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Abstract	<p>The aim of this chapter is to present the relevant degradation processes occurring at the micro-level in concrete exposed to high temperatures, with special interest to the differences associated with High Performance Concrete (HPC) and Self Compacted Concretes (SCC) in respect to Ordinary Concrete. The microstructure of concrete can be identified using appropriate techniques sensitive to detect changes in concrete components that occur at micro level. The main items considered in present chapter are:</p> <ol style="list-style-type: none"> 1. Chemical Degradation reactions 2. Physical degradation processes 3. Thermal changes. 	

Chapter 2

Degradation Reactions in Concretes Exposed to High Temperatures

Maria Cruz Alonso and Ulrich Schneider

Abstract The aim of this chapter is to present the relevant degradation processes occurring at the micro-level in concrete exposed to high temperatures, with special interest to the differences associated with High Performance Concrete (HPC) and Self Compacted Concretes (SCC) in respect to Ordinary Concrete. The microstructure of concrete can be identified using appropriate techniques sensitive to detect changes in concrete components that occur at micro level. The main items considered in present chapter are:

1. Chemical Degradation reactions
2. Physical degradation processes
3. Thermal changes.

2.1 Methodologies to Identify the Degradation Processes of Heated Concrete at Microstructural Level

The transformation processes taking place in concrete components (cement paste and aggregates) are usually determined in small pieces or powder obtained directly from the structure or from bigger samples, being destructive tests. The tests are usually performed after cooling, i.e. in residual state. Methods such as: X-Ray Diffraction Spectroscopy (XRD), Infra-Red Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), Near Edge X-Ray Absorption Fine Structure (NEXAFS), Scanning Electron Microscopy (SEM), micro X-Ray 3D computed tomography (μ X-3D-CT) and Mercury Intrusion Porosimetry (MIP) are those more commonly used. A few techniques allow the identification of the degradation reactions occurring at high temperature, such as: Thermal analysis (TG/DTA), Thermal changes (expansion,

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heat effects), Neutron Diffraction Spectroscopy (NDS), High Temperature X-Ray Diffraction (HT XRD) or High temperature Environmental microscopy (HTEM). All these techniques allow the identification of different aspects of microstructure degradation in concrete as a consequence of the action of temperature.

The specific information obtained from each type of technique is described below:

- *Crystal transformations*: XRD (residual), NDS (in situ at high temperature), Al-NMR (residual).
- Give information on the different crystalline components of concrete with the increase of temperature. In case of cement paste: ettringite ($\text{Ca}_6(\text{Al}(\text{OH})_6)_2(\text{SO}_4)_3(\text{H}_2\text{O})_{26}$), portlandite ($\text{Ca}(\text{OH})_2$), lime (CaO), calcite (CaCO_3), larnite (C_2S) and the crystalline forms of CSH (tobermorite, jenite, xonolite etc.), and of different crystalline aggregate transformations (like Quartz or carbonates).
- *Transformation of amorphous phases*: NEXAFS and Si NMR (in situ at high temperature)
These techniques give information about the alteration of Si chain of CSH gel. Si-NEXAFS or ^{29}Si -RMN inform on the local silicate tetrahedral environment in the CSH structure. In ^{27}Al -RMN the differentiation between tetrahedral [Al (4)] and octahedral [Al (6)] coordinated aluminium and so its incorporation to CSH structure is identified.
- *Molecular transformations*: IR (residual)
IR is a technique useful to determine molecular structures, identification of chemical species, quantitative/qualitative determination of chemical species; it can provide valuable information regarding the silicate, sulphate, and carbonate phases.
- *Thermal stability transformations*: DTA/TG (in situ at high temperature)
DTA gives information about the thermal stability of phases with increase in temperature. Using TG is possible to determinate the quantity of the transformation of the different phases at the different temperatures.
- *Microstructure transformations*: SEM, EDAX-SEM (residual) and HTEM (in situ at high temperature) and porosity (MIP) after cooling.

SEM is used to observe phase changes in the solid components, and the presence of micro-cracks. EDAX is a complement to identify local elemental analysis of the solid phases. The changes in density in concrete due to increase in porosity as a consequence of heat transformations are usually measured with MIP including total porosity and pore size distribution.

The small sample size (few grams) generally needed for identification of concrete damage at the micro-level is the main limitation of most of these techniques if the aim is to correlate what is taking place at the macro-level. However, sampling at different points and depths allows identification of the heterogeneity and gradients in degradation reactions of concrete exposed to high temperature.

2.2 Thermal Analytical Reactions of Concrete Components

When concrete made with plain Portland cement (OPC) or blended cements with mineral additions, such as Blast Furnace Slag (BFS), are subjected to heat, a number of chemical transformations and reactions of different kinds occur (Ehm and Schneider 1981; Mendes 2010). The main processes have been summarised in Table 2.1. The specific processes associated with High Performance (HP) cement paste, Self Compacted (SC) paste including filler and aggregate reactions are also considered.

Apart from the crystal transformations occurring mainly in the aggregates, the processes comprise the so called degradation reactions of cement paste, these being reactions which bring about a progressive breakdown in the structure of the concrete. They occur more particularly in the hardened cement paste hydrated components, but also in the aggregates depending on the type of rock concerned (Schneider et al. 1980) as described below.

- At temperatures from 100 °C to <500 °C the chemical reactions mainly take the form of dehydration of cement paste components (ettringite, CSH and portlandite) followed with water vapour expulsion. The main component of cement paste, the CSH, progressively decomposes its structure within this range of temperatures by breaking the silicon chains length (Alonso and Fernandez-Municio 2004; Mendes et al. 2010). The final stage of CSH dehydration is the formation of silicates with similar anhydrous cement structure type C2S (Ehm and Schneider 1981; Alonso and Fernandez-Municio 2004). In situ analyses using Neutron Diffraction Spectroscopy (NDS) of crystalline phase changes occurring during progressive heating confirmed these transformations (Castellote et al. 2004).
- At higher temperatures, up to 800 °C, crystalline transformation of aggregates occurs, e.g. α to β quartz transformation in siliceous aggregates. Decarbonation of carbonates plays a prominent part if the concrete contains limestone aggregates or filler such as in SCC (Schneider et al. 1977; Alarcon-Ruiz 2005).
- Above 1200 °C and up to 1300 °C, some components of the concrete begin to melt. During melting some aggregates (e.g. igneous rocks such as basalt) show degassing and expansion phenomena accompanied by release of gases trapped within the rock at the time of its formation (Schneider et al. 1977, 1980).
- Above 1300–1400 °C concrete exists in the form of a melt, i.e. it has then turned into a liquid (Schneider et al. 1977, 1980).

