excess of 200% of the unheated strength has been achieved. Furthermore, it is assumed that moisture has migrated away from the wall and the concrete that will experience the highest temperatures is effectively in a dry state. In this case, an increase in pore pressures would be expected due to the release of chemically bound water, however this will be small compared to those achieved on initial heating of the concrete. It is expected that the strength will reduce from its maximum achieved for 225°C, possibly to approximately the same strength as the unheated concrete. However, as the concrete is in an effectively dried state, it is unlikely that any further reactions will occur in the paste, i.e. once the concrete has reached 450°C, the strength should not change significantly.

Figure 6.6 is a SEM image of the concrete exposed to 7 days of sealed heating at 225°C.This image is remarkable in its evidence of new CSH gel formation, in support of duration of heating case 1 and 3. The whole upper left hand quadrant is covered with extensive formation of new CSH gel. This strongly supports the significant strength gain the concrete experiences in this environment. It is worth noting that this extensive formation of CSH is only in voids and cracks of the cement paste, as is illustrated in Figure 6.7, where there is little evidence of such extensive CSH formation.

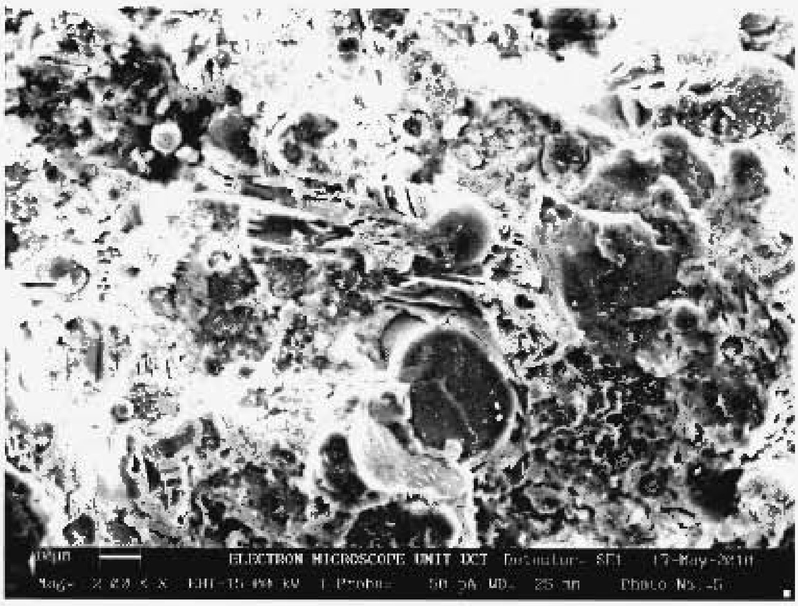


Figure 6.7: Conventional concrete exposed to 225°C for 7 days in a sealed environment

Figure 6.7 clearly demonstrates the dense nature of the concrete, with small cracking around the aggregate piece in the centre of the picture most likely being caused by crushing of the sample. The lower right hand quadrant illustrates a slight increase in porosity of the cement paste, supporting the loss of chemically bound water in the paste, leading to a denser solid phase with larger pores. There is evidence of some CSH formation on the fly ash particle in the middle left hand edge of the image.

The dense nature of the concrete and the evidence of significant CSH formation support case 1 and 3, as the concrete will undergo hydrothermal reactions, repairing any cracks and flaws in the concrete, creating a more amorphous solid with greater strength. This concrete will then gradually tend towards a dried state, which will limit the number of further hydrothermal reactions that can take place.

6.4 Other Criteria

Other criteria include factors that were not consequential to the selection of mix design but require consideration for the design of the structure.

6.4.1 Thermal Differences

Thermal differences in the structure, both through the wall from the hot face internal to the reactor cavity to the outside of the reactor cavity, and along the height of the cavity will play a significant role in developing thermal stresses in the concrete. Thermal modeling was carried out through the thickness of the wall that demonstrated at operating temperatures the temperature distribution through the wall falls quickly, being at 140°C about 0.8m into the wall. This suggests that using 225°C is a limiting case as much of the structure will be at significantly lower temperatures than this. A concern with this is the different response of concrete above and below 150°C, where there may be different causes for property change. This is supported by Kropp et al. [44] who point out that hydrothermal reactions only start occurring at temperatures in excess of 150°C. As such, further investigation is required of the response of sealed concretes for a range of values between room temperature and 225°C.

In the event of a LOCA the thermal model demonstrated that only the first 0.8m of the wall will be exposed to temperatures far in excess of 250°C. As such, it is likely that the 225°C response of the concrete will still dominate the overall structure. However, it has been shown that even the first 0.8m will be resistant to the higher temperatures of exposure.

6.4.2 Stress conditions

It has been quite clearly demonstrated in literature that the application of a confining stress to a concrete assists in the retention of properties. Abrams [58] suggests that there will be limited effect on strength up to 400°C for either limestone or siliceous aggregate concrete in an unsealed state, which is supported by Malhotra [61]. Schneider [38] demonstrated that a load of 30% at 450°C retains the modulus characteristics significantly more than no load.

6.4.3 Nature of and changes to the Surrounding Media

A brief discussion of the response of steel reinforcement was also carried out in this project, with information collected from literature. The following conclusions were made:

1. The mechanical properties of steel reinforcement and pre and post stressing cables needs special attention to ensure that the conditions of reinforcement and stressing of the concrete are maintained at temperature.

2. In terms of bond strength between steel reinforcement and concrete, the use of ribbed bars is strongly recommended as these retain bond strength significantly more than plain bars.

3. The concrete material constituents have an effect on the bond strength of the concrete. Hirano [79] has demonstrated that a significant increase in bond strength is possible in sealed conditions.

In conclusion literature and the results of testing suggest that a concrete can be designed for application in the PBMR that will meet the requirements put forward. Further research is required, particularly in areas where testing was not undertaken for the concrete (modulus of elasticity being an excellent example), and indeed further and more comprehensive testing is suggested. However, with the results of the project, it appears that a concrete can be designed for the environment of the PBMR reactor cavity structure.

