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DEVELOPMENTS IN LOW ENERGY CLINKERS

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INTRODUCTION

Ordinary Portland Cement (OPC) is the most widely used binding material in civil construction industries. With the high degree of industrialisation in addition to the massive construction of buildings, roads, bridges, dams, etc., its requirement is enormous in the present day modern society, throught out the world. Portland cement is conventionally produced in modern industries by the processing of natural raw materials such as limestone, clay and some amount of correctives, iron ore or bauxite in proper proportion to fine powder. Then the fine powder is sintered in rotary kiln at 1450 °C to produce clinker, requiring about 3244 kJ/kg (800 kcal/kg) of clinker. The clinker is ground to fine powder, in addition with gypsum in small proportion, to produce OPC. The whole process consumes enormous amount of energy, in terms of thermal as well as electrical. Thus OPC is one of the most energy consuming product in processing industries.

Since the invention of Portland cement by Joseph Aspdin in the year 1824, no efforts have been reported on modifying its potential compounds with the purpose of making a product capable of showing the same setting and hardening properties but requiring considerably lower energy input. In the year 1980 P. K. Mehta came out with a series of energy saving modified Portland cements. Portland cement derives its strength and water resistance mainly from the calcium silicate hydrates, paticularly due to the quick hydration of C_3S to form C-S-H gel. Instead of the high lime containing main silicate phase C_3S, which also requires high temperature for its formation, these modified Portland cements contain low lime containing phase C_2S. So the over-all lime requirement in these modified Portland cements is lower and leading to energy saving, as in the process of clinkerization the major amount of energy is consumed in the dissociation of $CaCO_3$ to CaO. Since the formation of C2S is completed at a much lower temperature than that of C_3S, is also another way of energy saving. Instead of C_3A these cements contain two low lime containing phases $C_4A_3\bar{S}$ and $C\bar{S}$. That means the over-all sulphate content in these cements is quite high in comparison to OPC. Cements of these type can accommodate higher amount of C_4AF, which is also a low lime containing phase leading to energy saving.

The sulphate and aluminate contents of these cements are quite high in comparison to OPC, which provides an opportunity to use industrial wastes such as gypsum containing high amount of sulphate and fly ash containing high amount of alumina. Such a modified cement can also accommodate high amount of iron. This provides another opportunity to utilise some of the wastes containing high amount of iron, such as red-mud. Besides the sulfoaluminate type modified cement there are some other approaches by which some energy can be saved such as active belite cement, alinite cement, fluroaluminate cement. The main aim of this paper is to review and discuss the present state of the art in the area of low energy clinkers with respect to their hydration behaviour, hardening property and durability aspects.

1. CLINKERS IN THE SYSTEM C-S-A-F

Ordinary Portland Cement clinker is traditionally prepared on the basis of four component oxide system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ and is a most energy consuming industrial product. To reduce the burning temperature in order to save some energy, without changing the potential phase composition some minor oxides are used as mineralizers and fluxes. These are added in the amounts up to 3 Wt. % to the raw mix. Mineralizers even in small amounts promote the formation of clinker compounds, especially the formation of C_3S. Fluxes are substances which lower the temperature at which the formation of liquid phase commences and decrease the viscosity of the clinker melt. But it is very difficult to derive a clear cut disticiton between these two, as many substances have both mineralising as well as fluxing action. Incorporation of such fluxes and mineralizers one can save only a very small amount of energy, approximately 5%. So there is a need of some other approaches to reduce the energy demand dramatically.

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Table I.

Compressive Strength of Belite Cement

Clinkers				Compressive Strength (MPa)			
	LSF	SM	AM	1 d	7 d	28 d	90 d
1	0.79	3.6	2.2	18	30	49	90
2	0.80	3.0	2.3	18	29	44	53
3	0.80	2.3	0.9	10	17	35	51

Active Belite Clinker (ABC):