2.2.1 Crystalline Phase Transformation in Cement Paste

Of concern with respect to cement paste of Portland cement are the in situ crystalline changes occurring during progressive heating has been identified using Neutron Diffraction Spectroscopy (NDS) (Castellote et al. 2004). As shown in Fig. 2.1 some peaks are identified corresponding to portlandite (P), ettringite (E), lime (L) and

Table 2.1 Transformation and decomposition reactions at high temperature in the main components of concrete (Schneider 1988; Bažant and Kaplan 1996; Ehm and Schneider 1981; Alonso and Fernandez-Municio 2004)

Temp. (°C)	OPC cement paste	OPC + BFS cement paste	HP cement paste	SC cement paste	Aggregate
20–80	Slow capillary water loss and water expansion	Slow capillary water loss and water expansion	Hydration cement grains	Slow capillary water loss and water expansion	
80–90	Ettringite decomposition		Ettringite decomposition	Ettringite decomposition	
80–100	Capillary water loss	Capillary water loss		Capillary water loss	
100–200	Physically bound CSH water loss CSH decomp. formation of $\alpha\text{C}_2\text{SH}$	Physically bound CSH water loss CSH decomp. formation of $\alpha\text{C}_2\text{SH}$	Physically bound CSH water loss CSH decomp. formation of $\alpha\text{C}_2\text{SH}$	Physically bound CSH water loss CSH decomp. formation of $\alpha\text{C}_2\text{SH}$	
200–350	Katoite and $\alpha\text{C}_2\text{SH}$ decomposition Formation of Mayemite Formation of Jaffeite and $\alpha\text{C}_2\text{S}$	Katoite and $\alpha\text{C}_2\text{SH}$ decomposition Formation of Mayemite Formation of Jaffeite and $\alpha\text{C}_2\text{S}$	Katoite and $\alpha\text{C}_2\text{SH}$ decomposition Formation of Mayemite Formation of Jaffeite and $\alpha\text{C}_2\text{S}$	Katoite and $\alpha\text{C}_2\text{SH}$ decomposition Formation of Mayemite Formation of Jaffeite and $\alpha\text{C}_2\text{S}$	
400–450	$\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$	$\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$ Less quantity		$\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$	
570					Quartz transformation $\alpha\text{SiO}_2 \rightarrow \beta\text{SiO}_2$
650–800				Filler decomposition $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	Lime decomposition $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
800–1200	Melting dehydrated phases		Melting dehydrated phases	Melting dehydrated phases	
>1200					Melting aggregates

Fig. 2.1 Degradation processes of OPC cement paste during heating by NDS: powdered sample, heating rate of 120 °C/h. P: Portlandite, E: Ettringite, L: Lime, T: CSH gel. (Castellote et al. 2004)

crystalline CSH, such as tobermorite (T). With regard to their changes with temperature increase, the first transformations observed are those of ettringite dehydrated at temperatures up to 90 °C. Further the CSH slightly decreases above 100 °C, as it gets dehydrated, disappearing at a temperature which depends on the structure of the CSH (between 200 and 450 °C). Part of the CSH decomposes and contributes to an increase in the content of calcite and a crystal phase identified as larnite. The portlandite decomposes abruptly when it reaches an internal temperature between 450 and 550 °C.

Analysing the intensity of the peaks as a function of the temperature, more details of the changes of concentration of these crystalline phases can be determined, as shown in Fig. 2.2 (Castellote et al. 2004):

- During heating up to 100 °C: two main processes are taking place simultaneously. One induces a decrease in intensity associated with the ettringite crystals dehydration due to the lack of thermal stability of this crystalline phase, while the other increases the intensity of portlandite due to new formation attributed to two reasons: (a) the loss of the free water in the pores with portlandite precipitation, (b) further hydration of anhydrous cement grains activated by the temperature. Furthermore, there is an additional release of calcium coming from the decomposition of ettringite, which certainly contributes to the precipitation of both portlandite and calcite, probably due to the reaction with the CO₂ present in the hot air.

Fig. 2.2 In situ evolution of ettringite, portlandite, lime and CSH gel (tobermorite) of Portland cement paste by NDS. During heating (dot signal), during cooling (open signal) (Castellote et al. 2004)

- In the region between 100 up to 400 °C: The peak corresponding to the crystalline form of CSH, the tobermorite, shows a wide scatter but a progressive decrease in intensity due to progressive dehydration and loss of crystal structure of CSH which disappears completely at 400 °C.
- At temperatures above 400 °C, up to 550 °C: the portlandite drastically decomposes in a narrow range of temperatures (450–550 °C) and at the same temperature that lime strongly increases.
- However, analysing in situ cooling processes (open signals in Fig. 2.2.), it can be observed that portlandite is partially recrystallised (but at lower temperatures, <450 °C) from partial lime hydration, the content of which decreases during cooling (also represented in the Fig. 2.2).

With HTXRD (Robert et al. 2009), it has also been possible to follow the integration of the intensity of the peak associated with different crystalline phases, as shown in Fig. 2.3. In the case of portlandite an increase is observed up to 200 °C and then a decrease before a sharp disappearance at 450 °C, which agrees well with the observation in NDS (Castellote et al. 2004). With the use of slag in the blend, the quantity of portlandite is less than in OPC. Katoite is not observed during in situ measurement. This may be connected with the formation kinetic of this compound.

Fig. 2.3 In situ measurements with HTXRD, Evolution of the integrated intensity for the peak (001) related to portlandite ($d = 0.49$) (Robert et al. 2009)

Some similar information can be obtained concerning the final components when using XRD in residual state (after cooling) from Fig. 2.4, and crystalline phases such as larnite, portlandite, brownmillerite, calcite, ettringite, and $\text{CA}_{1.5}\text{SiO}_{3.5}\text{xH}_2\text{O}$, in OPC cement paste can be observed. However, their evolution during heating cannot be deduced as with in situ test (NDS or HTXRD) (Castellote et al. 2004; Robert et al. 2009). After cooling, some reflections disappear, corresponding to ettringite (above 100 °C) and $\text{Ca}_{1.5}\text{SiO}_{3.5}\text{xH}_2\text{O}$ above 450 °C heating. A progressive reduction of the intensity of the peak related to portlandite is observed by increasing the temperature above 450 °C and it completely disappears at 750 °C. The presence of calcite is also detected (Handoo et al. 2002). Lime is well identified after heating at 750 °C, the origin of which is explained by portlandite and calcite transformations. The crystal phases brownmillerite and larnite are also identified (Robert et al. 2009; Alonso and Fernandez-Municio 2004, 2010).

