# Behaviour of Concretes Subjected to High Temperature

a) Fire

b) Refractory

*Dr. K. Prabriputaloong**

## Introduction

Structural concretes may be subjected to high temperature by either of the following two ways. The first one is unintentional ie by accidental fire. The second is the refractory concrete where it is designed for such service conditions.

The behaviour of concrete during and after fire is important. During the fire, if the strength of concrete deteriorates drastically, it could result in complete collapse of the structure. The knowledge of the behaviour of concrete after fire is also important in the restoration of the structure being damaged by fire.

For refractory concrete, this property is important because it will always be needed in proper design of any refractory structure.

To understand the behaviour well, it requires some experimental works. However, because of the nature of the subject, it is almost impossible to simulate the exact conditions for every components in a structure. Experimental works so far have been done only for such important elements as beams or columns. The others have to be approximated from the knowledge of the physical and chemical properties of concretes under such conditions.

---

* Lecturer, Faculty of Engineering, Khon Kaen University

In this paper, it is not claimed to cover all aspects of this subject. However the author is trying to discuss the physical, chemical properties of concretes at high temperature as much as possible. The factors that influence these properties will also be covered. Finally the ideal fire resistance concrete will be suggested including those for the refractory structure.

The behaviour of concrete subjected to high temperature may be predicted from its physical and chemical properties. Although in most cases, the physical properties are controlled by the chemicals which constitute the concrete. The most important physical property that should be watched when concrete is used at high temperature is the coefficient of thermal expansion.

Concrete has positive coefficient of thermal expansion. The value depends on the composition and hygral state of the concrete. The influence of the mix proportions arises form the fact that the two main constituents of concrete usually have different values for the above mentioned property and the value for concrete is resultant of the two values. The significance of the difference between the coefficient of aggregates and cement paste lies in the fact that if they differ too much from one another, a large change in temperature may introduce differential movement and a break in the bond between aggregates and the surrounding paste. Concrete with high coefficient of thermal expansion is less resistant to temperature change.

From the above discussion, it is obvious that the undertanding of the behaviour of these components both separately and as a concrete when they are subjected to high temperature is essential. So the properties of various cements and aggregates including the many types of concretes will be examined.

The properties of cement paste will be first looked into. The first cement to look at should be portland cement because it is the most widely used.

The composition of most portland cements should be in the limit given in table 1. The lime does not present itself as CaO but rather in the form of $C_3S$, $C_2S$ and $C_4AF$. When it is mixed with water, the hydration takes place leading to the formation of tobermorite gel and calcium hydroxide. For each mole of $C_3S$, three and one moles of calcium hydroxide will

TABLE 1

Composition of various cements

**Portland cement**

| | | | |
|---|---|---|---|
| CaO | 62....67 % | MgO | 0.5....5 % |
| $SiO_2$ | 18....25 % | Alkali | 0.5.... 1.5 % |
| $Al_2O_3$ | 4....8 % | $SO_3$ | 0.5....2 % |
| $Fe_2O_3$ | 2....5 % | | |

**Slag cement**

| | | | |
|---|---|---|---|
| CaO | 35....45 % | MgO | 2....16 % |
| $SiO_2$ | 28....40 % | MnO | 1....3 % |
| $Al_2O_3$ | 8....18 % | CaS | 2....5 % |

**Commercial aluminous cement**

| | | | |
|---|---|---|---|
| CaO | 32....44 % | FeO,$Fe_2O_3$ | 1....18 % |
| $Al_2O_3$ | 35....50 % | MgO | 0.2....1 % |
| $SiO_2$ | 4....14 % | $TiO_2$ | 1....2 % |

### High Alumina Cement

| | | | |
|---|---|---|---|
| CaO | 17....34 % | $Fe_2O_3$ | 1....18 % |
| $Al_2O_3$ | 62....81 % | MgO | 0....0.6 % |
| $SiO_2$ | 0....1 % | | |

be produced respectively. The amount of water used normally in mixing concrete is more than necessary for chemical reactions and the excess water usually disperses itself in fine capillaries in the mass of the concrete. Certain physical and chemical change when concrete is heated. The uncombined moisture evaporates and disappears at temperature in excess of $100^{0}$C and the dehydration of calcium hydroxide occurs when temperature exceeds 400° C. At higher temperature, it has been found that there is a phase separation taking place. The breaking down of $C_2S$ and the formation of free CaO are some of the reaction products.

