

Minimising Degradation of Concrete Structures through Cement Specifications

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Abstract

This paper examines the effectiveness of cements standards in promoting qualities that will mitigate deleterious effects in concrete. This objective is achieved through an examination of the potential harmful effects of some properties of cement and a determination of the adequacy of the standard in minimising harmful effects of these properties through limitation of the constituents in the cement. The scope of the discourse is limited to the chemical properties of ordinary Portland cement (OPC) and blended cements. Comparisons of the provisions for the chemical composition of these cements were made with the British standard (BS EN 197) and the American standards (ASTM C150 and C595). In some instances, comparison of the specification on OPC was also made with the Australian standard (AS 3972) in some instances.

Keywords: Concrete structures; Cement specifications; Durability; Chemical reactions

1. Introduction

The manufacturing of cement requires a careful balance of the proportion of the various ingredients to ensure that the material is not only produced with the highest level of economy and efficiency but that the finished product can attain the properties that are essential for assuring the materialization and sustainability of any resulting concrete elements.

It is said that concrete is a forgiving material, giving better performance than that which is anticipated, but the importance of the role of cement cannot be taken for granted. An incidence in the construction industry of a country less than a decade ago draws attention to this awareness [1]. For a period of approximately one year several medium and same scale projects constructed of reinforced concrete were abated mainly because there was significant delay in the development of strength in the concrete but there were other

associated that also impaired the quality of the concrete.

While there has always been fluctuation in the relative proportions of home-made and imported cement that supplied the local market, the industry was predominantly supplied with the former. In order to prevent the recurrence of such problem, the country's local regulatory body intervened and revised the cement standard and was resolute to monitor the quality of all types of cement used in the industry. This aberration in the performance of the cementitious material brings to light the contribution of the cement to the attainment of the essential properties in concrete.

The cementitious fraction plays a very important role in the performance of concrete, contributing not only to the mechanical properties but also having significant impact on the durability characteristics of the concrete. Ordinary Portland cement is made essentially from calcareous and argillaceous materials that supply oxides of calcium, silicon, aluminium, and iron. Usually limestone and clay are the respective sources for the calcareous and argillaceous materials. The production of cement involves alternately crushing, proportioning, mixing and eventually calcining the materials at about 1450°C in a kiln. The resulting clinker is then mixed with 5%, more or less, of calcium sulphate before grinding takes place. At the end of the process, hydraulic cement with Blaine fineness higher than 300 kg/m² and with approximately 95% of the particles being smaller than 45µm is produced. Fundamentally, this is the cementitious material that is used for most buildings and infrastructural developments worldwide. Concrete, and hence cement therefore has to perform many functions, one being to satisfy requirements relating to durability. The limits that are placed on the chemical properties of ordinary Portland cement should help to prevent or minimise

the degradation processes that are often associated with concrete.

Cement may display a certain degree of homogeneity but it is composed of four major compounds, namely tricalcium silicate C_3S , dicalcium silicate C_2S , tricalcium aluminate C_3A tetracalcium aluminoferrite C_4AF with several minor components, which depending on their relative proportion, can significantly influence the chemical reactivity, the rate of heat evolution, and the resistance to injurious substances [2].

This paper reviews the effect of the chemical constituents of ordinary Portland cement and their specified limits individually on harmful chemical process such as corrosion, sulphate attack and alkali-silica reaction in order to determine their effectiveness in abating deterioration factors.

2. Chlorides

Concrete per se is not susceptible to attack from chlorides but the steel which is embedded in reinforced concrete can corrode when exposed to chloride ions and consequently the concrete will suffer damage. Steel encased in concrete is protected from corrosion because of the high pH in the micro environment. The thin but dense passivity layer of iron oxide formed around the steel during hydration of the concrete also serves to insulate the steel from chloride attack. However chloride ions can break down the iron-oxide barrier despite the presence of the high alkalinity and initiate corrosion in the proximity of water and oxygen [3]. Corrosion is an electrochemical process. When an electrical potential difference exists cathodic and anodic sites are formed on the steel member. The pore water in the concrete which connects these sites now performs the function of an electrolyte [4]. At the anodic site electrons are liberated and ferrous ions are formed. The electrons travel through the metal to the cathodic site where they react with water and oxygen to produce hydroxyl ions. The latter then migrate through the electrolyte to combine with the ferrous ions to form ferric hydroxide. The reaction continues and the final product that is formed is rust. Figure. 1 summarises the schematics of steel in concrete undergoing electrochemical corrosion in

the presence of chlorides as proposed by Angst [5].