Although calcium aluminates and aluminate hydrates (ettringite and monosulphate hydrate) have very clear crystalline structure, their transformations occurring after heating can be characterised by ^{27}Al NMR (Mendes 2010) as shown in Fig. 2.5. It is possible to distinguish between tetrahedrally [Al (4)] and octahedrally [Al (6)] coordinated aluminium but the reflections found in a heated sample are more difficult to fit in the spectra. However, a significant conversion of octahedral sites to tetrahedral sites can be deduced [with the increase in temperature the hydrated Al(6) dehydrates into Al(4) unhydrated phases].

Fig. 2.4 XRD of after cooling heated Portland cement paste at various temperatures (Alonso and Fernandez-Municio 2004)

2.2.2 Amorphous Phase Transformation in Cement Paste

Although CSH of cement paste has phase structures that show crystalline forms (tobermorite or jennite), most of it has a gel structure that can be well identified using ^{29}Si MAS-NMR, after cooling (Alonso and Fernandez-Municio 2004). Figure 2.6 shows the main transformation processes of degradation of CSH using NMR:

- Temperatures up to 100 °C: alterations are initiated in the structure of CSH gel. The initial CSH structure is considered to be formed by chains of silicon tetrahedra, indicated by peaks Q^1 , associated with silicon tetrahedra at the extremities of the chain, and Q^2 , related to silicon tetrahedral in the middle of the chain. Temperatures above 200 °C: the Q^1/Q^2 ratio increases indicating that silicon chains start to break and at 400 °C the CSH structure has completely disappeared. Simultaneous to these transformations in CSH, a new nesosilicate phase of monomers of silicon tetrahedra is formed, Q^0 , having a similar but less crystalline structure than the anhydrous cement grains of larnite. The CSH degradation with temperature coincides with mechanical strength losses in OPC cement paste (Alonso and Fernandez-Municio 2007).

Fig. 2.5 Single pulse ^{27}Al NMR spectra of OPC and 35% slag pastes. After cooling (Mendes 2010)

If the binder contains slag the CSH has a more polymerised structure than OPC paste after exposure to the same temperature (Mendes 2010). This indicates that the slag cement paste CSH gel is less affected by temperature. At 800 °C Q^0 and a small Q^1 resonance are noticed, which indicates that slag pastes remain slightly more polymerised than the OPC cement pastes even after exposure to 800 °C.

Electronic configuration of amorphous CSH silicate structure can also be studied by NEXAFS spectra (Mendes 2010). In general, the main peak in the Si NEXAFS spectrum shifts to higher energy with increasing degree of polymerisation, as shown in Fig. 2.7.

The NEXAFS spectra in Fig. 2.7 show two first peaks related to single electron $1s \rightarrow \sigma^*$ Si–O transition of silicate. The latter is due to a broad σ^* Si–O continuum resonance and is probably made up of several overlapping σ^* (anti-bonding) orbitals due to differences in inter-atomic distances. However, with heating to 800 °C, the first peak shifts to a lower energy, indicating loss of polymerisation of CSH gel and the second peak increases significantly after exposure to 800 °C. This peak is related to

Fig. 2.6 Transformation in CSH gel of OPC cement paste after heating at high temperatures, by Si Mass NMR, after cooling (Alonso and Fernandez-Municio 2007)

monomer silicon tetrahedra and its increase is a result of depolymerisation of CSH due to rise in temperature, as also suggested from NMR (Alonso and Fernandez-Municio 2004). In cement paste with slag, after 800 °C the peaks have less intensity, which suggests that after exposure to high temperature OPC paste is less polymerised than the 35% slag cement paste.

2.2.3 Molecular Transformations in Cement Paste

The analysis of the changes happening after heating in bound hydroxyl (OH), bound H-bonded water (HOH), carbonate (CO₃), sulphate (SO₄), and silicate (SiO₂) ligands in cement paste can be followed using infrared technique (Mendes 2010). When a cement paste has been exposed to high temperature, the bonds are broken and some reflections decrease or disappear.

The main changes observed for OPC and 35% slag cement pastes are shown in Fig. 2.8 (Mendes 2010):

- Decreased Ca(OH)₂ peak intensity (35% slag is almost absent)
- Significant decrease in the carbonate peak
- Shift of the silicate/sulphate peak stretch to lower wave bands as a result of depolymerisation.

Fig. 2.7 Si NEXAFS spectra of OPC and 35% slag cement pastes RT and 800 °C (Mendes 2010)

2.2.4 Thermal Stability Transformations of Concrete Components

The reactions initiated during the heating of cement paste can also be studied with the aid of differential thermal analysis (DTA). In Fig. 2.9 the thermogravimetry analyses of a Portland cement paste occurring during high temperature exposure are compared with thermogravimetry of cement paste previously heated to specific temperatures, 100, 200, 450 and 750 °C (Schneider and Kordina 1976).

Fig. 2.8 FTIR spectra of OPC and 35% slag pastes RT and 800 °C. Spectra have been normalised to the OH bands near 3670 cm^{-1} to better display differences, after cooling (Mendes 2010)

Fig. 2.9 Degradation level of OPC cement paste after high temperature exposure, by TG/DTA (Alonso and Fernandez-Municio 2004)

The DTA of Fig. 2.9 left clearly shows the endothermic peak at 90 °C occurring in the cement paste labelled as reference (not-previously heated). This peak has disappeared in the other samples indicating that the ettringite is dehydrating. The next endothermic peak appears at 450 °C, attributed to portlandite decomposition. This peak maintains its transformation in samples heated at 100 and 200 °C. In samples heated at 450 and 750 °C only a small peak of transformation is present, which takes place at lower temperatures 430 °C indicating that this portlandite has been formed during cooling and is less crystalline (Alonso and Fernandez-Municio 2004). The mass losses occurring during the process can be seen in the TG of Fig. 2.9-right. The peak transformations shown in DTA are associated with mass losses in

Fig. 2.10 Differential thermal analysis of various normal weight concretes (Schneider and Diederichs 1981)

the samples due to the advance of the cement paste dehydration processes. Besides, in this Fig. 2.9-right the continuous mass loss between 100 and 400 °C is attributed to the progressive dehydration of CSH that has completely finished at 450 °C when portlandite decomposes.

Figure 2.10 shows the thermograms obtained for normal concretes made with quartzitic, calcitic and basalt aggregates and with portland cement (Schneider and Diederichs 1981). The DTA analyses clearly reveal the following reactions associated with heat effects: (a) water expulsion at about 100 °C; (b) breakdown of gel (first stage of dehydration) at 180 °C; (c) decomposition of portlandite at 500 °C; (d) transformation of quartz at 570 °C; (e) decarbonation of limestone from 800 °C; (f) start of melting from 1150 to 1200 °C onwards.