Chapter 7

Conclusions and Recommendations

This project has undertaken to assess concrete for high temperature structures in nuclear reactors. While various options are available in terms of materials that are resilient to temperature, Portland cement concrete was focussed on due to the breadth of literature available and the well documented response of the material. From literature it was concluded that a mix design with high quantities of fly ash (60%), low water:cement ratio, an amorphous igneous coarse aggregate and siliceous fine aggregate is best suited to a sealed environment as would be present in the PBMR.

Considering this mix design philosophy the following conclusions can be made with respect to the response of the concrete:

- The response of the concrete is governed by the moisture conditions of the concrete and the heating environment. Identifying the nature of the heating environment is of primary importance in determining the response of the concrete. The PBMR thermal environment is representative of steady state thermal conditions with moisture unable to migrate out of the structure, where chemical transformations govern the response of the material.

- An improvement in strength in the region of 100% could be expected for concrete in the PBMR environment (sealed conditions) under normal operating temperatures of 225°C, although this assertion would need to be verified due to concerns over the sealing of test specimens. This is due to hydrothermal reactions forming hydrogarnets and 11Å tobermorite from the presence of unreacted fly ash. These hydrothermal reactions can recover the response to accident temperatures of 450°C after an initial reduction of strength due to microcracking caused by differential expansion between the binder and aggregate phases.

- Unsealed concretes demonstrate either a reduction or increase in strength to a certain common strength value with exposure to 225°C. With exposure to 450°C a significant reduction in strength can be expected. This is most likely due to increased shrinkage of the binder phase related to the high quantity of fly ash, developing microcracking.

- The gas permeability of an unsealed concrete experiences a doubling of permeability with exposure to 225°C and an increase in excess of an order of magnitude with exposure to 450°C. The permeability increases with length of exposure to temperature. The 225ºC response is likely due to the evaporation of physically and chemically bound water, while the 450ºC response is more dependent on microcracking.

- The chloride diffusivity of an unsealed concrete increases on first exposure to 225°C, followed by a substantial recovery to close to room temperature properties with length of exposure. Considering 450°C there is a large increase on first heating with a slight reduction with length of exposure. This suggests that the concrete densifies with length of exposure, especially at 225ºC, reducing the ability for chlorides to transport through the concrete.

- The water sorptivity shows a small increase with initial exposure to 225°C, and a possible decrease with length of exposure. With exposure to 450°C there is a substantial increase in sorptivity that continues to increase with length of exposure. The results for 225ºC support the conclusion of densification of the concrete reducing the ability for transport through the concrete, while the 450ºC results support the development of microcracking.

- The porosity of the concrete supports the 225°C results for chloride diffusivity and sorptivity, showing an increase on first exposure followed by a substantial decrease with length of exposure. A lower porosity would hinder the transport of water and chlorides. The 450°C results of the concrete are in agreement with the water sorptivity results, showing a marked increase on first exposure with a further increase with length of exposure.

With these conclusions on the properties of concrete in mind, it is reasonable to suggest that further investigation of concretes with a similar mix design be carried out. It has been shown that, in terms of strength, the sealed concrete demonstrates an improvement in all circumstances except direct heating to 450°C. The likelihood of this occurring is low as this would require an accident with the PBMR on first heating. Furthermore, following the conclusion of Kropp et al. [44] that hydrothermal reactions can be complete within 20 hours, it is possible that a slight change in constituent quantities will lead to a strength improvement. Similarly, at 225°C the transport properties have been shown to have limited deterioration. As to the importance of the transport properties in terms durability of the structure, the hot face of the concrete will be effectively in a sealed state, preventing the ingress of deleterious chemicals, while the exposed cold face of the structure will be near room temperature. As such it is likely that the room temperature properties of the concrete are of greater importance in determining the durability of the structure, and these results were shown to be towards the high end of the durability index.

Following these comments the recommendations from the project include the following suggestions:

- Undertake temperature testing of concretes with unheated strengths above the design strength of 40 MPa. These concretes should have similar mix constituents to those used in this project, with investigations of the impact of different fly ash contents, within the region of 60% replacement, that would provide insight into the effect of higher or lower contents. It can be expected that these concretes may demonstrate an increase in strength in a sealed environment, however this increase would have to be quantified.

- Furthermore a quantification of the unsealed response would be useful in the characterization of the material, to preclude any questions around the use of the concrete in unsealed heated environments. Likewise, testing of the concrete once it has been heated in a sealed environment, and then dried out will be representative of the reactor cavity concrete after significant periods of heat exposure.

- Undertake testing of these concretes at temperature to characterize the strength, modulus of elasticity and Poisson's ratio. All tests carried out in this project were cooled (residual) tests, which was sufficient to identify a mix design that would be ideal for the PBMR, but is not sufficient to characterize the material for the design of the reactor cavity. It has been shown that all mechanical properties have different responses at temperature and post heating, with the modulus of elasticity being of particular interest as this demonstrates a much lower response at temperature in a sealed environment.

- Investigate moisture migration and pore pressures to identify the transport rate of water through the structure with a sealed heated face. Of particular interest will be the effect of hydrothermal reactions that would densify the microstructure, likely significantly reducing the transport rate. These results can then be used to determine for how long the concrete would be in a sealed environment and when it would be reasonable to assume the concrete is effectively dried (i.e. has no notable moisture content to cause hydrothermal reactions and pore pressures).

- Investigate the effect of creep at temperature, particularly focusing on concretes with similar mix designs to that suggested here. Temperature will likely cause an increase in creep, but this would need to be quantified for the design of the structure.

- Consider other forms of binder, examples being high aluminate cement (HAC), geopolymers or polymers, that have a more stable response to temperature exposure than Portland cement concrete. Developing a justification to use HAC may be more effective than attempting to manage the temperature related reactions of Portland cement.

These recommendations conclude this dissertation.