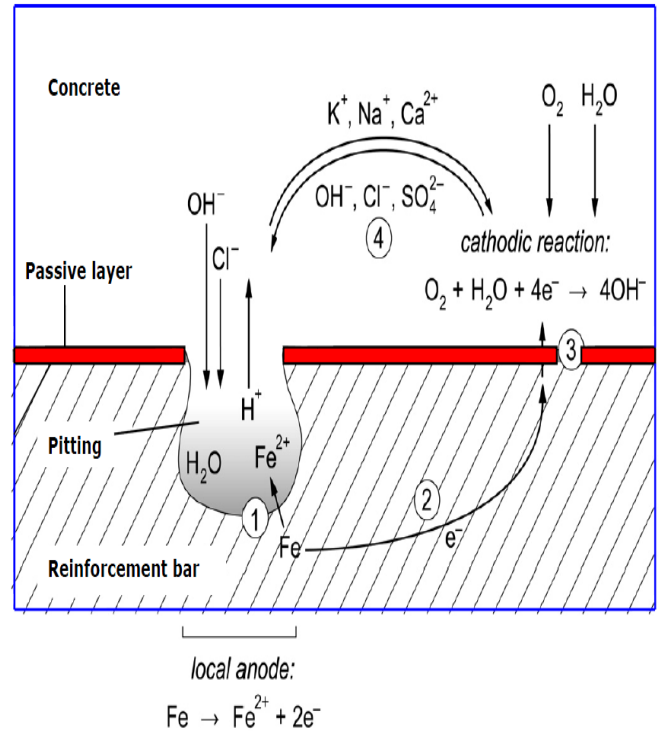
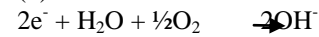


Figure.1 Representation of steel in concrete undergoing electrochemical corrosion in the presence of chlorides (Adapted and modified from [5])



(Reaction at the anode)

(1)



(Reaction at the cathode)

(2)

The concomitant deterioration of concrete occurs as a result of the increase in the volume of the corroded metal. The volumetric increase in the corroded metal is several times higher than the original material [6] and this creates tensile stresses in the concrete surrounding the corroding reinforcing bar and can lead to cracking and spalling, as schematically illustrated in Figure.2 [7].

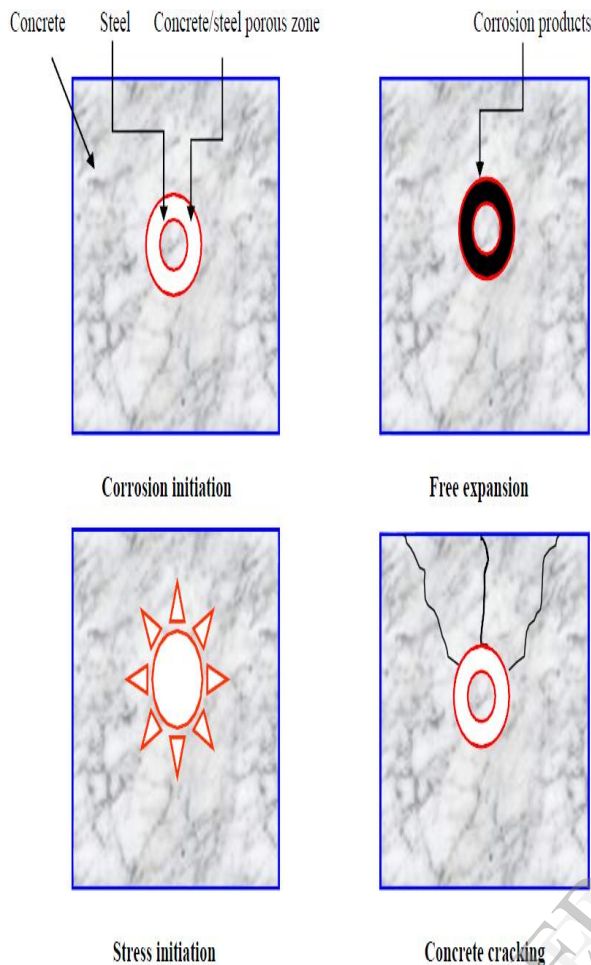


Figure.2 Schematic illustrations of damaged concrete resulting from steel corrosion (Adapted and modified from [7])

Corrosion is the result of contamination of concrete by internal and external chlorides. One source of internal chloride is the cement. The entry of chlorides into ordinary Portland cement is through the raw materials, mainly clay from marine environments [8]. In the case of cement made with ground granulated blast furnace slag (CEM II and CEM III blends) the chloride may also enter the cement clinker through seawater if it is used for quenching the slag [3]. Another entry point for domestic chloride is through the fuel that is used in the kiln for burning the raw mix. As combustion takes place, the chlorides volatilise and later condense. Some of these chloride ions become intimately mixed in the clinker [8].

Portland cement normally contains very low amounts of chloride, typically less of 0.05 as shown by technical report from Lafarge [9]. The total chlorides in concrete can be broken down into free and bound chlorides [10]. Bound chlorides are adsorbed or chemically bond to the hydrating products. With adsorption, the chloride ions are physically bond to the walls of the C-S-H. In chemical binding, the chloride reacts with C_3A to form Friedel's salt but it is further mentioned by Yuan et al. [11] that C_4F , C_2S and C_3S can also

contribute to the binding of chloride ions. As the binding of the ions usually takes place early in the hydration process of the cement, the binding is mostly confined to internal chlorides, that is chlorides that resides in the ingredients of the concrete at the time of mixing. With regards to physically and chemically bound chlorides, it was generally believed that only the residue, referred to as the free chloride, contributes to corrosion in reinforced concrete [10-11] but the bound chloride can become free and move towards the reinforcing bar [11]. Justness [12] summarised research works on the release of bound chlorides and showed that, in the presence of sulphates, bound chlorides are released, increasing the Cl^- concentration in the pore solution. The explanation provided is that there is a greater affinity for C_3A and SO_3^- bonding than for C_3A and Cl^- bonding. Another phenomenon that is responsible for the liberation for the bound chlorides is carbonation. It is postulated that as the reduction in pH that accompanies carbonation is proliferated, the binding capacity of the cement paste is reduced. Nowadays, internationally recognised standard specifications have placed a ceiling on the levels of domestic chlorides.