Quantitatively it is more practicable to study those reactions which are associated with a conversion of mass which manifests itself in a distinct change in weight. Investigations relating to this were carried out for concrete with the aid of a large

Fig. 2.11 Thermograms of normal weight concretes made with Portland cement (Schneider and Diederichs 1981)

thermo-balance. Figure 2.11 shows the results of the measurements performed in these thermogravimetric investigations. The ordinates in this diagram represent the loss of weight (referred to the initial weight of the sample for analysis) of three concretes, made with Portland cement and with quartzite, basalt and calcite aggregates respectively, plotted against the temperature. The specimens employed in these tests were small concrete cylinders, 12 mm in diameter and 40 mm long, obtained as cores drilled from thick concrete slabs which had been stored at 20 °C and 65% RH. The core specimens were stored under the same environmental conditions until immediately before the start of testing (Schneider and Diederichs 1981).

Figure 2.11 clearly shows that even at temperatures below 100 °C a loss of weight occurs in the concrete, which is due to the evaporation of water from the large pores. Just above 100 °C the loss of weight from this cause proceeds at an increased rate due to dehydration of paste components as explained above. Up to about 200 °C the slope of the curves is practically constant and practically independent of the pressure in the thermo-balance. It is not possible, with the aid of the thermogram to detect a discrete boiling point. This is because at the chosen heating rate of 5°K/min a temperature gradient in the direction of the axis of the test specimen blurs the boiling point and because, furthermore, there exists for each volume element of constant temperature a whole range of boiling points corresponding to the different pore sizes (more particularly corresponding to the capillary forces associated with the different values of pore radii). Furthermore, transport of matter and transport of heat are interlinked

phenomena, so that, also on account of the finite thermal conductivity of concrete, no definite pronounced boiling point can occur in the test (Schneider and Diederichs 1981).

Above 220 °C the curves rise somewhat less steeply. At these temperatures the water is liberated from the finer pores. Furthermore, water held by chemisorptions is also released (breakdown of the gel, first stage of dehydration).

The released amounts of water up to 500 °C are equivalent to about 2–4% by weight (corresponding to about 50–100 L of water per m³ of concrete). At temperatures between 100 and 450 °C decomposition of the CSH phases occurs. In the temperature range from 500 to approximately 700 °C the weight loss again shows a marked increase, this being due to the decomposition of portlandite ($\text{Ca}[\text{OH}]_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$) at between 450 and 550 °C, followed by formation of $\beta\text{-C}_2\text{S}$. Both reactions are accompanied by release of water, approximately amounting to 3% by weight (about 75 L of water per m³ of concrete) (Schneider and Diederichs 1981). In addition to the phenomena discussed above, with some aggregates (e.g., serpentine) there occurs the release of zeolithically bound water or water held by chemisorptions; these dehydration reactions take place in the temperature range from 120 to 600 °C, depending on the bonding strength.

Concretes made with limestone aggregates, show an additional loss of weight at temperatures above 600 °C, this being due to the decarbonation reaction, i.e., the decomposition of calcium carbonate ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), in which 44% by weight of CaCO_3 can be given off as CO_2 . The overall weight loss of the limestone concrete is 34 and 5–6% is attributable to elimination of water (Schneider and Diederichs 1981). In the temperature range from 900 °C up to incipient melting at about 1150–1200 °C no measurable further loss of weight was found to occur. However, in some melts an expansion or bloating of the aggregates (e.g., basalt) can be observed, these phenomena evidently being caused by escaping gases. Another important observation is that, irrespective of the aggregate, in all concretes the matrix of hardened cement paste in any case undergoes conversion into a glassy phase.

For the cases of High Performance Concretes, HPC or Self Compacting Concrete, SCC, the thermograms follow a similar change with temperature, as shown in Fig. 2.12. The transformation of portlandite also occurs at 450 °C although the mass loss diminishes depending on the amount of cement and blend addition employed (e.g. fly ash or silica fume). Other differences are in the type of aggregate. Gabbro and quartzite do not suffer mass loss but limestone aggregates decompose above 750 °C (Alonso et al. 1998, 2005).

A clear difference in the amount of mass loss is detected in SCC due to lime transformation coming from the aggregate but also from the filler. In SCC the loss of weight due to calcium carbonate is about 60% by weight of concrete, because it has limestone aggregate and filler (Alonso et al. 1998, 2005; Alonso and Rodrigues 2009; Hanaa et al. 2010).

The thermograms of Fig. 2.13 compile the thermal transformations for three HPC containing different types of cement; low heat Portland cement [including 9% silica fume (SF) (denoted as Si in the figure)], rapid hardening Portland cement with 25%

Fig. 2.12 Thermograms of HPC for DTA (top)/2.14/and SCC for TG (bottom) (Alonso and Rodrigues 2009)

fly ash (denoted as Lt) and blast furnace slag cement (content over 70%) (Denoted as Tr) (Hanaa et al. 2010):

- The peak caused by dewatering at about 100 °C is clearly broader in the thermogram for Tr-concrete than in the others
- The portlandite peak near 500 °C is much smaller in the thermogram for Si-concrete than in the others

Fig. 2.13 Thermal transformations of HPC. Si: Low heat Portland cement + 9% SF including, Lt: Rapid hardening Portland cement + 25% fly ash, Tr.: Slag Cement (>70%) (Hanaa et al. 2010)

- The peak caused by the transformation of quartz at 573 °C can be seen in all the thermograms
- At about 770 °C a peak caused by decomposition of CaCO_3 and calcium-rich CSH-phases can be seen in all the thermograms, but in that for Si-concrete it is distinctly smaller than in the others
- In the thermogram for Si-concrete an exothermic reaction can be seen at about 850 °C.

The incorporation of microfibres in HPC and SCC introduces alterations in the thermal performance. The size of these changes depends on the type and proportion of fibre employed (Alonso et al. 2005; Alonso and Rodrigues 2009). In addition to those described above for concrete components (cement paste and aggregates) for HPC and SCC the use of fibres results in transformations at high temperatures that change the fire resistance of these types of concretes.

Table 2.2 Thermal transformations in polypropylene and steel fibres

T [°C]	PPF	SF
160–170	Melting of fibre	
200–350	Degradation of fibre	
500		Fibre oxidation

Fig. 2.14 Thermograms (DTA and TG) of PPF (Alonso and Rodrigues 2009)

Table 2.2 shows the transformations occurring in fibres at high temperature for polypropylene (PPF) and steel fibres (SF). The polypropylene fibres melt around 150–200 °C with the aim to create open paths for vapour release. But the degradation of the polypropylene, with mass loss, occurs at higher temperatures above 300 °C, varying with the type of polypropylene, as can be noted in Fig. 2.14 (Kalifa et al. 2001; Alonso et al. 2013). After 500 °C the altered PPF have completely disappeared, while steel fibres do not decompose but oxidise above 500 °C (Alonso et al. 2005; Alonso and Rodrigues 2009).