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Appendix A

Testing Results

In Appendix A the testing results are presented in tabular format. The codes used in the tables are:

- RT – Room Temperature
- S – Sealed
- US – Unsealed
- S* – Failed sealing results – removed from consideration
- S** – Sealing results that lost mass but demonstrated different property development from unsealed concretes – results considered
- - – No result

A.1 Strength Results

A.1.1 Preliminary Results

Table A.1: 28 day results for testing series 1

	Strength (MPa)					
	Sample 1	Sample 2	Sample 3	Average	Range	% Range
Conventional Concrete	33	26	41	33	15	45
Conventional Mortar	33	34	30	33	4	14
Low Cement Concrete	25	25	20	23	5	22
Low Cement Mortar	23	20	18	20	5	25

Table A.2: 90 Day conventional concrete results

		RT	225ºC - 1 Day		225ºC - 5 Days		450ºC - 1 Day		450ºC - 5 Days	
			S*	US	S*	US	S*	US	S*	US
Sample 1	MPa	64	56	52	57	57	34	34	42	26
Sample 2	MPa	56	41	40	49	47	26	34	56	19
Sample 3	MPa	50	49	50	42	-	32	-	48	-
Average	MPa	57	49	47	49	52	30	34	49	22
Range	MPa	14	15	12	15	10	8	0	14	7
% Range	%	25	26	21	26	18	14	0	25	12
Mass Values (unheated)										
Sample 1	g	-	84.3	78.7	88.8	80.2	-	83.7	-	80.3
Sample 2	g	-	91.1	78.2	89.1	84.5	-	77.3	-	77.5
Sample 3	g	-	84.0	79.0	87.5	-	-	-	-	-
Container	g	-	-	-	-	-	673	-	688	-
Mass Loss										
Sample 1	g	-	7.5	5.4	6.6	4.8	-	5.8	-	5.5
Sample 2	g	-	8.0	5.1	6.2	5.1	-	5.6	-	5.6
Sample 3	g	-	7.8	5.3	6.1	-	-	-	-	-
Container	g	-	-	-	-	-	26	-	19	-

Table A.3: 90 Day conventional mortar results

		RT	225ºC - 1 Day		225ºC - 5 Days		450ºC - 1 Day		450ºC - 5 Days	
			S*	US	S*	US	S*	US	S*	US
Sample 1	MPa	70	53	58	45	47	-	35	-	28
Sample 2	MPa	66	49	57	44	41	-	33	-	28
Sample 3	MPa	59	45	51	41	50	-	32	-	29
Average	MPa	65	49	55	43	46	-	33	-	28
Range	MPa	11	8	7	4	9	-	3	-	1
% Range	%	17	12	11	6	14	-	5	-	2
Mass Values (unheated)										
Sample 1	g	-	84.3	72.8	83.0	73.9	-	71.2	-	72.6
Sample 2	g	-	81.8	71.1	82.2	73.4	-	79.1	-	73.5
Sample 3	g	-	83.0	73.8	83.7	73.3	-	73.7	-	73.8
Container	g	-	-	-	-	-	-	-	-	-
Mass Loss										
Sample 1	g	-	8.7	8.2	10.5	9.0	-	8.6	-	8.9
Sample 2	g	-	8.3	7.9	9.5	8.5	-	9.5	-	9.0
Sample 3	g	-	8.3	8.6	9.6	8.0	-	9.0	-	9.0
Container	g	-	-	-	-	-	-	-	-	-

Table A.4: 90 Day low cement concrete

		RT	225ºC - 1 Day		225ºC - 5 Days		450ºC - 1 Day		450ºC - 5 Days	
			S*	US	S*	US	S*	US	S*	US
Sample 1	MPa	33	32	31	28	23	43	20	59	19
Sample 2	MPa	36	24	39	33	30	54	24	52	28
Sample 3	MPa	41	34	-	31	29	47	17	56	21
Average	MPa	37	30	35	31	27	48	20	56	23
Range	MPa	8	10	8	5	7	11	7	7	9
% Range	%	22	27	22	14	19	30	19	19	24
Mass Values (unheated)										
Sample 1	g	-	88.2	77.3	87.3	78.4	-	77.5	-	84.3
Sample 2	g	-	86.8	79.9	86.5	85.2	-	78.7	-	82.8
Sample 3	g	-	86.5	-	88.5	77.5	-	77.6	-	85.3
Container	g	-	-	-	-	-	690.0	-	691.0	-
Mass Loss										
Sample 1	g	-	4.9	4.8	6.5	5.8	-	4.5	-	5.7
Sample 2	g	-	4.8	5.0	5.8	5.0	-	5.0	-	5.0
Sample 3	g	-	5.2	-	6.0	4.0	-	5.0	-	5.4
Container	g	-	-	-	-	-	25.0	-	23.0	-

Table A.5: 90 Day low cement mortar results

		RT	225ºC - 1 Day		225ºC - 5 Days		450ºC - 1 Day		450ºC - 5 Days	
			S*	US	S*	US	S*	US	S*	US
Sample 1	MPa	30	31	28	19	27	24	17	28	11
Sample 2	MPa	31	33	29	20	24	35	20	31	10
Sample 3	MPa	36	25	30	24	22	27	19	28	16
Average	MPa	32	29	29	21	24	28	18	29	13
Range	MPa	6	8	2	5	5	11	3	3	6
% Range	%	19	25	6	16	16	34	9	9	19
Mass Values (unheated)										
Sample 1	g	-	88.9	75.0	82.3	73.9	-	74.5	-	74.9
Sample 2	g	-	88.2	74.8	83.8	80.3	-	80.9	-	74.1
Sample 3	g	-	93.6	79.7	85.6	80.6	-	80.6	-	79.6
Container	g	-	-	-	-	-	671.0	-	669.0	-
Mass Loss										
Sample 1	g	-	5.2	8.0	8.4	7.6	-	7.9	-	8.0
Sample 2	g	-	5.1	7.5	9.2	8.3	-	8.3	-	8.2
Sample 3	g	-	5.4	14.4	8.2	8.1	-	7.9	-	8.9
Container	g	-	-	-	-	-	15.0	-	28.0	-

A.1.2 Conventional Concrete Results

28 Day Results

Table A.6: 28 day Strength Results

	Compressive Strength
	MPa
Sample 1	25.1
Sample 2	32.6
Sample 3	31.4
Average	29.7
Range	7.5
% Range	25.4