Several studies have been conducted to determine the threshold level of chloride concentration for the depassivation of steel but there is no general agreement on the value, particularly because there are several factors that influence the threshold level. The threshold value is expressed as a concentration ratio Cl^-/OH^- . Work carried out by Alonso and co-workers [13] showed that threshold for the initiation of corrosion of steel in mortar under different conditions, ranged from 1.17 – 3.98% and the total chloride contents ranged from 1.24 – 3.08% by weight of cement. Table 1 shows the percentages of reinforced concrete highway bridges with corrosion related cracking by chloride content.

Table 1: Relationship between chloride content and incidence of corrosion-induced cracking in UK Reinforced Concrete Highway Bridge (Adapted from [4])

Chloride range (% by mass cement)	Proportion showing corrosion (%)
<0.2	2.0
0.2-0.4	22.5
0.4-1.0	32.4
1.0-1.5	64.4
>1.5	75.9

AS 3972 [14] stipulates a maximum chloride content of 0.1% by mass of cement for this type of Portland. From all indications this value falls below the perceived threshold levels that will initiate corrosion and therefore chloride-induced corrosion by this domestic source should be inhibited in concrete if the cement used complies with the Australian standard. When the Australian standard is compared to BS EN 197-1 [15], the specified limit on chloride content for ordinary Portland cement (CEM 1) is identical to that for the AS GP cement –AS 3972 [14] and like the Australian, the British have made provision of a lower chloride limit on cements that will be used for pre-stressed works. In fact the BS EN standard for CEM 1 - V cements have a maximum permissible limit of 0.1%. There is no specified limit on chlorides in ASTM C150-07 [16] but ACI 201.2R [17] for example gives guidance for the prevention of metal corrosion in concrete. To get a better perspective of the limits that are placed on chlorides in concrete, other standards should be examined. BS EN 206-1 [18] gives maximum acceptable chloride limits on concrete for various uses. The range is from 0.1% to 0.4% based on the mass of cement as shown in Table 2.

Table 2: Maximum chloride content for concrete (Adapted from [18])

Concrete Use	Chloride Content Class	Max. Cl ⁻ Content (by mass of cement) %
Without any form of metal with the exception of corrosion-resisting lifting devices	Cl 1.0	1.0
Containing steel reinforcement or other embedded metal	Cl 0.2	0.20
	Cl 0.4	0.40
Containing pre-stressing steel reinforcement	Cl 0.1	0.10
	Cl 0.2	0.20

Reinforced concrete can be protected from chloride attack from external sources by ensuring that there is adequate concrete cover, using a low water/cement ratio, incorporating adequate proportion of cement [19-20], and using mineral admixtures such as fly ash [21], silica fume and granulated ground blast furnace slag. It is believed that the mineral admixture reduces the size and the

connectivity of the pores in the concrete and hence minimises penetrability. However, if the internal chloride load is high, the effectiveness of these measures is reduced. Therefore, from the researches, it can be seen that if the maximum permissible domestic chloride from cement does not exceed 0.1%, the risk of chloride-induced corrosion from Cl⁻ ions in cement is negligible for the normal reinforced concrete.

3. Sulphates

As before mentioned, the manufacture of cement requires the use of materials from an argillaceous source such as clay or shale and from a calcareous source such as limestone, just to name a few. Some of these materials, depending on the source, introduce sulphates into the cement. Taylor [22] shows that there are alkali sulphates in the form of arcanite (K₂SO₄), aphythalite (3K₂SO₄·NaSO₄) and thenardite (Na₂SO₄) in the clinker. Calcium langbeinite (K₂SO₄·2CaSO₄) and anhydrite (CaSO₄) are other examples of sulphate-containing compounds that can be found in cement clinker. The materials used for the combustion in the kiln can contribute to the sulphate load in the clinker. Traditionally, fossil fuel such as coal is used for the processing of the raw meal. Approximately 220 kg of coal is needed to produce 1 ton of cement [3]. With a worldwide thrust to reduce the dependence on fossil fuel, alternative fuel such as substandard oils, alcohols, solvents, tar mud and tires inter alia are now partially replaces the traditional fuels [23] Although these materials have to meet certain criteria, their use may contribute to higher levels of sulphur in the clinker in the combustion stage [24].

Another source of sulphate in cement is calcium sulphate, often in the form of gypsum, which is deliberately introduced in end-stage clinker as a retarder. Tricalcium aluminate, one of the main phases of the cement, generates large amount of heat in the setting period [25]. The setting time of the cement is reduced as C₃A rapidly reacts in water [26]. Calcium sulphate is therefore introduced in the clinker to control the rate of the reaction and hence regulate the setting time. At the same time reduced shrinkage and enhanced strength development is imparted from gypsum addition [25]. The quantity of gypsum used usually ranges from 3% to 6% of the mass of cement and the addition is made to the clinker at the cooling and pulverization stage.