2.2.5 Microscopy of Microstructure Transformations in Concrete Components

The microstructure of the concrete components altered due to the thermal processes (Alonso et al. 1998, 2005) shows clear changes in microscopy observation. Cement paste and aggregate structure after heating to high temperature can be analysed using

Fig. 2.15 Microstructural changes in HPC after high temperature exposure. **a** Dehydrated portlandite 500 °C in C60 OPC concrete. **b** Alteration of a gabbro aggregate and cement paste in a C70 concrete after 600 °C. **c** Dehydration of cement paste and anhydrous grains C60 after 500 °C and **d** Microcracking in dehydrated cement paste and aggregates in C90 (9%SF) concrete after 500 °C (Alonso et al. 1998, 2005)

scanning electron microscopy (SEM) in fractured samples and using SEM-Back Scattering mode on polished samples, as shown in Fig. 2.15:

- CSH has suffered a full dehydration at 400 °C and the initial high density of cement paste and cohesive structure with anhydrous grains of cement is lost
- The ettringite and portlandite crystals are completely altered after dehydration
- Crack initiation and propagation in concrete can be followed with SEM at high temperature (Alonso et al. 1998, 2005; Diederichs et al. 1989), as shown in Figs. 2.15 and 2.16. It can be observed that the temperature plays an important role in the microcracking of concrete. Cracking initiates at temperatures between 100 and 200 °C and as the temperature increases, the density of microcracks increases (Alonso et al. 1998; Diederichs et al. 1989). The microcrack initiation mechanism at high temperature in concrete is associated to differences in thermal expansion between cement paste and aggregates, or differences in the local material properties and local temperature gradients. At temperatures above 300 °C microcracks crossing the dehydrated CSH, through the interface with aggregates and anhydrous cement grains, become massive. The microcracks grow with the temperature

Fig. 2.16 Surface cracking of the cement paste after elevating the temperature to 100 °C and holding for 60 min in HTEM, 20 μm) (Xi-Shu et al. 2005)

increase, and become macrocracks above 500 °C (Alonso et al. 2005). So that, the growth of microcracks to macrocracks is consequence of two processes: dehydration reactions and thermal stresses. The evidence of the microcracking in the bulk dehydrated cement paste and interface with aggregates has been described above through the analysis of microscopy, although always after cooling (Diederichs et al. 1989). The reason for the microcracking degradation process in concrete is not yet fully understood. Several investigations (Bažant and Kaplan 1996) pointed out that the deterioration of concrete is mainly caused by thermal incompatibilities of the aggregates and the cement paste matrix

- At temperatures above 500 °C aggregates are altered and cracks crossing the aggregates are developed. The bonding of cement paste and aggregate is also altered (Alonso et al. 2005).

The use of fibres in HPC or SCC also alters the microstructure changes at high temperature. In the case of polypropylene, after melting penetration into the surrounding cement paste is noted by some authors (Alonso et al. 1998, 2013; Kalifa et al. 2001) (see Fig. 2.17) but also the nucleation of microcracking initiated in the bed of the PPF (Alonso and Rodrigues 2008; Alonso et al. 2013) has been seen under SEM and backscattering microscopy (see Fig. 2.17 top). These increases in microcracking with PPF were also pointed out by Pistol et al. (2011) with an increase of acoustic events and ultrasonic velocity and observations under SEM and μX-3D-CT microscopy (Fig. 2.18).

The SF act to confine dehydrated cement paste and control cracking developing but above 500 °C oxide formation contributes to the growth of microcracks as observed in Fig. 2.19 (Alonso et al. 1998, 2005).

Fig. 2.17 HPC after 700 °C (Alonso et al. 2005, 2013) (top) and SCC containing polypropylene fibres after 350 °C (bottom). The fibre is visible at initial state but the PP disappears above 200 °C and only the fibre bed is visible (Kalifa et al. 2001)

2.3 Physical Transformations at Microstructural Level

The chemical degradation reactions described during heating of concrete also follow physical changes due to the heat, i.e. the development of microcracks as a consequence of chemical degradation reactions and thermal stresses. The evidence of the microcracking in the bulk dehydrated cement paste and interface with aggregates has been described above through the analysis of microscopy tests, although always after cooling. The reason for the microcracking degradation process in concrete is not yet fully understood.

Several investigations (Bažant and Kaplan 1996) pointed out that the deterioration of concrete is mainly caused by thermal incompatibilities of the aggregates and the cement paste matrix. Analysing the main components of concrete in more detail, it is found that aggregates, like almost all solids, show expansion with increasing temperatures while the hardened cement paste shrinks after exceeding a certain temperature level, as shown in Fig. 2.20 for several cements paste (Diederichs et al.

Fig. 2.18 Microcracking observed in HPC concrete containing PPF after exposure to high temperature events (Pistol et al. 2011)

Fig. 2.19 Steel fibre, right in HPC after 700 °C (Alonso et al. 2005)

1989). Why bulk cement paste does not show a response similar to other solids with respect to volumetric changes under heating conditions has no easy explanation. It should be considered that most of the solid phases of cement paste incorporate water molecules in their structure and during heating dehydration occurs together

Fig. 2.20 Thermal expansion of cement pastes using different types of binder (Diederichs et al. 1989)

with degradation of structure (Alarcon-Ruiz et al. 2005; Castellote et al. 2004; Alonso and Fernandez-Municio 2007). These processes can result in an increase in the porosity, also measured in cement paste and concrete but in a cooling state, particularly for temperatures above 100 °C when the degradation of solid hydrated cement paste compounds (mainly CSH) is extensive.

Changes in the volumetric stability of cement paste compounds have also been demonstrated to occur at high temperature as shown in Fig. 2.21. The d-spacing associated with changes in the size of the unit cell of crystals phases is presented for portlandite and CSH (tobermorite) during heating. The values have been calculated from an NDS test at high temperature (Castellote et al. 2004).

The d-spacing (in Å) of each diffraction peak shows that when temperature increases, an expansion of the unit cell of the respective crystal takes place. The evolution of the d-spacing can be qualitatively linked with the evolution of the volume of the unit cell with temperature. In the case of portlandite, there is an initial increase in the size of the cell, and when a certain precipitation takes place at about

Fig. 2.21 Evolution of the d-spacing (Å) for Portlandite and CSH gel (Castellote et al. 2004)

100 °C, it starts to decrease steadily up to about 300–400 °C. The d-spacing of CSH is also seen to remain steady up to 100 °C before increasing in size indicating that an expansion takes place.

An increase in the size of isolated crystals can be expected with the increase of temperature but some contradiction can be deduced with thermal expansion measurements of the bulk cement paste with heating shown in Castellote et al. (2004) in comparison to others (Bažant and Kaplan 1996).