Table A.7: Strength Development of Conventional Concrete

	Sample 1	Sample 2	Sample 3	Average	Range	% Range
	MPa	MPa	MPa	MPa	MPa	%
7 Days	19	16	13	16	6	35.2
14 Days	25	24	24	24	1	5.1
28 Days	29	27	29	29	2	8.3

70 Day Results

Table A.8: Sealed strength and mass results for conventional concrete

		Units	Sample 1	Sample 2	Sample 3	Average	Range	% Strength	% Range
Room Temp.	Strength	MPa	30	28	36	31	8	100	23.9
	Mass	g	-	-	-	-	-	-	-
	Mass Loss	g	-	-	-	-	-	-	-
1 Day 225ºC	Strength	MPa	55	49	45	50	10	158	18.9
	Mass	g	100.1	99.9	101.0	100.3	-	-	-
	Mass Loss	g	6.3	6.1	6.2	6.2	-	-	-
	Container Mass	g	-	-	-	750	-	-	-
	Cont. Mass Loss	g	-	-	-	25	-	-	-
7 Days 225ºC	Strength	MPa	76	67	76	73	9	233	11.9
	Mass	g	99.9	100.4	101.3	100.5	-	-	-
	Mass Loss	g	6.1	6.4	6.2	6.2	-	-	-
	Container Mass	g	-	-	-	750	-	-	-
	Cont. Mass Loss	g	-	-	-	25	-	-	-
14 Days 225ºC	Strength	MPa	68	80	69	72	12	230	15.9
	Mass	g	100.6	100.4	99.3	100.1	-	-	-
	Mass Loss	g	6.0	6.2	7.0	6.4	-	-	-
	Container Mass	g	-	-	-	750	-	-	-
	Cont. Mass Loss	g	-	-	-	20	-	-	-
14 Days 225ºC + 1 cycle to 225ºC	Strength	MPa	84	77	74	78	10	249	12.1
	Mass	g	100.8	99.4	99.5	99.9	-	-	-
	Mass Loss	g	6.5	6.2	6.5	6.4	-	-	-
	Container Mass	g	-	-	-	760	-	-	-
	Cont. Mass Loss	g	-	-	-	35	-	-	-
14 Days 225ºC + 2 cycles to 225ºC	Strength	MPa	60	62	52	58	10	184	17.5
	Mass	g	100.4	100.9	100.0	100.4	-	-	-
	Mass Loss	g	6.4	6.3	6.6	6.4	-	-	-
	Container Mass	g	-	-	-	735	-	-	-
	Cont. Mass Loss	g	-	-	-	25	-	-	-
14 Days 225ºC + 2 cycles to 225ºC + 1 cycle to 450ºC	Strength	MPa	48	53	52	51	5	162	9.6
	Mass	g	101.1	99.5	100.7	100.5	-	-	-
	Mass Loss	g	7.4	7.1	6.8	7.1	-	-	-
	Container Mass	g	-	-	-	745	-	-	-
	Cont. Mass Loss	g	-	-	-	25	-	-	-

Table A.9: Unsealed strength and mass results for conventional concrete

		Units	Sample 1	Sample 2	Sample 3	Average	Range	% Strength	% Range
Room Temp.	Strength	MPa	34	34	28	32	6	100	18.2
	Mass	g	-	-	-	-	-	-	-
	Mass Loss	g	-	-	-	-	-	-	-
1 Day 225ºC	Strength	MPa	45	41	33	40	12	124	30
	Mass	g	100.7	101.2	100.2	100.7	-	-	-
	Mass Loss	g	6.4	6.5	6.6	6.5	-	-	-
7 Days 225ºC	Strength	MPa	37	42	45	41	8	128	18.2
	Mass	g	99.3	100.1	100.9	100.1	-	-	-
	Mass Loss	g	6.2	6.5	6.7	6.5	-	-	-
14 Days 225ºC	Strength	MPa	43	53	52	49	10	153	20.9
	Mass	g	99.8	100.3	99.9	100.0	-	-	-
	Mass Loss	g	6.2	6.7	6.5	6.4	-	-	-
14 Days 225ºC + 1 cycle to 225ºC	Strength	MPa	51	44	36	43	15	135	34.4
	Mass	g	100.9	100.0	100.3	100.4	-	-	-
	Mass Loss	g	6.2	6.3	6.7	6.4	-	-	-
14 Days 225ºC + 2 cycles to 225ºC	Strength	MPa	49	42	46	46	7	142	13.7
	Mass	g	100.0	100.4	99.5	100.0	-	-	-
	Mass Loss	g	6.4	6.4	6.4	6.4	-	-	-
14 Days 225ºC + 2 cycles to 225ºC + 1 cycle to 450ºC	Strength	MPa	28	30	33	30	5	94	17.0
	Mass	g	100.0	99.8	100.3	100.0	-	-	-
	Mass Loss	g	7.0	6.9	6.9	6.9	-	-	-