Sulphates in cement however, increase the vulnerability of concrete to internal sulphate attack. When water is intimately mixed with cement, the reaction of C₃A commences and a simultaneous reaction is triggered with the sulphates; the alkali sulphates being very soluble react immediately followed by the slower reacting calcium sulphates [10]. The dissolution of the C₃A is subsequently retarded by increased concentration of the soluble

K^+ and Na^+ [27] in the presence of the sulphate and hydroxyl ions [10,27]. During this early stage of hydration, the aluminate phases react to produce ettringite, often referred to as primary ettringite (see Figure.3 [28]) and formulated as seen in Equation 3. If the sulphates are within tolerable levels, this reaction is short lived and as the reaction of the aluminates continues, the existing ettringite is transformed to monosulphate (Equation 4). In early ettringite formation (EEF), any resulting stress from growth of crystals can be accommodated in the plastic concrete and hence the concrete suffers no noticeable damage [24]. Further, as the characteristic needle-shaped crystals proliferate in the aqueous solution, they contribute to the development of strength in the concrete [27]. Therefore, there is usually no adverse effect stemming from EEF.

Conversely, the delay in the development of ettringite can have severe consequences. When concrete is cured at temperature above $70^\circ C$, ettringite formation is 'thermally decomposed' but subsequently appears when the temperature is lowered [24]. This may occur in steam curing or in concrete with a high heat of evolution. In this case, the hardened concrete may not be able to contain the concomitant expansion resulting from delayed ettringite formation (DEF) and hence the dimensional stability of the hardened concrete is altered [24]. The manifestations are, spalling, expansion, reduction in strength and significant physical deterioration of concrete as shown in Figure.4 [4, 29]. To reduce the probability of internal sulphate attack, limits are placed on the sulphates in the cements. It is said that the sulphates supplied by fuel is chemically bound in the clinker [3] but it is shown by Horkoss et al. [23] that some of the sulphates from fuel can adversely affect the resistance of cement to internal sulphate attack. Therefore sulphates from all internal sources will have to be considered in order to control the total level of internal sulphate.

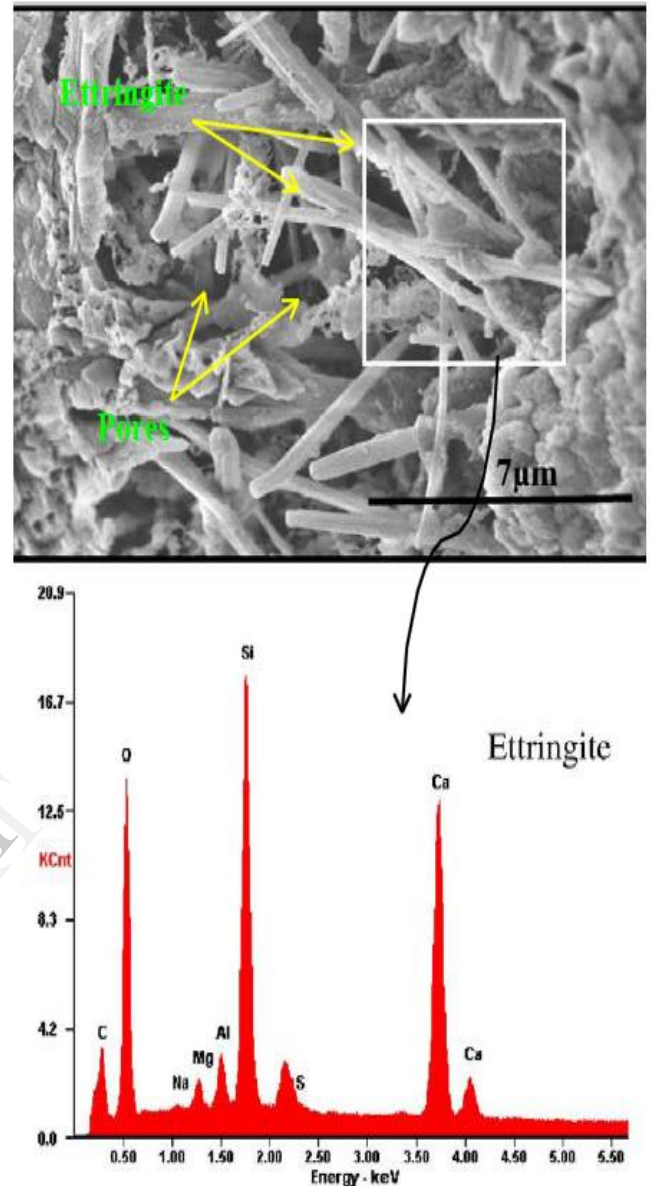
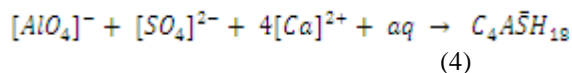
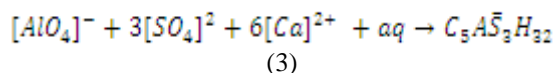


Figure.3 Scanning electron microscopy micrograph of ettringite (Adapted and modified from [28])