The above transformations, either due to dehydration processes in cement paste or differences in thermal expansion of concrete components occurring due to heating result also in evolution of porosity, the extent of which depends on the initial pore size distribution and on the type of concrete (Mendes 2010; Alonso et al. 1998; Diederichs et al. 1989, 2009; Kalifa et al. 2001; Tsimbrowska et al. 1997; Ye et al. 2007; Persson 2004). In HPC and SCC, all agree that total porosity (either from water

Fig. 2.22 Distribution of pore diameters in HPM (Tsimbrovska et al. 1997)

Fig. 2.23 Gel pore transformation with temperature in C60 concrete, from NAI (Alonso et al. 1998)

porosity or mercury intrusion porosimetry, MPI) undergoes an increase with temperature, although the pore size evolution will depend on the type and microstructure of concrete particularly for ultra-high strength concretes.

In the study carried out by Tsimbrovska et al. (1997) with high performance mortar, shown in Fig. 2.22, a clear increase in porosity (MIP) with increasing temperature is observed. Initially it is capillary pores most affected by heating, evolving to larger pore sizes. Similar results were found by Alonso et al. (1998) but for HPC, as reflected in Figs. 2.23 and 2.24.

The progressive destruction of gel pores on the order of 3 nm is clearly identifiable in Fig. 2.23 for a C60 concrete. These low pore sizes were determined with Nitrogen Absorption Isotherms (NAI) (Alonso et al. 1998). At 200 °C most of the gel pores have been destroyed probably due to CSH dehydration and there is an increase in the

Fig. 2.24 Mean pore size distribution of C60 and C90 HPC with temperature (Alonso et al. 1998)

formation of small capillary pores (>10 nm). At 400°C the gel pores have completely transformed to sizes larger than 100 nm.

The evolution of larger pore size diameters with temperature can be clearly seen in Fig. 2.24 (top) for HPC. The pore size increases progressively from the lower capillary pores, $0.01\text{ }\mu\text{m}$ (100 nm), of the main peak, to $0.1\text{ }\mu\text{m}$ and larger sizes up to $5\text{ }\mu\text{m}$. This holds mainly for heating above 500°C probably not only due to dehydration of cement paste up to 300°C but also due to the initiation of microcracking. In contrast in C90 concrete the pore size peak moves from around $0.01\text{--}0.1\text{ }\mu\text{m}$. However, while this peak movement is also caused by dehydration processes of cement paste, microporosity seems not to increase to higher micropore sizes. Instead, a new region of larger pore size, $>10\text{--}100\text{ }\mu\text{m}$, appears after 300°C , as shown in Fig. 2.24 (bottom), which can be associated with more severe microcracking, as suggesting by Alonso et al. (1998, 2005), Persson (2004) for HPC and SCC.

In Fig. 2.25 the evolution of pore size distribution is also seen after heating HPC (>90 MPa) (Diederichs et al. 1989). It is known from investigations with aggregates

Fig. 2.25 Differential pore size distribution of heated HPC (Diederichs et al. 1989)

and neat cement paste that the first area beneath the distribution curves represents the capillary porosity of the cement paste whereas the second dotted area shows the porosity of the interfacial zone connecting the bulk cement paste matrix and the aggregates as well as voids due to incomplete compaction and cracks caused by shrinkage of the paste. Temperature rise up to 105 °C does not seem to change porosity of the interfacial zone, although this will depend on the type of concrete and binder. At temperatures above 105 °C, independent of the type of binder, increases in the pore volume and crack widths of the interfacial zone and matrix always occur.

One aspect studied concerning pore size evolution during heating is the case of HPC or SCC incorporating PPF (Alonso and Rodrigues 2009; Alonso et al. 1989; Kalifa et al. 2001; Zeiml et al. 2006; Klingch and Frangi 2011; Huismann 2010).

In the case of some concrete with PPF, depending on the initial pore size distribution and particularly those with very low porosity such as UHPC, the melting of PPF does not represent an increase of capillary pores at temperatures higher than 200 °C, where the fibres and the CSH have been completely transformed, as can be observed in figures presented by Persson (2004), Alonso et al. (2005, 2013).

The capillary pores between 0.01 and 10 μm increase in content and size, as noticed in Figs. 2.26 and 2.27 (Alonso et al. 1998, 2013; Klingsch and Frengi 2011)

Fig. 2.26 Pore size distribution change with temperature of UHPC with PPF (Alonso et al. 2005)

Fig. 2.27 Pore size distribution for a HPC with different amounts of PPF heated to several temperatures (Klingsch and Frengi 2011)

similarly to concrete without PPF. The dehydration evolution of cement paste strongly contributes in this pore region.

Rather, the capillary pores of larger size, $>100\ \mu\text{m}$, are those more affected in PPF concretes, as can also be observed in Figs. 2.26 and 2.27 both with HPC and UHPC. Particularly the increase of pore size above $100\ \mu\text{m}$ is clearly observed in Fig. 2.28 (Huisman 2010). So a double effect can be deduced from PPF after melting; a decrease in very small capillary pores probably due to closing of pores as a consequence of penetration of melted PP [as stated in Kalifa et al. (2001), Alonso et al. (2013)] but also an increase of larger pore sizes due to the generation of microcracks [as suggested by Alonso et al. (1998), Pistol et al. (2011)].

Fig. 2.28 Pore size distribution of concrete with PPF exposed to temperature (Huisman 2010)

2.4 Thermal Changes

2.4.1 Determination of Heat of Reactions

With regard to the prediction, by calculation, of the thermal behaviour of massive concrete members, not only are the quantities of material involved in the decomposition transformations of interest, but of course also the heat effects associated with the individual reactions occurring in the concrete, together with their temperature ranges, the heats of reaction or transformation, and the reacted quantities. These are listed in Table 2.3, for limestone and quartzite concretes made with blastfurnace slag cement. The mix composition of the calcite concrete is indicated in Table 2.4. For calculating the heats of reaction and reacted quantities for the quartzite concrete the mix composition was assumed to be similar to that of the calcite concrete. It was further assumed that both materials under investigation were mass concretes almost 100% saturated with water (Schneider and Diederichs 1981). In the range of evaporation of physically bound water a considerable amount of water will be liberated from the mass concrete.