90 Day Results

Table A.10: 90 Day sealed results for conventional concrete

		Units	Sample 1	Sample 2	Sample 3	Average	Range	% Strength	% Range
Room Temp.	Strength	MPa	30	29	34	31	5	100	17.2
	Mass	g	-	-	-	-	-	-	-
	Mass Loss	g	-	-	-	-	-	-	-
1 Day 225ºC	Strength	MPa	64	62	60	62	4	200	6.3
	Mass	g	98.2	101.0	100.1	99.8	-	-	-
	Mass Loss	g	6.3	6.6	6.1	6.3	-	-	-
	Container Mass	g	-	-	-	731	-	-	-
	Cont. Mass Loss	g	-	-	-	27	-	-	-
5 Days 225ºC	Strength	MPa	53	68	63	62	15	199	24.9
	Mass	g	101.5	101.1	100.8	101.2	-	-	-
	Mass Loss	g	6.5	6.2	6.6	6.4	-	-	-
	Container Mass	g	-	-	-	-	-	-	-
	Cont. Mass Loss	g	-	-	-	-	-	-	-
5 Days 225ºC | 1 Day 450ºC	Strength	MPa	52	43	44	46	8	149	19.2
	Mass	g	100.0	101.1	98.8	100.0	-	-	-
	Mass Loss	g	7.5	7.5	7.0	7.3	-	-	-
	Container Mass	g	-	-	-	-	-	-	-
	Cont. Mass Loss	g	-	-	-	-	-	-	-
5 Days 225ºC | 2 Days 450ºC	Strength	MPa	42	46	46	45	4	144	8.4
	Mass	g	101.5	101.4	100.9	101.2	-	-	-
	Mass Loss	g	7.1	7.2	7.2	7.2	-	-	-
	Container Mass	g	-	-	-	-	-	-	-
	Cont. Mass Loss	g	-	-	-	-	-	-	-
5 Days 225ºC | 3 Days 450ºC	Strength	MPa	45	62	53	53	17	171	31.6
	Mass	g	101.3	99.1	100.8	100.4	-	-	-
	Mass Loss	g	9.4	5.7	7.0	7.3	-	-	-
	Container Mass	g	-	-	-	-	-	-	-
	Cont. Mass Loss	g	-	-	-	-	-	-	-

Table A.11: 90 Day unsealed results for conventional concrete

		Units	Sample 1	Sample 2	Sample 3	Average	Range	% Strength	% Range
Room Temp.	Strength	MPa	30	29	34	31	5	100	17.2
	Mass	g	-	-	-	-	-	-	-
	Mass Loss	g	-	-	-	-	-	-	-
1 Day 225ºC	Strength	MPa	49	47	46	47	3	152	6.5
	Mass	g	99.9	100.6	100.6	100.3	-	-	-
	Mass Loss	g	6.7	6.4	6.1	6.4	-	-	-
5 Days 225ºC	Strength	MPa	43	50	-	46	7	149	14.9
	Mass	g	99.5	100.9	-	100.2	-	-	-
	Mass Loss	g	6.5	6.2	-	6.4	-	-	-
5 Days 225ºC | 1 Day 450ºC	Strength	MPa	52	43	44	46	8	149	19.2
	Mass	g	100.0	101.1	98.8	100.0	-	-	-
	Mass Loss	g	7.5	7.5	7.0	7.3	-	-	-
5 Days 225ºC | 2 Days 450ºC	Strength	MPa	38	34	33	35	5	113	15.0
	Mass	g	100.8	96.1	100.8	99.2	-	-	-
	Mass Loss	g	7.2	7.3	7.2	7.2	-	-	-
5 Days 225ºC | 3 Days 450ºC	Strength	MPa	34	40	40	38	6	123	16.2
	Mass	g	99.8	99.7	100.8	100.1	-	-	-
	Mass Loss	g	7.5	7.7	7.3	7.5	-	-	-

A.2 Durability Index Results

A.2.1 28 Day Tests

Property		Value
Oxygen Permeability Test	Diffusivity	1.8 * 10^{-11} m/s
	OPI value	10.7
Chloride Conductivity Test	Chloride conductivity	0.21 mS/cm
	Porosity	5.7%
Sorptivity Test	Sorptivity	7.3 mm/hr
	Porosity	6%

Table A.12: 28 Day durability index test results for conventional concrete

A.2.2 90 Day Heated Tests

Oxygen Permeability Results

Table A.13: Diffusivity and oxygen permeability index for conventional concrete

	RT		225°C - 1 Day		225°C - 5 Day		450°C - 1 Day		450°C - 5 Day	
	k (m/s)	OPI	k (m/s)	OPI	k (m/s)	OPI	k (m/s)	OPI	k (m/s)	OPI
Sample 1	3.2E-11	10.5	1.0E-10	10.0	6.7E-11	10.2	4.5E-10	9.3	7.4E-10	9.1
Sample 2	2.6E-11	10.6	5.9E-11	10.2	9.2E-11	10.0	4.2E-10	9.4	1.3E-09	8.9
Sample 3	4.9E-11	10.3	5.2E-11	10.3	7.2E-11	10.1	4.5E-10	9.4	9.9E-10	9.0
Sample 4	-	-	3.4E-11	10.5	5.9E-11	10.2	4.9E-10	9.3	1.3E-09	8.9
Average	3.6E-11	10.4	6.1E-11	10.2	7.3E-11	10.1	4.5E-10	9.3	1.1E-09	9.0

Table A.14: Diffusivity and oxygen permeability index for low cement concrete

	RT		225°C - 1 Day		225°C - 5 Day		450°C - 1 Day		450°C - 5 Day	
	k (m/s)	OPI	k (m/s)	OPI	k (m/s)	OPI	k (m/s)	OPI	k (m/s)	OPI
Sample 1	9.9E-12	11.0	6.3E-11	10.2	1.1E-10	9.9	1.4E-09	8.9	1.8E-09	8.7
Sample 2	1.0E-11	11.0	7.2E-11	10.1	1.2E-10	9.9	1.2E-09	8.9	1.7E-09	8.8
Sample 3	1.8E-11	10.7	5.9E-11	10.2	8.4E-11	10.1	1.3E-09	8.9	2.1E-09	8.7
Sample 4	5.7E-12	11.2	6.1E-11	10.2	1.1E-10	10.0	1.5E-09	8.8	2.0E-09	8.7
Average	1.1E-11	11.0	6.4E-11	10.2	1.1E-10	10.0	1.3E-09	8.9	1.9E-09	8.7

Chloride Conductivity Results

Table A.15: Chloride conductivity results for conventional concrete

	RT (mS/cm)	225°C-1 Day (mS/cm)	225°C-5 Day (mS/cm)	450°C-1 Day (mS/cm)	450°C-5 Day (mS/cm)
Sample 1	0.19	1.07	0.36	2.12	1.73
Sample 2	0.24	0.71	0.28	1.87	1.58
Sample 3	0.17	0.77	0.28	1.85	1.51
Sample 4	0.19	0.72	0.25	1.61	1.46
Average	0.20	0.82	0.29	1.87	1.57
Average Porosity	5.00%	11.20%	1.20%	13.50%	15.80%