The basic concept that reduction in lime saturation factor can reduce energy consumption during the burning process initiated the research attention to develop an active belite cement. The average theoretical heat required to prepare OPC is 1750 kJ/kg (420 kcal/kg). For example a clinker having the lime saturation factor (LSF) 0.97 the theoretical heat required is 1850 kJ/kg (440 kcal/kg), this can be reduced to 1650 kJ/kg (390 kcal/kg) by lowering the LSF to 0.80 that means a net decrease of 210 kJ/kg. The clinkerisation temperature can thus be reduced from 1450° C to 1300° C. By reducing the LSF the dominant silicate phase is dicalcium silicate at the cost of tricalcium silicate, the main early hydrating phase responsible for hardening and strength development. The problem associated in having high percentage of dicalcium silicate in the clinker is that, it is a slow hydrating phase and leading to very low early strength. Moreover this phase has different polymorphism and γ C_2S is non hydraulic. Whereas the β, α, and α' modifications are hydraulic. So there is a need to stabilise the β C_2S or the high temperature modifications in the system, which is also the common form in the Portland cement. The stabilisation of this form can be achieved by fast cooling. On the other hand fast cooling means more heat losses from the cooler. So the over-all saving in energy is questionable. So far the application is concerned the initial strength development is low so the use is limited. The literature survey shows that a lot of research attention has been paid to improve the hardening capacity [1–10]. The several approaches of improving the hardening capacity are as follows.

I. Rapid quenching of clinker by which the high temperature polymorph of C_2S are stabilised and the reactivity of the cement is improved [1–4].
II. Introduction of some minor oxides (Alkalies, Sulfates) to stabilise the β, α, or α' form of C_2S [5, 6].
III. Addition of ground clinker of normal composition by which the hydration process is accelerated [7–10].

Principally the hydration of ABC is not different form that of OPC. But the only main difference is that ABC hydrates more slowly and less portlandite is produced during hydration. There are two different results reported regarding the stability of ettringite in belite cement. According to Ftikos [13] part of the ettringite is transformed to monosulphate. The less workability of belite cement has been explained due to the rapid formation of ettringite in the relatively lower alkaline medium than that of alite rich cement [14]. On the other hand it has been established that monosulphate is the stable phase in higher pH than ettringite [15]. The strength development of some of the industrial clinkers are summarised in Table I [16]. The durability of belite cement concrete is expected to be more than that of OPC as very small amount of $Ca(OH)_2$ is released during hydration.

2. CLINKERS IN THE SYSTEM C-S-A-$\bar{S}$

Several attempts have been made to develop cements in the system containing the phases C_2S, $C_{12}A_7$, CA, $C_4A_3\bar{S}$, $C\bar{S}$ and some amount of free lime [18–22 and 30–32]. The presented results are varying from each other. In the presence of gypsum/anhydrite in the system CaO-SiO_2-Al_2O_3 two ternary compounds containing sulphate are formed, they are $C_5S_2\bar{S}$ and $C_4A_3\bar{S}$. Out of these two phases the former phase is stable at a narrow range of temperature from 1100–1180° C [17] which decomposes to form C_2S and $C\bar{S}$, whereas the phase $C_4A_3\bar{S}$ is stable up to 1400 °C. The sequence of reactions that take place in the presence of sulfate are as follows, at about 800–900°C intensive formation of C_2S takes place in addition to the phase C_2AS. Above 1000° C $C\bar{S}$ takes part in the reaction to form $C_5S_2\bar{S}$ and $C_4A_3\bar{S}$, and C_2AS disappears form the system. Intensive formation of these ternary sulphate phases takes

Table II.

Phase Composition and Compressive Strength of Some of the Typical Cements

Phase Compositions of cements					Compressive Strength (MPa)			
	C_2S	$C_4A_3\bar{S}$	$C\bar{S}$	CA	1 d	7 d	28 d	Ref.
1.	74.2	17.8	1.2	–	8	10	12	21
2	56.3	20.1	1.7	13	15	26	30	
3.	40.8	28.8	1.2	20	28	35	55	
4.	32.8	38.7	0.7	19	31	55	60	
5.	20	80	–	–	42.5	44.0	–	20
6.	16.9	64.35	19.56	–	24.5	34.5	–	
7.	10.14	40.55	49.31	–	18.5	25.0	–	

place above 1100° C. The Phase $C_5S_2\bar{S}$ than decomposes above 1180° C to form $\alpha'C_2S$ and $C\bar{S}$. About 1200° C the quantity of $C_4A_3\bar{S}$ reaches its maximum. The phase $C_5S_2\bar{S}$ does not have hydraulic property [30], whereas the phase $C_4A_3\bar{S}$ is the most important hydraulic phase. That is why for the preparation of clinkers in this system the preferred temperature regime is above 1200° C. Depending upon the ratio of C / S+A+$\bar{S}$ and A / $\bar{S}$, the phases $C_{12}A_7$ and CA also appear in the system. The phase $C_4A_3\bar{S}$ reacts in the presence of calcium sulphate and lime to form ettringite according to the following schemes:

$$C_4S_3\bar{S} + C\bar{S} + H_2O \rightarrow C_2A.(C\bar{S})H_{32} + Al(OH)_3 \quad (1)$$

$$C_4A_3\bar{S} + CaO + C\bar{S} + H_2O \rightarrow C_3A.3(C\bar{S})H_{32} \quad (2)$$

$$C_2S + H_2O \rightarrow C - S - H + Ca(OH)_2 \quad (3)$$

$$Ca(OH)_2 + AlOH_3 + C\bar{S}H_2 + H_2O \rightarrow \quad (4)$$

$$\rightarrow C_3A.(C\bar{S})H_{32}$$

Den Jun-An et al. [20] investigated the possibility of obtaining a series of cements by taking the phases C_2S-$C_4A_3\bar{S}$-$C\bar{S}H_2$ in different proportions to produce rapid hardening, slight expansive, expansive and self stressing cements. Some attempts were made to develop such type of cements from industrial wastes, K. Ikeda tried to prepare them from blast furnace slag and waste gypsum [21]. These cements also contain the CA phase. The results show that such type of cements can very well be prepared from waste materials for common applications. Some of the strength development data reported by different authors are given in Table II. It is very important to note that depending upon the proportion of different phases the development in mechanical properties, porosity, microstructure as well as the expansive behaviour changes. When higher amount of $C_4A_3\bar{S}$ is present in the system than the cement has high early strength, but the ratio of $C_4A_3\bar{S}/C\bar{S}$ has significant influence in determining the ratio of AFm to AFt phase in the hydrated product and the microstructure. The type of calcium sulphate supplied has a role in changing the mechanism of ettringite formation as well as in the microstructure development [23].

3. CLINKERS IN THE SYSTEM C-S-A-F-$\bar{S}$

The phase composition of this type of clinker is almost the same as in the system C-S-A-$\bar{S}$. The introduction of Fe_2O_3 in the system leads to the initial formation of C_4AF, which starts at about 850° C and reaches its maximum at 1200° C. This system has additional interest in preparing high iron cement besides the normal sulfoaluminate cement. Several results are existing regarding the preparation of cements in this system containing the main phases C_2S, $C_4A_3\bar{S}$, C_4AF, $C\bar{S}$ from natural raw materials or pure chemicals [24–33]. Mehta P. K., for the first time undertook more detailed study on the phase composition and their influence and a wide verity of cements are reported [24]. Depending upon the phase composition various cements such as normal hardening, rapid hardening, slow hardening and low durable cements can be prepared. Similarly a series of cements containing the phases C_2S, $C_4A_3\bar{S}$, C_4AF, $C\bar{S}H_2$ and free CaO is prepared by Sudho et al. from natural raw materials and pure chemicals [25]. It is observed that such type of cement can accommodate upto 10–12% of free lime without any adverse effect. Wang Yanmou et al. have reported the industrial production of cements containing the phases C_2S, $C_4A_3\bar{S}$,