First, substantial water evaporation occurs out of the larger pores close to the surface of the concrete. Then, from 100 °C onwards, the evaporation will proceed at a faster rate, water being expelled as a result of above-atmospheric vapour pressure (>760 Torr) from the parts near the surface (steam flow). The rate of vapour discharge from the concrete can become quite high if rapid heating-up is applied. Thus, discharge rates of 2.5 L/m² h were measured on a mass concrete specimen weighting

Table 2.3 Transformation and decomposition reactions of concretes made with slag cement and quartzite and limestone aggregates (Schneider and Diederichs 1981)

Temperature [°C]	Transformation or decomposition reaction	Reactions-/Heat Conversion [kJ/kg]	Reactions-/Heat Conversion [MJ/m ³ Concrete]	Implemented quantity [kg/m ³ Concrete]
30–120	Evaporation of physically bound water	Heat of vaportisation of water 2258	290	130 kg Water
30–300	Dehydration 1. Stage	Hydration heat: 250	<20	<78 kg Cement
120–600	Release of chemisorbed water or bound water	Heat of vaporisation of water >2258	>135	60 kg Water
450–550	Decomposition of portlandite $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$	1000	<40	<40 kg CaO
570	Quartz transformation $\alpha \rightarrow \beta \text{ SiO}_2$	5.9	8.8 1.2	1500 kg Quartz 200 kg Quartz
600–700	Decomposition of the CSH-phases; Formation of $\beta\text{-C}_2\text{S}$	Hydration heat: 500	<120	<240 kg Cement
600–900	Only limestone: decarbonation of limestone	Heat of decomposition: 1637	2360	1600 kg Cement CaCO_3 —Share about 90%
1100–1200	Melting of concrete, formation of glassy substances	Heat of fusion: 500–1000	Quartzitic: 1575 Calcite: 1125	2100 kg Concrete 1500 kg Concrete

about 11 mg (rate of temperature rise was approximately 40 °C/h at the hot surface) (Schneider and Kordina 1976).

At 120 °C the expulsion of the water physically bound in the smaller pores, or held by chemisorption, commences; this continues up to about 500 °C, by which point this process is virtually completed. It is known that up to 120 °C about 130 kg of water per m³ can be driven out of saturated concrete.

In the range from 120 to 600 °C the further release will be 50–60 kg of water per m³ of concrete. The heat of transformation can be taken as approximately equal to the heat of evaporation of water (strictly speaking, this is correct only for temperatures below 120 °C, because for the water bound by chemisorption it will additionally be necessary to supply the bond energy for achieving desorption). Thus, per m³ of

Table 2.4 Composition of a limestone concrete (Schneider and Diederichs 1981)

Substance	Granulation (mm)	Content
Cement: HOZ450L		350 kg/m ³
Rhine sand	0–2	275 kg/m ³
Limestone-Crushed stone	0–2	375 kg/m ³
Limestone-Stone	2–5	300 kg/m ³
Limestone-Stone	8–11	545 kg/m ³
Limestone-Stone	16–22	375 kg/m ³
EFA-Filler (RM)		50 kg/m ³
Total water		170 kg/m ³
Additive: BV		4 cm ³ /kg Cement

concrete, the heat of reaction is about 290 MJ for water expulsion up to 120 °C and about 135 MJ for water expulsion in the temperature from 120 to 600 °C.

From 30 to 300 °C, along with the evaporation process, there occurs the dehydration of the hardened cement paste (first stage of dehydration). The maximum rate of dehydration occurs around 180 °C. For calculating the heat of transformation it was presupposed that about 20% (approximately the C₂S proportion in the hardened cement paste) participates in these degradation reactions. The heat of reaction was taken as equal to the heat of hydration of β-C₂S (about 250 kJ/kg) (Zement Taschenbuch 1974). For this first stage of breakdown of the gel about 20 MJ must be supplied per m³ of concrete.

A further process of decomposition of the hardened cement paste takes place between 180 and 400 °C; the decomposition of the CSH phases. For an OPC containing 60% C₃S on average, and since the heat of hydration is about 500 kJ/kg, a heat of reaction of about 120 MJ/m³ of concrete must be assumed.

In the temperature range from 450 to 550 °C in concrete made with Portland cement decomposition of portlandite occurs, i.e. Ca(OH)₂ → CaO + H₂O, with approximately 1000 kJ/kg heat of reaction. The quantity of portlandite which is formed as a result of the hydration of the cement in the concrete is about 40 kg/m³ for a concrete of medium cement content. With cements (containing 15–64% Portland cement clinker and 36–85% of blast furnace slag) Ca(OH)₂ is formed only from the Portland cement ingredient, so that the content of Ca(OH)₂, referred to the amount of CaO formed on decomposition, is clearly below 40 kg/m³. The related heat of reaction of 40 MJ/m³ must be taken to represent merely an upper limit.

At 570 °C the α → β conversion of quartz takes place. This crystal transformation is reversible and endothermic, involving a heat of transformation of 5.9 kJ/kg of SiO₂. On the assumption that about 75% of the quartzite aggregate in the concrete participates in the transformation, the heat of transformation is found to be 8.8 MJ/m³ for quartzite and about 1.2 MJ/m³ for calcite concrete.

A further process of degradation takes place between 600 and 700 °C in quartzitic aggregates the formation of β -C₂S). Around 780 °C the unhydrated blast furnace slag can be expected to undergo recrystallisation. Even if it is assumed that a high content of blast furnace slag (100 kg) has not been hydrated, the exothermic heat of reaction is only 5 MJ/m³.

In the range between 600 and 900 °C the limestone begins to undergo decarbonation ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). The heat of dissociation is dependent on temperature and pressure and is approximately 1637 kJ/kg for limestone at 900 °C and 1 bar (Schiele and Berens 1972). The rate of decomposition and the temperature at which it occurs are not only dependent to a great extent on temperature and pressure, but are also affected by the content of SiO₂, which is always present in limestone. At a partial CO₂ pressure of 760 Torr the decomposition temperature may be anywhere within the range from 850 °C (for pure calcium carbonate limestone) to 560 °C ($\text{CaCO}_3 + \text{SiO}_2$) (Zement Taschenbuch 1974). For calcite concrete the total heat of dissociation can be put at about 2360 MJ/m³, on the assumption that about 90% of the limestone consists of CaCO₃. This gives rise to the formation of about 630 kg of carbon dioxide which occupies a volume of 1400 m³ at 900 °C and 760 Torr.

2.4.2 Ablation, Heat of Melting and Erosion of Concrete

Some constituents of concrete begin to melt from a temperature of about 1150–1200 °C onwards, but little information on the actual process itself and the phases that are formed in connection with melting has been found in the literature. From such observations as have been reported however, it would appear that the liquefaction of the concrete commences with the melting of the matrix of hardened cement paste and that melting of the aggregates takes place only after this (Tze 1978; Hildenbrand et al. 1978; Muir 1977).

A hardened cement paste whose main chemical constituents is lime (63–71%), silica (18–30%), and alumina + iron oxide (5–15%) begins to melt at about 1200 °C. The melting point depends substantially upon the content of Al₂O₃ and of Fe₂O₃. For example, if the iron oxide content is about 7%, the melting temperature may fall below 1200 °C. Similarly, in the reaction of lime (CaO) with silica (SiO₂) and alumina (Al₂O₃) for Al₂O₃ contents from 15 to 35% two eutectic fields with melting points at 1170 and 1265 °C are detected in the ternary system (Muir 1977). Other elements and compounds which are always present in traces in the clinker minerals lower the melting point still further, so that the occurrence of the first melting areas can be expected at about 1100 °C.