The occurrence of CaO denotes a weakness in portland cement, because hydration will take place in a damp environment and as a result cracks may be formed leading to damage to the cement structure. The formation of $Ca\left(OH\right)_2$ from CaO results in a volumetric expansion of about 44%.

When the reactions in the cement died down after the first baking process, the cement structure exhibits quite normal, reversible expansion with temperature of approximately 1% at 100°C. The linear coefficient of thermal expansion is therefore about $100 \times 10^{-7}$ per °C.

The heating of cements to temperature in the middle to high range results in noticeable deterioration of the strength, due to disintegrating reactions and the associated phase-building. This fact is the reason for the critical strength range of refractory concrete, which can extend over a varying region of temperature scale, depending upon the type of cement, the additives and so on, until the point is reached at which a renewed increase in strength caused by ceramic bonding.

## Slag cement

This type of cement is made from finely ground portland cement clinker, quenched blast furnace slag and gypsum or anhydrite stone. The composition of slag cement lies within the limits shown in table 1.

The blast furnace slags which form important constituents of the slag cements are waste products which arise during the manufacturing of pig iron from the cooling of lime based silica smelt and which in a certain condition can be hardened by a hydraulic process. They contain essentially $CaO$, $SiO_2.Al_2O_3$ and $MgO$ but nevertheless are poorer in lime and richer in silicic acid and alumina than portland cement clinker.

The slag cements harden in a manner similar to portland cement; the gain of strength is, however slower. An important fact which influences the behaviour of refractory concrete is that no, or very little, free $Ca(OH)_2$ occurs during hydration. For this reason so called ceramic stabilizers necessary in the case of portland cement, are not necessarily required. The relationship between strength and temperature for slag cements is much the same as that of portland cement.

## Aluminous cements

a) Commercial aluminous cement is an hydraulic binding agent, consisting of compounds of calcium oxide and aluminum oxide together with small quantities of silicon dioxide, iron oxide, titanium oxide, and magnesium oxide. It is obtained by the smelting of limestone or quicklime together with bauxite or other materials having a high alumina content, in an electric furnace, followed finally by grinding of the cooled clinker without any further additives. The chemical composition of well known commercial aluminous cements is found to lie within the limits shown in table 1.

The characteristic hardening process and the phase building which are determining factors in the behaviour of a cement when heated, were a major reason why for a long time aluminous cement was used almost exclusively in refractory concretes.

In contrast to $C_3A$ contained in portland cement, the aluminates of low lime content, particularly CA and $CA_2$, exhibit very valuable characteristics when hardening. The most evident is the high initial strength which distinguishes smelted aluminous cement. Hydration process takes place, not by the separation of lime, but by the formation of $Al(OH)_3$ and lime rich hydroaluminates. The separated $Al(OH)_3$ is amorphous in the first place, then adheres to other particles and subsequently changes into crystalline hydrargillite. The other clinker minerals, such as $C_2S$ and $C_4AF$ hydrate in the well known manner. Hardening takes place accompanied by the evolution of large amount of heat, due to the high heat of hydration of the aluminate and the concentration of the released heat as the result of rapid hydration. Hardening is considerably influenced by temerture; lower temperatures are advantageous, while above 25°C the strength deteriorates appreciably.

Aluminous cement, like all other set cements, loses its adsorbed and chemically combined water upon being heated. The complex endothermic effect between room temperature and about 300°C denotes the loss of adsorbed water and the dehydration of calcium aluminate hydrate and aluminum hydroxide or aluminum oxide hydrate. (This result is obtained from differential thermal analysis study by Zschornewitz). The dehydration reactions of hydroaluminate should be completed by 400°–500°C at the highest. Since it is evident that the rejection of water takes place gradually, the term zeolitically combined water is sometime used in this connection.