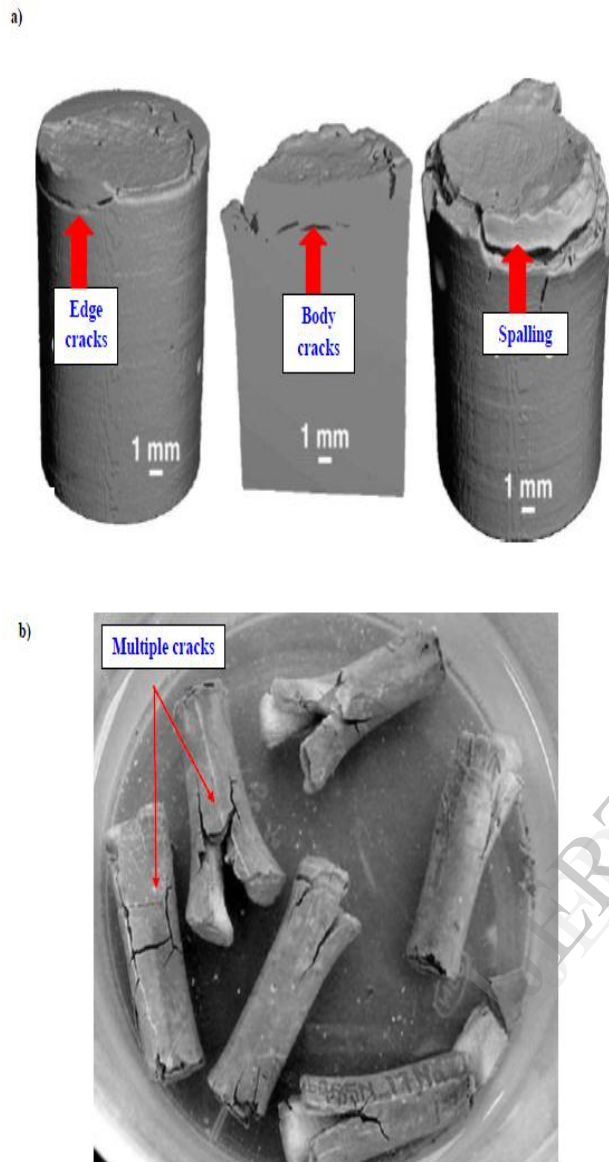


Figure.4 Cement paste samples exposed to sulphate concentrations showing a) 3D reconstructions of the specimens and b) multiple cracks and some spalling (Adapted and modified from [30])

Two ways of expressing the amount of sulphates in cement are by using SO_3 and SO_4 contents. When limits are quoted as SO_4 , their equivalence in SO_3 can be determined by dividing SO_4 values by 1.2 [3]. As shown in Table 3, all three standard specifications for Portland cement that are used in this paper express the limits for sulphates as sulphur trioxide. The Australian standard AS 3972 [14] prescribes a maximum sulphate content of 3.0% by mass of cement if C_3A content is less than or equal to 8.0% and a maximum of 3.5% if the C_3A content is higher than 8%.

Table 3: Specification limits: Sulphate in Portland cement

	AS 3972:2010 [14] Ordinary Portland Cement	BS EN 197- 1:2000 [15] CEM I	ASTM C150-07 [16] Type 1
Sulphate Content (as SO_3) %	≤ 3.0 (≤ 3.5)	3.5	≤ 3.0 (≤ 3.5)

*Values in the brackets are the values of SO_3 when C_3A is greater than 8%

*All requirements are expressed as percentage by mass of cement

For the ordinary Portland cement (CEM I) and the composite (CEM II) with strength classes 32.5 (both rapid and normal hardening) and 42.5 (normal hardening), the British standard has stipulated that the sulphate content should not exceed 3.5%. The AS 3972 [14] also stipulates a maximum sulphate content of 3.5% for the GP cement. However, the British has at least a 0.5% higher limit on all other types of CEM II cements. The explanation is that the lower permeability that is reported to have been obtained in high strength concrete made with cement of high strength class (CEM1-II 52.5) helps to mitigate deterioration due to sulphate attack. Similarly, mineral admixtures such as fly ash, silica fume and GGBS are purported to help in producing pore refinement in concrete [31] and therefore concrete produced with these admixtures are expected to exhibit a lower level of penetrability. The rationale is that, if the use of mineral admixtures and high strength class cements make the concrete less susceptible to sulphate attack, then the maximum permissible limit for sulphates in cement made from these materials can be increased. The ASTM C150 [16] specifies a maximum sulphate content of 3.5% for Type 1 cement when the C_3A content is greater than 8.0% but further mandates that at lower C_3A levels, the SO_3 should not be greater than 3.0%. It should be stated that the alkali content of the cement has an impact on the gypsum content but the CaSO_4 requirement is largely predicated on the levels of C_3A [3]. Therefore, the importance of the introduction of the two sets of limits by ASTM is to prevent 'quick' and 'false' sets, phenomenon that are brought about when the available SO_3 is lower and higher respectively than the levels of reactive aluminates in the C_3A [27]. For blended cements, the American standard, ASTM C595 [32], also has a limit of 3% for some types of blended cements and 4% for other types.

A point to note is that C_3A is important in the manufacturing process of cement as it is one of the components that act as a flux [30] and hence facilitates the burning of clinker at a lower temperature. High levels, however, increase the energy needed to pulverize the clinker [3]. Tricalcium aluminate also helps to bind chloride ions and hence is believed to increase the resistance of reinforced concrete to chloride attack [33], but there are other ways of reducing the concrete's susceptibility to corrosion. Besides, the contribution of C_3A to the strength of concrete is marginal and it increases the concrete's susceptibility to sulphate attack [33]. From the authors' observations from technical reports and research works, in many instances the C_3A content of Portland ranges from 6 to just over 9% [34].