Table A.16: Chloride conductivity results for low cement concrete

	RT (mS/cm)	225°C-1 Day (mS/cm)	225°C-5 Day (mS/cm)	450°C-1 Day (mS/cm)	450°C-5 Day (mS/cm)
Sample 1	0.19	0.72	0.51	2.17	2.27
Sample 2	0.27	0.69	0.60	1.79	2.37
Sample 3	0.21	0.68	0.54	2.06	2.17
Sample 4	0.23	0.75	0.42	2.21	2.13
Average	0.23	0.71	0.52	2.06	2.23
Average Porosity	5.60%	11.90%	4.00%	15.90%	16.60%

Water Sorptivity Results

Table A.17: Water sorptivity results for conventional concrete

	RT	225°C - 1 Day	225°C - 5 Day	450°C - 1 Day	450°C - 5 Day
	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)
Sample 1	1.7	2.7	1.7	11.7	15.5
Sample 2	3.4	2.2	1.3	11.0	14.8
Sample 3	3.3	1.9	1.6	10.0	16.1
Sample 4	3.0	4.6	-	12.7	16.9
Average	2.8	2.9	1.5	11.4	15.8

Table A.18: Porosity results from the sorptivity tests for conventional concrete

	RT	225°C - 1 Day	225°C - 5 Day	450°C - 1 Day	450°C - 5 Day
	(%)	(%)	(%)	(%)	(%)
Sample 1	11.7	29.4	5.2	16.8	18.0
Sample 2	11.5	14.8	5.7	17.1	18.8
Sample 3	11.3	14.9	5.2	16.9	17.9
Sample 4	11.5	15.0	-	17.0	18.2
Average	11.5	18.5	5.4	17.0	18.2

Table A.19: Water sorptivity results for low cement concrete

	RT	225°C - 1 Day	225°C - 5 Day	450°C - 1 Day	450°C - 5 Day
	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)	(mm/hr$^{0.5}$)
Sample 1	-	2.8	0.8	18.1	20.0
Sample 2	3.8	3.9	0.4	20.2	20.9
Sample 3	3.1	4.5	0.7	18.3	22.4
Sample 4	3.5	4.1	0.5	19.8	22.6
Average	3.5	3.8	0.6	19.1	21.5

Table A.20: Porosity results from the sorptivity tests for low cement concrete

	RT	225°C - 1 Day	225°C - 5 Day	450°C - 1 Day	450°C - 5 Day
	(%)	(%)	(%)	(%)	(%)
Sample 1	-	15.8	11.1	17.2	17.3
Sample 2	11.8	15.2	11.7	17.1	17.5
Sample 3	12.2	15.4	10.3	17.2	17.8
Sample 4	11.9	16.1	11.3	17.2	18.7
Average	12.0	15.6	11.1	17.2	17.8