With regard to phase building under the effect of temperature, it has been found that $\gamma$ -alumina can occur temporalily above 500°C, and $CA_2$ above about 1000°C. It has also been shown that in cements which have a low iron content, at a temperature of about 900°C, CA. $C_2AS$, $CaTiO_3$, $C_{12}A_7$ and $Fe_3O_4$ are produced; these phases with the exception of $C_{12}A_7$, are retained even at 1400°C. In the iron rich cements, at 900°C,CA $C_{12}A_7$, $C_2AS$, $C_2F$ and $CaTiO_3$ are formed; in this case also $C_{12}A_7$ disappears finally at 1300°C.

Irreversible shrinkage takes place in parallel with the reaction of dehydration. The character of the shrinkage is very similar for the separate aluminate and for their hydrated phases. The maximum shrinkage usually occurs at about 800°C. However it has been also observed that there is also a second shrinkage at higher temperature (1100°C). This was explained as being due to ceramic sintering. The cement with low iron content has lower overall shrinkage which must be considered as a great advantage for use in refractory concrete (1 2 %)

Subsequent reheating of aluminous cement causes the normal reversible thermal expansion. The average value of the coefficient of expansion up to 900°C. is $60-80 \times 10^{-7}$ per °C. Above 1000 °C. the stage of irreversible shrinkage as a result of sintering has been reached.

The loss of strength in actual aluminous cements extends over a wide range of temperature, usually between 100° and 1000°C, but the minimum value of strength is usually found at about 900°C. The critical temperature can be higher or lower, however, depending upon the nature of the cement; the amount of loss of strength may also vary considerably, from 40–80 %.

## b) High alumina cements

High alumina cements are those with $Al_2O_3$ content greater than 60%. It has a very good fire resistant characteristics and is therefore used for special refractory concrete. The chemical composition of these cements is shown in table 1.

The hardening process in aluminous cements with high alumina content is similar in principle to that of normal commercial smelted aluminous cements. It is therefore to be expected that the cement structure will show similar chemical effects and processes when subjected to heat.

The shrinkage behaviour when the cement is heated is dependent upon the chemical composition. The smallest shrinkage values (0.3–0.5% between 100°–800°C) are found with an $Al_2O_3$ content of 70%. High alumina cement with alumina content of 81% was found to exhibit a noticeable irreversible expansion of about 2% from about 1000°C which was said to be caused by the formation of $CA_2$. In this case of course, the total resultant effect is a net expansion, not shrinkage of about 0.5%.

The strength of high alumina cements does not decrease appreciably upon heating, however many of its other properties are very much the same as those of normal aluminous cements.

## Aggregates

This is a component which may have the most influence on the behaviour of concrete. Aggregates constitute up to 70% of the bulk of concrete and its behaviour under high temperature will certainly have much effect on the properties of concrete. Aggregates can be obtained either from naturally occurring or by manufacturing. Concrete for normal usage is usually made from natural aggregates because of its convenience and low cost. The chemical composition of naturally occurring aggregates tends to vary from source to source. The general aggregates, however, will be of the following types.

### a) Heavy aggregate

This type includes sands, gravels and crushed rock aggregates. Sands normally compose of quartz, small amount of feldspar and some other impurities. Gravels contain flint, chert (silica), quartz and quartzite. Crushed rock will be mainly granite, dolerite, basalt, sandstone and limestone.

### a) Light weight aggregate

Pumice is one of the naturally occurring aggregates. Most of other light weight aggregates are either manufactured or parts of an industrial wastes. The most important one would be the slag from blast furnaces. Expanded shale, broken bricks are also classified as being this type of aggregates.

Besides these, there are aggregates which are used specially for high temperature service concretes. An example of these is the high alumina aggregate.

The properties of these aggregates will vary depending upon its chemical composition and impurities content. For high temperature use, the purity of the aggregate could be critical or the inclusion of some metal oxide ie iron oxide has to be avoided. This is because this oxide is a flux material and it will weaken the concrete when it is subjected to high temperature.

## Discussion

Causes of failure of concrete subjected to high temperature

1) Difference in coefficient of thermal expansion

If the coefficent of thermal expansion of cement paste and aggregate are very much different, it could lead to differential movement between cement paste and aggregate when the concrete is heated. This could result in the breakage of the bond between the two components and hence the reduction in the strength of the concrete.