4. Alkalis

Cement mixtures are highly alkaline having pH ranging from 12.7 – 13.9 [3]. When cement is mixed with water, the ensuing chemical reaction produces $Ca(OH)_2$ which promotes alkalinity. The other sources of alkali in cement are potassium and sodium, usually expressed in oxides as K_2O and Na_2O respectively. These latter two are known as the alkalis in cement nomenclature [3]. A sodium oxide equivalent form $(Na_2O)_e$ is often used when referring to the alkalis of these compounds; $(Na_2O)_e = 0.658 \times (\%K_2O) + \%Na_2O$ [8]. The alkalis are usually listed as minor constituents, which belie their potential to contribute to adverse effects on concrete.

The alkalis in the cement can react with susceptible aggregate particles used in concrete [3]. One type of alkali-aggregate reaction is alkali-silica reaction. The reaction is initiated when the pore solution becomes concentrated in alkalinity such as after the reduction of water in the concrete. At a high concentration, alkaline hydroxides in the pores then react with certain siliceous aggregates to produce an alkali-silica gel around the aggregate particles [36]. The gel attracts water and becomes distended, a condition that can result in fracture and cracks in the surrounding hardened cement paste as shown in Figure.5 [37]. The alkali-silica reaction in concrete does not necessarily lead to cracking as significant production of gel is required before cracks are manifested.

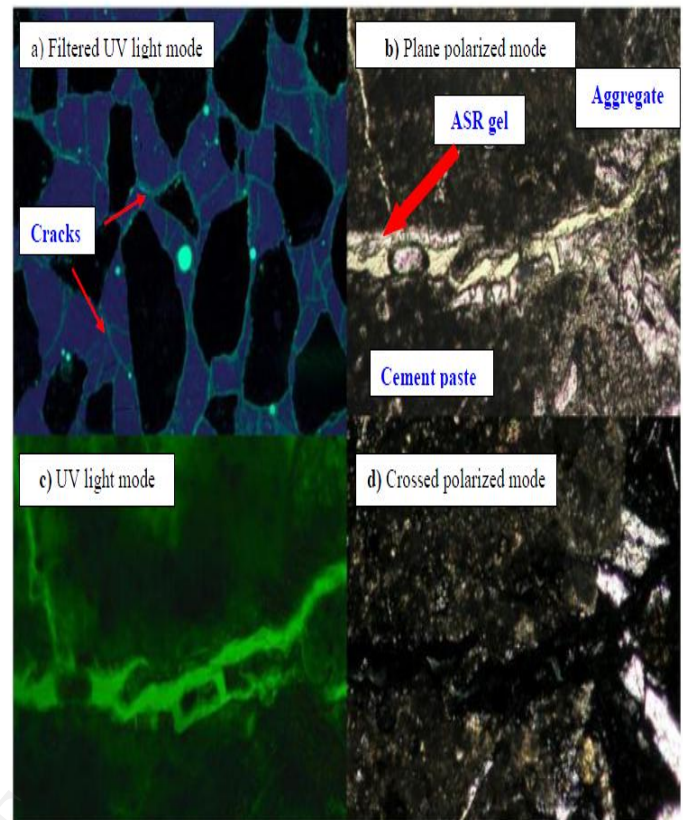


Figure.5 ASR-induced cracks in the micro concrete bar sample (Adapted and modified from [37])

The other type of alkali-aggregate reaction is alkali-carbonate reaction (ACR) which is triggered by the use of certain types of dolomitic limestone aggregate in concrete work [36]. This reaction does not appear to be common and there is a paucity of information on the mechanism involved in this reaction. There is general assent that the reaction results in de-dolomitisation of the particles which is accompanied by swelling of the newly formed product. This ultimately leads to expansion in the concrete. There are however alkali-carbonate reactions that do not cause expansion.

ASTM does not present a limit on alkali content for Type 1 and Blended cements in its mandatory requirements in the C150 and C 595/595M specifications. The limit for OPC is however placed as an optional requirement. It provides the option of specifying a maximum limit in ordinary Portland cement where it is envisaged that alkali-aggregate reaction (AAR) in the concrete is probable and not adequately provided for otherwise. The provisional requirement for equivalent alkalis in ASTM C150 [16] is a maximum of 0.6% of the mass of cement for Type 1 cement. The allowable limit for alkalis is also omitted from the chemical requirements in BS EN 197-1 [15] but the standard states that an agreement on the supply of low alkali cement can be made between manufacturer and purchaser. Whereas the precursor to BS EN 197-1 referred to a maximum

valve of 0.6% for the alkali limit in agreements made between purchasers and manufacturers, this is now removed from the specification as greater emphasis is placed on performance. Again, AS 3972 [14] does not give a general mandate on the permissible alkali content of the cement but rather made provision for test results on alkali content to be made available to the purchaser.

5. Alumina/Iron ratio

It is mentioned that one of the principal criteria in cement manufacturing is the Al_2O_3 and Fe_2O_3 ratio or alumina modulus (AM), mainly because it helps to control the C_3A/C_4AF ratio which impacts sulphate resistance and heat evolution [39]. When the alumina/iron ratio is minimised to values less than 0.64, C_3A formation in the clinker is abated but C_4AF and C_2F will be present [40]. With regards to C_2F , it does not exhibit a permanent cementing quality and hence does not contribute to the strength of concrete [41]. Typical value of AM in ordinary Portland cement clinker falls in the range of 1.0 to 4.0.