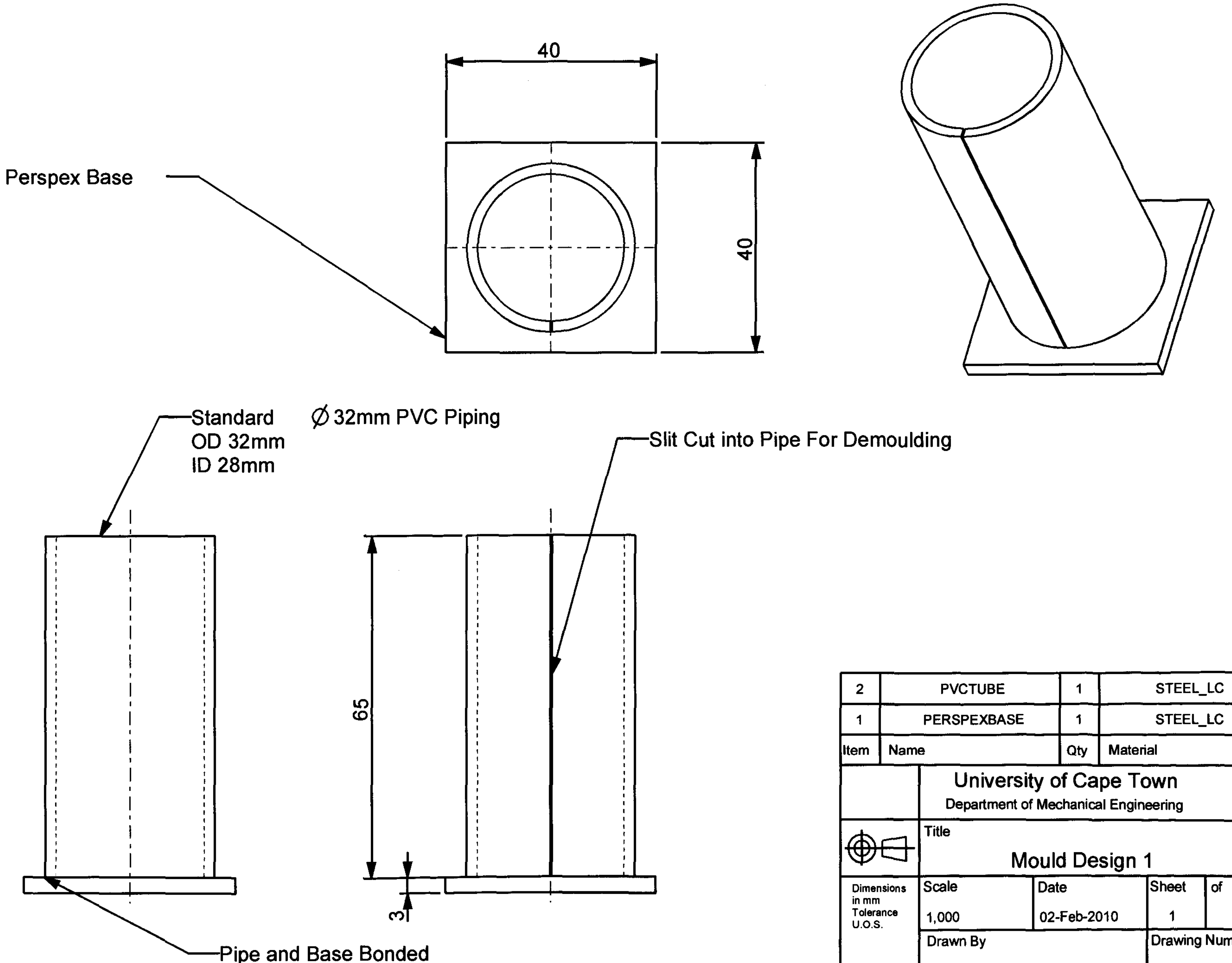
A.3 Shrinkage Tests

Age	Mean Shrinkage (Microstrains)			Cumu. Mean
(Days)	Sample 1	Sample 2	Sample 3	(Microstrains)
0	0	0	0	0
1	-10	50	15	18
2	10	5	160	77
3	30	55	65	127
5	70	20	15	162
8	0	35	30	183
14	65	60	65	247
21	45	55	35	292
35	80	90	95	380
56	0	10	45	398

Table A.21: Shrinkage data for conventional concrete

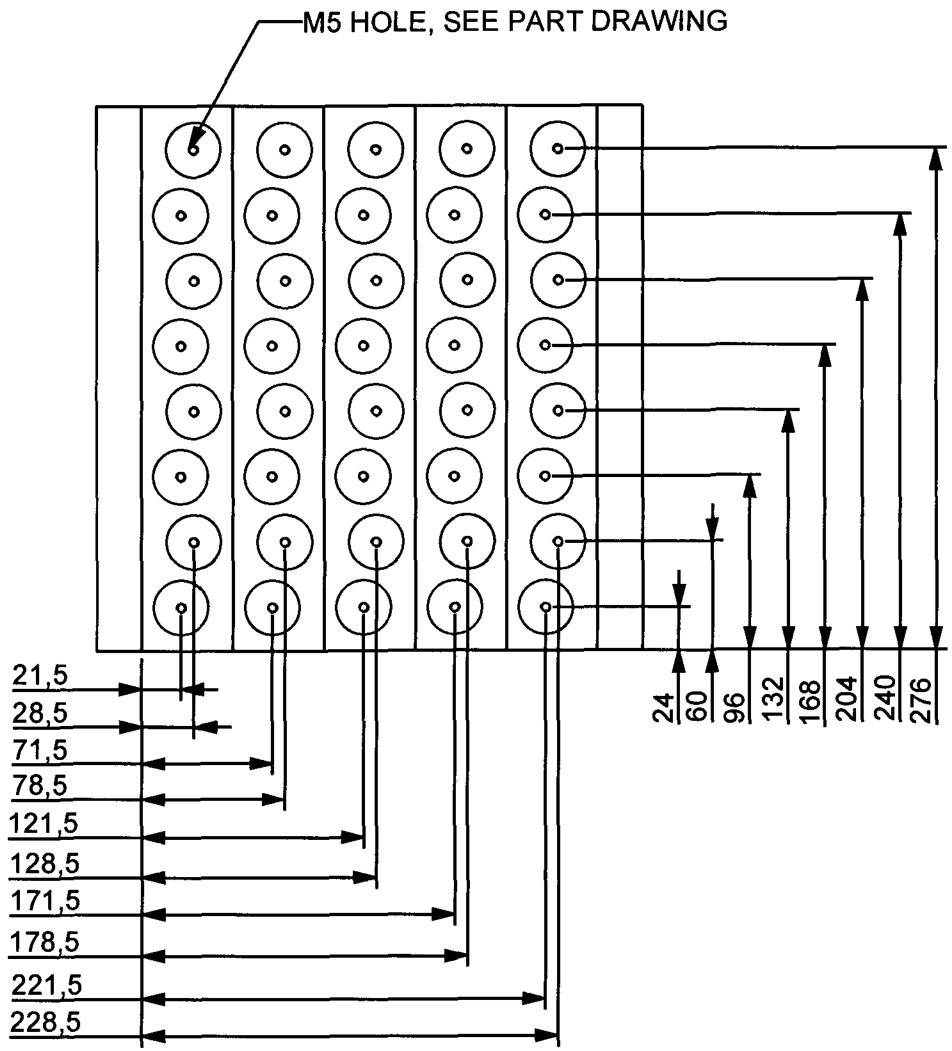
Appendix B

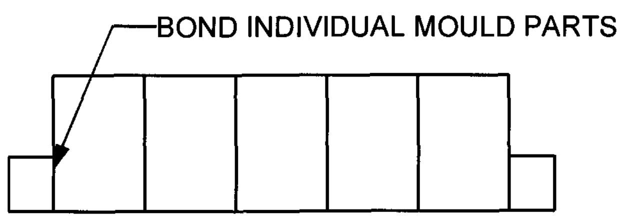
Designs

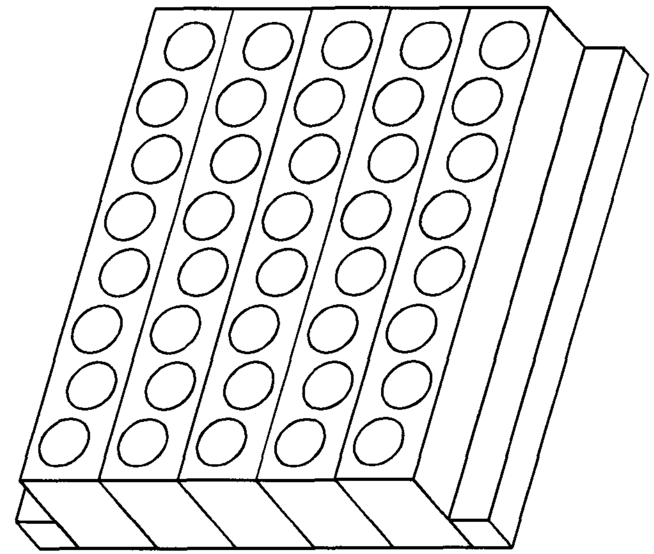


Item	Name	Qty	Material
2	PVCTUBE	1	STEEL_LC
1	PERSPEXBASE	1	STEEL_LC

	University of Cape Town Department of Mechanical Engineering			
	Title Mould Design 1			
Dimensions in mm Tolerance U.O.S.	Scale 1,000	Date 02-Feb-2010	Sheet 1	of 1
0.1	Drawn By Darryn McCormick		Drawing Number 001-001	