2) Phase change

This phase change could be either of cement paste or aggregate or both. In cement paste, the dehydration of $Ca(OH)_2$ usually results in the reduction in volume of concrete. This problem can be serious only for aggregates with high siliceous content. For example, the transformation of $\alpha$ quartz to beta quartz and beta quartz to tridymite, the volume change accompanying these processes is as high as 14%.

3) Chemical reaction

Chemical reactions between components of cement paste and aggregate can lead to either better or worse quality concrete. If the reaction occurs at the interfaces, it may strengthen the bond between aggregates and paste and hence increase the overall strength. On the other hand if the reaction leads to a severe contraction or expansion of the concrete volume, it could become a serious problem.

So far only the effect of aggregates and cement paste has been discussed. The concrete properties can be affected by other factors as well. The water/cement ratio, the aggregate grading, the homogeneity of the aggregate, the way in which it is subjected to heat, and the rate of heating and cooling are just some of the factors that could affect the property of concrete at high temperature.

Among these, the water/cement ratio seems to have the least effect whereas the effect of heating and cooling rate is quite important. From Maholtra's work (4), the effect of water/cement ratio was found to be very slight but quenched concrete had lower strength than the same concrete that was cooled slowly. This effect can be explained in the following way. The fast cooling concrete, the contraction at the outside core is much faster than the inner one, so it tends to develop stresses and eventually cracks. These cracks weaken the concrete and this is more so for flexural strength. The compressive strength is not affected as much because the applying loads tend to close some of these cracks. So the service conditions of concrete determine much of its properties.

The range of temperature to which concrete is subjected is also important. Normally the concrete will decrease in strength drastically say between $200^{o}-800^{o}$C, and in this range the strength of concrete could be as low as 20% of its original strength. However as temperature increases the concrete could regain some strength because of ceramic bonding.

The effect of aggregates on the behaviour of concretes has been studied by Zoldners (5) Zoldners et al (6). For normal portland cement concrete prepared with commercial aggregates, it was found to deteriorate on exposure to dry heat at elevated temperatures. The extent of the deterioration is dependent, to a large degree, on the type of the aggregate. Concretes made with gravel, consisting predominantly of crystalline igneous and metamorphic rocks, deteriorated more rapidly than limestone concrete. After 400°C exposure, the residual flexural strength of gravel concrete was only 26% and the compressive strength only 85% of its original strength.

Sandstone concrete showed a significant compressive strength in the lower temperature ranges. It was explained that heating stimulated the hydration process in the concrete with water available in the room dried test specimens.

However after 500°C exposure, it lost strength very rapidly. This was because of the transformation of alpha to beta quartz at 573°C causes a volume expansion of about 2.4%. An even more detrimental expansion of sandstone concrete may be expected at 800°C, when quartz inverts to tridymite with an accompanying volume change of 14% Limestone performed best after being exposed to temperature up to 700°C.

Expanded slag concrete was strong in compression, retaining 71% of its original strength after exposure at 600°C, but it retained only 16% of its flexural strength after exposure to 400°C. This was because of its higher drying shrinkage which is maximum at 300°C.

Aluminous cement concrete is similarly affected by the type of aggregate (6). Concrete made with expanded shale, anathosite, ilmenite, or phonolite aggregate lost more than 50% of their strength after exposure to 400°C. At temperature between 400° and 1000°C the loss in strength continues but at relatively lower rate.

Expanded shale concrete showed the greatest stability whereas phonolite concrete was the least heat resistant of the four types investigated. The reduction of strength of concrete made with phonolite, anorthosite, and ilmenite aggregates at temperature as low as 200°C was explained as owing to deterioration of cement-aggregate bonds. However the concrete will recover the strength as it is being heated above 1000°C. because of the formation of ceramic bonding.

The reduction in the residual compressive and flexural strengths of aluminous cement concretes at lower ranges of elevated temperatures is related primarily to change in the principal compound composition of the cement, although the type of aggregate also affects the strength of fired concrete greatly. The major decrease in strangths of cement between 110° and 300° to 500°C could be due to the dehydration of its principal compounds $C_3AH_6$, $AH_3$ and $CAH_{10}$ and the formation of their dehydration products. Above 700°C the loss in strength was possibly due to grain growth and the formation of the new compounds. The other possible reason for the loss in strength of aluminous cement concrete is the crystalization of $AH_3$ from alumina gel.