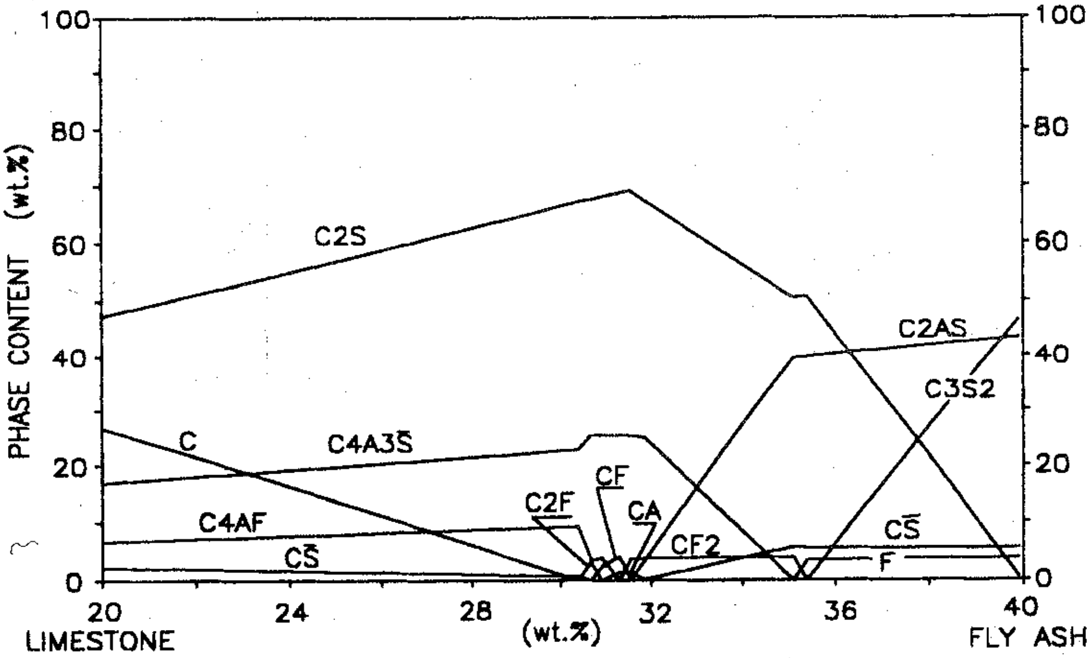

Fig. 1. Changes in phase composition in the system Limestone-Fly Ash-Gypsum (5 wt. % of Gypsum)

Table III.

Phase Composition and Compressive Strengths of Some of the Typical Cements

	Phase Composition (Wt. %)					Compressive Strength (MPa)			
	C_2S	C_4AF	C_4A_3S	CS	CaO	1 d	7 d	28 d	Ref.
1.	25	40	20	15	–	34.8	37.4	–	24
2.	45	15	20	20	–	9.5	27.1	49.8	
3.	36	4	41	18	–	15.0	25.1	31.2	25
4.	17	4	40	31	9	40.6	45.4	52.0	
5.	53	8	16	13	10	31.0	35.0	37.0	28
6.	50	8	15	17	10	20.3	42.5	50.0	

C_4AF, $C\bar{S}$ from natural raw materials [26]. Mudbhatkul et al. have reported that cement having the following parameters: $A/S = 2.5$, $A/\bar{S} = 3.81$, show better strength properties and is suitable for zub-zero applications [27].

Considering the potentials of using a variety of industrial waste products to prepare such type of cements, a systematic study was carried out [38]. The scattered thermodynamic and phase compatibility data in the system C-S-A-F-$\bar{S}$ were collected and the phases which are compatible with C_2S in this system were established [34]. As we have seen from the earlier studies [24–27] the variation in quantities of phases and the changes in chemical composition lead to the formation of different type of cements from high early strength and long durable to low strength and low durable cements. So stringent quality control is required to prepare such type of cements. These phase compatibility data have been used to establish the phase assemblies and consequently the phase field map. For this purpose three component raw mix system Limestone-Fly ash-Gypsum has been used for computation to study their feasibility for the preparation of such type of cements [35]. Figure 1, the result of such a computation showing the changes in mineralogical composition with change in the proportion of the raw mix. Cements of this type has been prepared from industrial wastes showing superior properties [28–30].

The hydration of these type of cements are similar to that of cements in the system C-S-A-$\bar{S}$ and C_4AF also participates in the formation of AFm or AFt phase in the system depending upon the SO_3 available in the system. Some of the typical results of strength development reported by different authors are given in Table III.

The speciality of these type of cements are as follows

- Excellent high early strength (1 day strength up to 40 MPa).
- Good anti seepage properties due to low porosity.
- Good frost resistance ability.
- Good low temperature strength development due to liberation of high heat of hydration
- High Corrosion resistance, especially SO_4^{2-}, Cl^-
- Controlled expansion

4. CLINKERS IN THE SYSTEM C-S-A-F-M-$\bar{S}$

Only one work [36] has been reported in the last congress in New Delhi regarding the possibility of preparation of clinkers in this oxide system, it is of paramount importance in the utilisation of low grade limestone containing high amount of magnesia and in certain cases dolomite. These raw materials are not usable in OPC clinker preparation due to the formation of periclase, which hydrates slowly in the hardened cement paste thus leading to unsoundness.