The AS 3972 standard [14] places a minimum permissible limit of 0.66 on the alumina/iron ratio in Portland cement. This requirement is omitted from the standard specification of the other two standards, namely ASTM C150-7 [16] and BS EN 197-1:2000 [15]. ASTM C150-07 [16] however makes other provisions for the control of C_3A and C_4AF .

6. Insoluble residue

Typically, ordinary Portland cement is composed of 95% clinker and 5% gypsum. The gypsum can be obtained from natural deposits or from industries as a by-product of chemical processes. Whatever the source, the gypsum invariably contains impurities. However, it is worth mentioning that another source of impurity is un-reacted silica found in the clinker [42]. In order to safeguard the cement against adulteration, the standards include an insoluble residue test.

According to the provision sets out in ASTM C150 [16], the maximum permissible amount of insoluble residue in Type 1 cement is 0.75% and the limit is increased to 1% of the mass of the cement for blended cements where this property applies. The addition of mineral admixtures to ordinary Portland cements should make it difficult to place limits on the insoluble residue on blended cements but the mineral additions are required to satisfy some requirements before use and this reduces the difficulty in monitoring the insoluble residue. The British counterpart however sets an upper limit of 5% for CEM I types of cement but does not address the CEM II cements directly.

7. Loss on ignition

Loss of ignition (LOI) is a test that is done on a pre-weighed sample of cement to determine the mass that is lost after exposure to a temperature of $900^\circ C$ to $1000^\circ C$ [25]. Usually high loss on ignition values in cement corresponds to low strength [8]. One condition that can influence LOI results is weathering of the clinker. Clinker that is left outdoors for an extended period can have the free lime and free magnesia undergo appreciable pre-hydration and carbonation [3] which will result in a high LOI [25]. Contamination of cement can also negatively influence LOI results.

The BS EN 197 standard permits a maximum of 5% by mass of cement loss on ignition for CEM I cement while the ASTM C150 [16] permits a maximum of 3% for Type 1 cements and up to 10% for blended cement, with the exact percentage depending on the type of the blend (Table 4). In the Australian standard, loss of ignition is basically treated as an informative requirement that should be provided to the purchaser upon request.

Table 4: Specification limits: loss on ignition of ordinary Portland cement

	AS 3972:2010 [14] Ordinary Portland Cement	BS EN 197- 1:2000 [15] CEM I	ASTM C150-07 [16] Type 1
Loss on ignition %	4	≤ 5	3

*All requirements are expressed as percentage by mass of cement

8. Magnesium oxide content

Magnesia is one of the constituents that can lead to lack of soundness in cement (free lime and calcium sulphate are the other constituents). In the context of cement chemistry, soundness can be defined as the ability of the hardened cement to remain dimensionally stable. Only the reactive magnesium oxide constituent (referred to as periclase) contributes to unsoundness of cement. More specifically, as a portion of the periclase is bound in the cement, only the free periclase adversely impacts soundness [25]. Usually, magnesia contents in the range of 4% to 6% based on the mass of cement will not result in marked dimensional changes in the concrete but it is reported that higher percentages of MgO can contribute to expansion, hence affecting the

soundness of the cement [8]. Gao et al [43] studied the soundness of concrete samples with various percentages of fly ash and magnesia that were cured via autoclaved devices at various temperatures. The result showed that the expansion of the concrete increased as the magnesia increased, but the most noticeable expansion occurred when 8 and 12% MgO was used. Additionally, the autoclave expansion of the concrete decreased as the level of fly ash replacement in the cement increased. This attribute is at least partly ascribed to the fact that the magnesia level was higher in the cement than in the fly ash. ASTM specifies an upper limit of 6% for OPC and Portland pozzolanic cements but did not set limits for the other blended cements. The Australian standard specifies a maximum of 4.5% by mass of cement for GP while BS EN 197 permits a maximum of 5% on the clinker of Portland.

9. Setting Times

This property is usually determined via physical means and hence is placed under physical properties in most specifications. However, the process of setting is actually a chemical activity and therefore it is included in this discourse. The setting of concrete is separated into two categories; a) initial set and b) final set. The setting time that is associated with each is described by standards as the time that a specified degree of solidification that restricts the penetration of a designated needle to a particular depth in a sample of cement under stated conditions. The practical application of the initial setting time is that it gives an estimate of the relative time that the concrete will remain workable; facilitating mixing, conveying, placing, compaction and finishing of concrete. The final setting time of cement gives an indication of the initiation of strength development in concrete. It is imperative to point out the setting times of cement does not coincide with the setting times of concrete but there is correlation between the two that can be used to indicate slump loss and strength initiation in concrete as schematically illustrated in Figure.6.