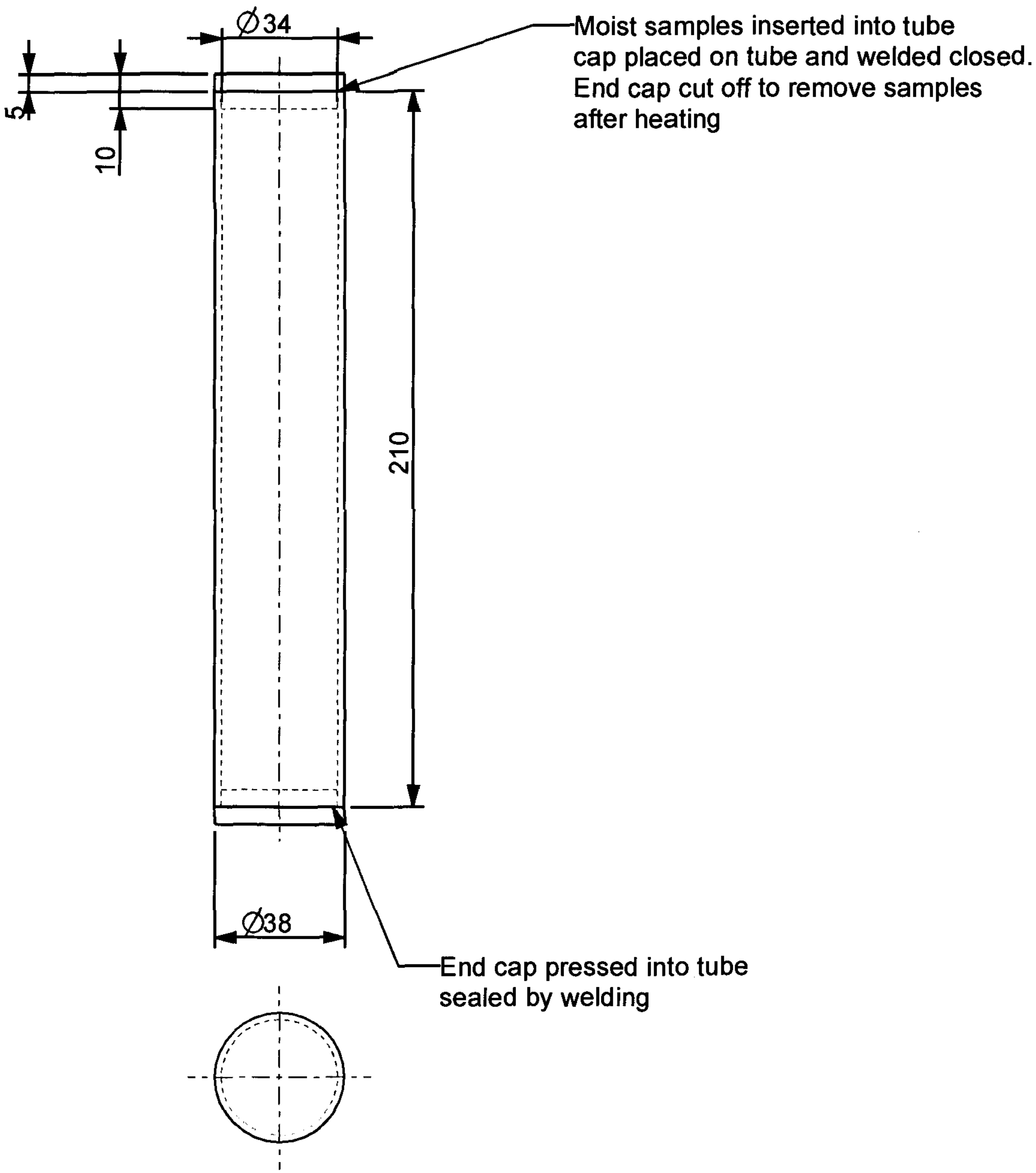


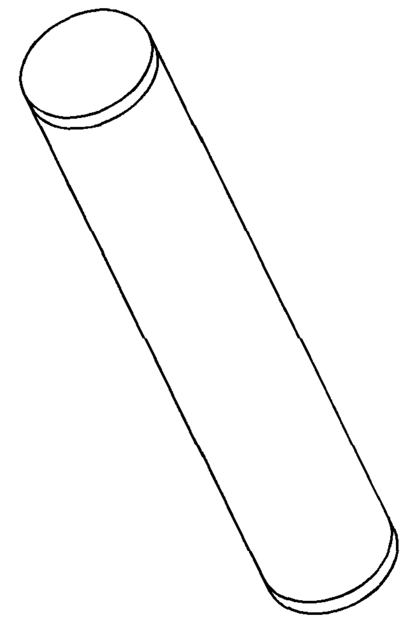




2	SINGLEMOULDBODYOUTSIDES	2	STEEL_LC
1	SINGLEMOULDBODY	5	STEEL_LC
Item	Name	Qty	Material

	University of Cape Town Department of Mechanical Engineering			
	Title Assembled Mould			
Dimensions in mm Tolerance U.O.S.	Scale 0,250	Date 26 Jan. 2010	Sheet 03	of 03
0.1	Drawn By Darryn McCormick		Drawing Number 01-03	





Item	Name	Qty	Material
2	SEALEDCYLINDERENDCAPS	2	STEEL_LC
1	SEALEDCYLINDER	1	STEEL_LC

University of Cape Town
Department of Mechanical Engineering

Title
Steel Sealing Container

Dimensions in mm Tolerance U.O.S.	Scale	Date	Sheet	of
	0,500	02-Feb-2010	01	01
	Drawn By		Drawing Number	
0.1	Darryn McCormick		001-001	