Though there are no detailed phase equilibrium studies in this system but it has been shown MgO present up to 12 Wt. % forms the stable phase C_3MS2 at the cost of C_2S at 1350° C. The stable phase composition of the clinker in this temperature range is C_2S, C_3MS_2, C_4A_3S, CS. In some clinkers the presence of additional phase C_2AS is also observed.

The main hydrated product in the initial period is ettringite. The one and twenty-eight days compressive strength was 37 and 49 MPa respectively. This shows that high early strength cements can be prepared on this basis. The dimensional change measurement by autoclave shows that in the presence of M_gO up to 10% there is shrinkage in the range of 0.02 to 0.05% but further increase in the content shows expansion.

5. CLINKERS IN THE SYSTEM C-S-A-F-T-$\bar{S}$

Sulfoaluminate belite cement is generally prepared from the natural raw materials such as limestone, bauxite, and gypsum. Bauxite being the source of aluminiumoxide, the other oxides present are iron and titanium. The presence of CT phase in industrial sulfoaluminate belite clinkers is reported [37]. So far industrial waste product utilisation is concerned some of them contain TiO_2 e.g. fly ash and red mud. An attempt was made to establish phase compatibility in the system C-S-A-F-T-$\bar{S}$ and it was observed that all the three calcium titanate compounds C_3T_2, C_4T_3, CT are compatible with $C_4A_3\bar{S}$, and $C\bar{S}$ [38]. There are altogether thirty phase assemblages containing C_2S, the main compound of sulfoaluminate belite clinker was established. On the basis of the computation [35] in order to establish the phase field map form the phase compatibility data a fly ash containing 6.96 Wt. % of TiO_2 has been estimated for the preparation of clinkers. A clinker prepared at 1200° C by using 16.5 Wt. % of this fly ash, 20 Wt. % gypsum and limestone have the phase composition C_2S, $C_4A_3\bar{S}$, C_4AF and $C\bar{S}$, calcium titanate and free lime [38]. The main hydrated product in the initial period is ettringite. The one day and twenty-eight days compressive strength of this cement mortar is 23 and 55 MPa respectively. The presence of calcium titanate as a minor phase has no harmful effect in the strength development in the initial period.

6. CLINKERS IN THE SYSTEM C-S-A-CaF_2

If one will review the presentations in the last New Delhi Congress, it is obvious that numerous papers have been devoted to study the influence of CaF_2 as a mineraliser in lowering the clinkerisation temperature and its influence in the phase development, microstructure of the clinker and its hydration behaviour. But how a low energy clinkers have been developed on the basis of these informations gathered is pointed out here.

It is well established that the incorporation of CaF_2 in the above system lowers the clinkering temperature significantly. In the presence of CaF_2, formation of $\alpha'C_2S$ takes place at about 800° C and this compound reacts with CaF_2 at about 900° C to form an intermediate non-hydraulic phase $2C_2S.CaF_2$ which is stable in the temperature range 900–1040° C. This compound decomposes at higher temperature to CaO + Liquid [32]. At about 1100° C another non-hydraulic phase $C_{11}S_4$. CaF_2 forms [39]. This phase decomposes at about 1150 °C to form C_3S (Containing about 1.5% fluorine). So the formation temperature of C_3S is dropped by et least 200 °C. In the presence of Al_2O_3 another ternary compound $C_{11}A_7CaF_2$ is formed at about 1050° C being stable up to 1300° C and above this temperature it decomposes to form C_3A [33]. The compatible phase assemblage which is of interest to prepare low energy clinker is CaO-C_3A-$C_{11}A_7CaF_2$-C_2S. The presence of C_3A is dependent on the quantity of CaF_2 introduced into the system and the temperature of burning. By adjusting the proportion of limestone, alumina and fluorine two types of clinkers are produced having the following mineralogy [33].