The melting points of the aggregates vary greatly (Schneider and Diederichs 1981). With a melting point of 1060 °C basalt is at the lower limit of all types of rock in this respect, whereas quartzite does not melt below about 1700 °C (cristobalite begins to produce a melt at 1713 ± 5 °C). The low-temperature quartz (α -quartz) in this rock spontaneously undergoes conversion into the β -quartz modification at temperatures above 575 °C. At temperatures between 1000 and 1200 °C the β -quartz slowly

changes irreversibly in conjunction with complete breakdown of its structure into α -cristobalite, the cubic SiO_2 modification. Then, between about 1300 and 1470 °C, this substance in turn is transformed, under the influence of the impurities that are present (more particularly: alkalis and alkaline earths), into α -tridymite. At 1470 °C there occurs gradual re-formation of stable α -cristobalite, and from 1700 °C onwards the material undergoes melting.

If small islands of melting areas of dehydrated hardened cement paste are present, however, incipient melting of the quartzite aggregates may occur at lower temperatures by virtue of the composition of the melts in the contact zones. If 1% Al_2O_3 is added, the transition temperature for quartz $\rightarrow$ SiO_2 glass is lowered to 1315 °C. Similarly, the formation of the vitreous phase is accelerated also by CaO , B_2O_3 , P_2O_5 and Na_2CO_3 . Calcite aggregates are decomposed in the temperature range between 600 and 900 °C (see Table 2.3). The CaO that is formed has, in its pure state, the exceedingly high melting point of 2570 °C. If iron oxide and silica (from the fine aggregates, the cement and/or the CaO impurities) are present, the melting point may under certain circumstances be lowered to below 1400 °C as a result of the formation of various calcium silicates or ferrites.

The latent heat to be supplied for the transition of concrete from a “solid” to a “melt” is sometimes called the heat of melting in the literature (Tze 1978; Hildenbrand et al. 1978; Muir 1977). In reality, however, a whole series of reactions take place particularly in the range of temperatures in which the melting is observed, and these reactions are themselves in turn bound up with heats of transformation, which can sometimes be much greater than the actual heat of melting. The thermal process during the melting of concrete has hitherto not been investigated at all from this point of view.

The heat of melting of silicate concrete is 204 kJ/kg, a value which is very close to that for quartz (237 kJ/kg) (Kühl 1958). An effective latent heat, i.e. the sum of all the dehydration and other heats of transformation, including those of melting and solution is in the order of 2560–3600 kJ/kg, (Muir 1977; Perinic et al. 1979). On deducting from this heat balance the entire heat of dehydration [which amounts to 445 kJ/kg (Zement Taschenbuch 1974) and to 263 kJ/kg], the effective heat of melting of concrete would presumably be between 2000 and 3000 kJ/kg. By effective heat of melting is to be understood the total latent heat which is needed for transforming the dehydrated and (with calcite aggregates) decarbonated concrete from the solid to the liquid state at the melting point.

For calcite concrete (Muir 1977; Tze 1978) likewise state the effective latent heat to be between 2560 and 3600 kJ/kg. On deducting the heats of dehydration and decarbonation, this would result in an effective heat of melting of 1300–2300 kJ/kg. The occurrence of an exothermic reaction in connection with the melting of calcite concrete and attributed to the formation of calcium silicates was observed by Hildenbrand et al. (1978). They ascertained the heat of reaction and melting as 1100 kJ/kg. On the basis of considerations of analogy between glass manufacture and cement manufacture (Schneider and Diederichs 1981) have come to the conclusion that the effective heat of melting of concrete, calcite and quartzite, is of the order of 500–1000 kJ/kg for dehydrated and decarbonated concrete.

Table 2.5 Erosion rates of different concretes

Type of concrete	Erosion rate (mm/min)	Test set up	Researches
Basalt	20	Thermite reaction	H. J. Sutherland
Limestone			
Quartzite	40	Thermite reaction	Perinic (1979)
Basalt	22	Metal melting + Arc heating	Hildenbrand and Peehs (1978)
Limestone	35		
Basalt	12	Plasma jet	Muir (1977)
Limestone			
Limestone	66	Immersed in molten steel	Ehm and Schneider (1981)
Quartzite	44		
Quartzite	25	Thermite reaction	

In connection with the accidental situation of a nuclear reactor core melting it is of special interest to know how much energy can be dissipated by the concrete of the containment structure. The heat of ablation is defined as the heat which is dissipated per unit mass of the material during a steady state erosion process resulting in the removal of this unit mass. It is composed of the sensible heat to be provided and of the heats of reaction and transformation. The heat of ablation for concrete is 6 ± 3 MJ/kg according to Muir (1977). For an incoming heat flow of $20\text{--}200\text{ W/cm}^2$ it is independent of the nature of aggregates (basalt, limestone). As reported in Tze (1978) the sensible heat is $1.09\text{ kJ/kg } ^\circ\text{C} \times 1330\text{ }^\circ\text{C} = 1450\text{ kJ/kg}$; correspondingly, for the heat of ablation $1450 + 2560\text{--}3600$, i.e., a range of approximately $4050\text{--}5050\text{ kJ/kg}$. The heats calculated as integral melting enthalpies are 2227 kJ/kg for silicate concrete and 1474 kJ/kg for calcite concrete, these values being at the lower limit (Hildenbrand et al. 1978). Realistic values for the heat of ablation are 3200 and 2400 kJ/kg for calcite and quartzite concretes respectively (Schneider and Diederichs 1981).

In a case where concrete is subjected to the direct action of molten metal, there may, in addition to the phenomena discussed here, occur substantial changes in the melting temperatures and melting enthalpies, because at least some constituents of concrete react very violently with molten metal. The most familiar phenomenon is the decomposition of the water in the concrete. The degradation of a concrete surface by liquid metal attack in this context is generally called erosion. Therefore the erosion rate can also be defined as the rate of penetration of molten metal into a concrete structure. Table 2.5 shows results for a range of temperatures from $1600\text{ }^\circ\text{C}$ (molten steel) to $2600\text{ }^\circ\text{C}$ (metallothermic reaction). There is a wide scatter in the data because of different mixtures of concrete and different test conditions (Ehm and Schneider 1981).

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Author Queries

Chapter 2

Query Refs.	Details Required	Author's response
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AQ2	Kindly note that the closing parenthesis does not have a corresponding opening parenthesis in the caption of 'Fig. 2.16'. Please insert the parenthesis in the appropriate position.	

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