So as can be seen from this discussion, the behaviour of concrete subjected to high temperature is quite complicated. It is complicated because there are so many types of cement and aggregate that can be used. The variation of service conditions is also a main factor contributing to the complication of the design of concrete. So appropriate selection of cement and aggregate for the right type of work is very important.

As a general guide, concrete that will be subjected to high temperature not exceeding 400°C can be made from almost any type of cement and aggregate. In this case, economic factor may be more important. For medium high temperature, say up to 700°C, the high siliceous aggregate is probably not suitable because of the possible expansion accompanying phase change of silica. The service condition which includes steam or high humidity will not be suitable for the calcareous type of aggregate because of the spalling effect which is caused by the hydration of CaO.

For service at very high temperature, the use of high alumina cement is recommended. The aggregate should be of the calcareous type where the reactions leading to the formation of calcium aluminate and ceramic bonding are possible. This would increase both the strength and the stability of the concrete. Above 2200°C, the use of pure alumina and calcium carbonate was found to be satisfactory. (3)

## Conclusion

Concrete made from portland cement is not a good fire-resistant material because of the dehydration of $Ca(OH)_2$ to form CaO on heating and the rehydration of CaO upon cooling. Both processes cause volume change in concrete which could lead to the destruction of the structure. The problem is very serious especially with the latter process because the increase in volume is as high as 40%.

To improve the quality of portland cement concrete, cement with low lime content should be used. In other work cement with high $C_2S$ and low $C_3S$ should give better fire-resistant quality. $C_2S$ forms only one mole of $Ca(OH)_2$ on hydration comparing to 3 moles by $C_3S$. This is probably a reason leading to the use of slag cement for high temperature concrete. Another possility is to use high siliceous aggregates. In this the reaction between aggregates and cement paste will help to improve the quality of concrete. The main reaction is the one between free lime and silica to form calcium silicate. This will help to reduce the volume change by rehydration of CaO. This solution is, however, not easy because excess silica also has adverse effect on the property of concrete.

The third solution is to use cement which does not give $Ca(OH)_2$ as a hydration product. This leads to the use of aluminous and high aluminous cements. The use of this type of cement coupled with appropriate selection of aggregates leads to the discovery of excellent fire resistant quality concrete. The formation of ceramic bond when it is heated to high temperature is a very desirable quality bacause of the formation of stable bonds and compounds that do not change on cooling.

The cost of high alumina concrete is, however, much higher. This limits its use to only special refractory structures. So for general constructions ie buildings or bridges etc the ordinary portland cement is still used. The strength of concrete measured at high temperature is usually higher than the same concrete being cooled down to room temperature. (4)

## References

1) H. Woods, Durability of Concrete Construction, ACI monograph no 4

2) A.H. Meville, Hardened Concrete Physical and Mechanical Aspects, ACI monograph no. 6.

3) P.H. Harris, the Engineering Journal, March 1956, 219-222.

4) Malhotra, V.M., Mag. of Concrete Research, S (23) 85-94, August 1956.

5) N.G. Zoldners, Proc. ASTM Phila., 63 (1963).

6) Zoldners N.G., Malhotra V.H., and Wilson A.S., Proceedings, ASTM, Philadelphia, V. 63, pp 966-992, 1963.

7) Power T.C., The Properties of Fresh Concrete, John Wiley, New York, 1968.

8) W.H. Gitzen, D.D. Hart, and G. McZura,J. Amer. Ceram. Soc., 40 (5), 158-167, May 1957.

9) Livovich A.F., Amer. Ceram. Soc. Bull., 40 (9), Sept 1961.

10) G.E. Troxell, H.E. Davis, and J.W. Kelly, Composition and Properties of Concretes, McGraw Hill (1968).

11) A. Petzold and M. Rohrs, Concrete for High Temperatures Elsevier Publishing Co., 1970.

12) F.M. Lea and C.H. Desch, The Chemistry of Cement and Concrete, Edwork Arnold & Co, London, 1935.