Clinker I $C_{11}A_7CaF_2 = 65–75\%$, $C_2S = 25–15\%$

Clinker II $C_{11}A_7CaF_2 = 20–30\%$, $C_2S = 10–15\%$,
$C_3S = 50–60\%$

Hydration Behaviour: The hydration mechanism of the phase $C_{11}A_7CaF_2$ in the presence of different forms of calcium sulfates, calcium hydroxide and carboxylic acid was studied by Uchikawa et al. [40–42]. Conduction calorimetric study shows the presence of three peaks. The second and third peak usually appeared after 1h and 1 day of hydration. The second peak corresponds to the formation of hexagonal calcium aluminate hydrate C_2AH_6 and C_4AH_{13}. The third peak represents the conversion of hexagonal calcium aluminate hydrate to cubic C_3AH_6. In the presence of $Ca(OH)_2$ the formation of hexagonal calcium hydrates and their conversion to cubic hydrates are accelerated. In the presence of sulfates the main hydrated product is ettringite. In the presence of plaster of paris the rate of reaction is faster. The rate of hydration of alite in Jet cement (cement corresponding to the clinker II) is almost twice as faster as monoclinic alite in Portland cement. So a much denser structure of hardened Jet cement than Portland cement was also confirmed. The hydrated produts of these cements are ettringite and C-S-H gel.

$$C_{11}A_7.CaF_2 + CaSO_4 + H_2O \rightarrow \tag{5}$$

$$\rightarrow C_3A3(CaSO_4).32H_2O + CaF_2$$

$$C_2S + H_2O \rightarrow C-S-H \text{ gel} + Ca(OH)_2 \tag{6}$$

These are quick setting and rapid hardening cements. The final setting time is less than 10 min. The compressive strength fo the cement paste after one hour is about 30 MPa, and concrete strength of 20–30 MPa can be achieved after 3–4 hours of hydration [43]. This cement is generally used in rapid repair work and in sub-zero application.

7. CLINKERS IN THE SYSTEM C-S-A-F-CaF_2

The introduction of high amount of iron oxide in the basic system C-S-A-CaF_2 has further possibility of reducing the clinkering temperature. A clinker containing high amount of iron in the above system can be prepared at 1050° C. The reactions in the system take place according to the following sequence [44].

800°C – $CaCO_3 \rightarrow CaO + CO_2$

860°C – $CaO + Fe_2O_3 \rightarrow CaO.Fe_2O_3 \rightarrow$
$\rightarrow CaO.Fe_2O_3$

900°C – $CaO + Al_2O_3 \rightarrow CaO.Al_2O_3 \rightarrow$
$\rightarrow 12CaO.7Al_2O_3$

950°C – $CaO + SiO_2 \rightarrow 2CaO.SiO_2$

980°C – $2CaO.Al_2O_3 + Fe_2O_3 \rightarrow$
$\rightarrow 6CaO.Al_2O_3.2Fe_2O_3$

1000°C – $12CaO.7Al_2O_3 + CaF_2 \rightarrow$
$\rightarrow 11CaO.7Al_2O_3.CaF_2$

The composition of feroaluminate phase present in the system is C_6AF_2 instead of C_4AF. The phase composition of the clinkers varies in the following range:

$C_{11}A_7 = 5 - 60\%$

$C_6AF_2 = 20 - 80\%$

$C_2S = 10 - 40\%$

The main hydrated products in the initial period are ettringite and AH_3 gel + CaF_2. As the hydration continues C4AF participates, increasing the AFt phase further and formation of FH_3 gel takes place. And C_2S hydrates to form C-S-H gel. Due to the formation of ettringite it gives the skeletal structure which is filled by the formation of large amount of gels and a compact structure is resulted, which contributes for high compressive strength. An industrial clinker containing 40 and 50% of ferrite phase gave 17.5 and 19.5 MPa after 6 hrs and 56.4 and 63.5 MPa after 28 days of hydration, respectively. The setting time of iron rich fluroaluminate cement is relatively higher than the only fluroaluminate cement (around 1.30 min).