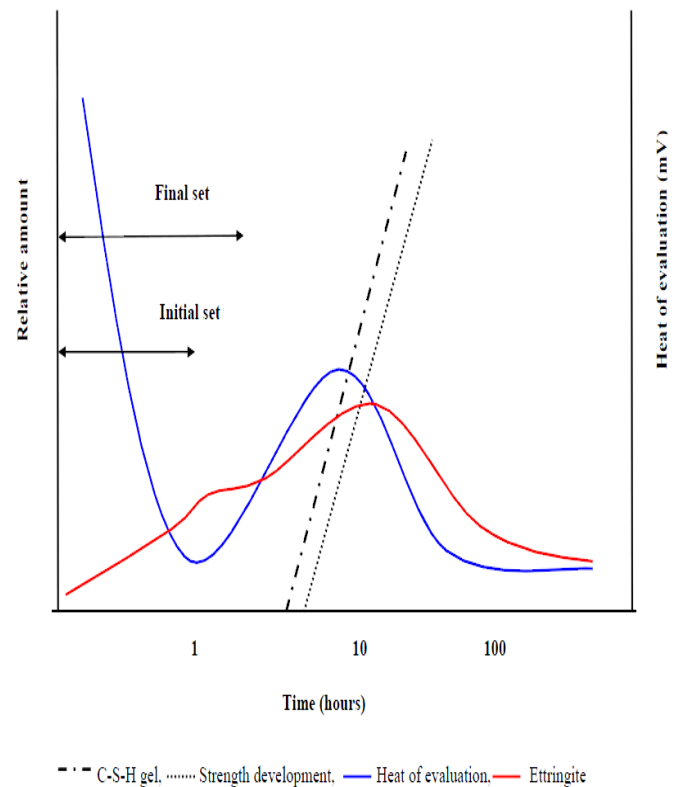


Figure.6 Relationship between the initial and final setting time of cement and the strength development in concrete

Cement is composed of several major and minor chemical phases and this, with the variation in the relative proportions of these phases, makes the setting of the cementitious material quite complex. However, it is postulated that in pure cement paste with 5 – 6 % gypsum, the reaction of C_3A is suppressed but, nevertheless, its limited activity contributes to the formation of needle-like crystals that are produced under the influence of the calcium sulphate [27]. These crystals results in stiffening but the most important phases that contribute to solidification of the cement paste are the silicates of which the C_3S plays a significant part at the very early age. The commencement of the reaction of the silicates is slower than that of the more reactive aluminates but the strength of the cement paste is advanced at a high rate once this reaction is underway. As the reaction progresses, the production of cement gel increases and setting, which leads to development in strength, takes effect.

Setting times of cement are however, influenced by a number of factors, many of which are predicated on the production conditions. For example, the duration and degree of heat exposure affect the production of alite and belite in the clinker. When clinker, that was rich in oxides of magnesium and sulphur, was reheated to high temperature for two hours and was tested, there was noticeable increase in the alite and decrease in the belite phases [44]. This kind of adjustment in the

proportions of the alite and belite phases will affect the early age hydration and by extension the setting times of the cement. Clinker rich in C_3S will result in a higher rate of heat evolution when the cement undergoes hydration and the consequence is an increase in the setting time. Researchers have also shown that increases in the C_3A content and in the fineness of the cement will have the same type of effect. The use of mineral admixtures in cement can also retard or accelerate initial setting of concrete. Many of the adverse effects in the cement are also interrelated. As mentioned, an excess of lime leads to higher levels of uncombined CaO which delays the hydration process. Low quantities have the reversed effect [45]. The setting times of cement is therefore affected by the levels of free lime [46].

The setting times of cement are largely determined by the Vicat apparatus, although in recent times ultrasonic measurements and other means are explored but there is no documentation to suggest that these techniques are standardized. The ASTM standard stipulates that when determined by the Vicat apparatus, the initial setting time should not be less than 45 minutes and the final setting time should not exceed 375 minutes. The minimum time that is allocated to the initial set is reasonable as lower values would not allow adequate time for handling fresh traditional concrete. Besides, low setting times are indicative of accelerated hydration which may result in high rate of heat evolution and its associated problems. However, the use of high range water-reducing admixture is becoming more prevalent and this may reduce the significance of the initial setting time. The final setting time is useful as increases in this time are early signs that the concrete may be faulty. BS EN 197 set out different values for each strength class but the lowest minimum initial setting times, which is assigned to strength class 52.5 (normal early strength and high early strength), is 45 minutes but the final setting time is omitted from this standard. The Australian standard also concur with a minimum initial setting time of 45 minutes but specifies that the maximum time for the setting of GP cement is 360 minutes.

10. Conclusions

In this paper, the manufacturing and the development in the hydration of cement was briefly discussed to provide a background to some of the properties of the concrete. The effects of the properties of the cement were also shown in order to establish the relevance of the limits on each of its parameters. Three recognised standards were used to illustrate the limits that are placed on some of the parameters of the ordinary Portland cement and the Portland cements blended with silica fume, fly ash, GGBS and/or limestone. It was seen that, although the limits were not always the same, in most instances there were not any significant deviations

in limits of properties that were provided. The limits on harmful chemical properties such as chlorides in cementitious materials were not always covered fully in the cement standard specifications but other related standards were needed to provide understanding of how to control deleterious consequences in concrete.

More importantly however, it was seen that when the standard limits were compared to what is normally obtained in the cement or thresholds for the initiation of injurious effects in concrete, the limits appeared reasonable and in some cases, the limits were conservatively placed on the side of safety as regards values necessary for limiting the initiation of adverse condition. It is therefore concluded that if the type of cement that is manufactured bear similarities to those reviewed in this paper and closely conforms to the specification limits in these three standards, the incidences of deleterious attacks from the studied properties will be minimised. It is also seen that the current knowledge implies that the use of regulated mineral admixtures in cement in many instances can help to improve the performance of concrete.

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