8. CLINKERS IN THE SYSTEM C-S-A-F-$CaSO_4$-CaF_2

In the studies of influence of different mineralisers in the production of OPC it was found that CaF_2 has a good mineralising effect. But the combination of $CaSO_4$ nad CaF_2 has much more effect than CaF_2 alone, or vice versa. The combined influence of sulfate and fluoride was studied in works [45–56]. After reviewing the literature [46–56] the following important information can be derived. There are four aluminate phases present in the high lime region which are important to cement chemistry i.e. C_3A, C_6AF_2, $C_4A_3\bar{S}$, $C_{11}A_7CaF_2$. The phases C_3A and $C_{11}A_7CaF_2$ are coexisting [56]. But in the clinker coexistence of these phases is dependent upon the ratio $A/F+S+\bar{F}$ and the temperature regime. At temperature $\geq 1350°$ C the phase $C_{11}A_7CaF_2$ decomposes to form more C_3A, whereas at lower temperature $C_{11}A_7CaF_2$ is the dominant phase. The ratio of $C_{11}A_7CaF_2$ to $C_4A_3\bar{S}$ is dependent on $\bar{F}/\bar{S}$. From the change in free energy of formation of C_4AF, $C_{11}A_7CaF_2$, $C_4A_3\bar{S}$ the reactivity of CaF_2, $CaSO_4$, Fe2O3 with CaO and Al_2O_3 in the following order was determined: $CaF_2 > CaSO_4 > Fe_2O_3$. During the clinkerization process there are four intermediate silicate phases formed, these are $2C_2S.CaSO_4$, $2C_2S.CaF_2$, $3C_2S.3CaSO_4.CaF_2$ and $C_{11}S_4.CaF_2$. The phases $2C_2S.CaF_2$ and $C_{11}S_7CaF_2$ do not co-exist. The thermal stability of these phases are as follows: formation of the quaternary phase fluro-ellestadite, $3C_2S.3CaSO_4.CaF_2$ begins at 900° C and is stable up to its incongruent melting at 1240° C. But according to [56] it decomposes at 1035° C. During the clinkerization process $2C_2S.CaSO_4$, $2C_2S.CaF_2$, and $C_{11}S_4.CaF_2$ are not formed directly from their oxides but through the intermediate phase C_2S. The introduction of sufficient amount of $\bar{F}$ and $\bar{S}$ into the system lowers the formation temperature of liquid phase in the system by 200° C compared to the system C-S-A-F. From the point of intermediate mineral formation this system is much more complicated but in the temperature range of 1250–1300° C the stable phases present in the system are C_3S, C_2S, $C_4A_3\bar{S}$, C_4AF, $C_{11}A_7CaF_2$, or C_3A. The phase composition of the clinker produced in this system is C_3S = 30–50%, C_2S = 30–50%, $C_4A_3\bar{S}$ = 5–20%, C_4AF = 3 10%.

AS C_3S is present in the system it hydrates quickly to form C-S-H gel in addition to ettringite in the initial period of hydration. The typical strength development of this cement is 34 MPa after one day and 63.5 MPa after 28 days.

9. CLINKERS IN THE SYSTEM C-S-A-F-$CaCl_2$

So far the production of alinite cement is concerned this system is very important. Alinite cement has been developed in the former USSR, where it has been patented since May 1977 and also produced industrially. B. I. Noudelman and his co-workers are the inventors [57, 58, 66, 67]. The raw mix for making alinite clinker contains between 6–23 Wt. % CaCl2, and the proportion of other oxides remains almost the same as in OPC except MgO, which has to be increased a little in order to stabilize alinite. But the optimum $CaCl_2$ addition to the raw mix was found to be 7–8 wt % [59]. Since calcium chloride melts at 772 °C, a salt melt (eutectic $CaCl_2$-$CaCO_3$ or $CaCl_2$-CaO) is formed already at relatively lower temperature. This promotes the chemical reaction between components of the raw mix. At temperatures below that of the melt formation solid state reaction occurs in which calcium chloride participates or promotes the reaction. The formation and decomposition of the compound $CaCO_3.CaCl_2$ takes place close to the temperature 570 °C [60, 61]. The decomposition of $CaCO_3$ to CaO and CO_2 starts at 780 °C. Small amount of $C_2S.CaCl_2$ forms at 600° C and reaches the maximum at 950° C. At 1037° C $C_2S.CaCl_2$ melts incongruently and decomposes to C_2S and $CaCl_2$. In this way the presence of $CaCl_2$ in this system accelerates the formation of C_2S [62, 63]. The compound $C_2S.CaCl_2$ is not hydraulic. At about 700° C the formation of another compound Calcium Chloroaluminate ($C_{11}A_7CaCl_2$) starts and this compound is stable upto 1350° C. At about 1050° C the formation of alinite begins and is stable up to 1250° C. At about 1100° C the main co-existing stable phases in the system are $C_{21}S_6A.CaCl_2$ (alinite), C_2S, $C_{11}A_7CaCl_2$ and C_4AF. So the clinkerization temperature of alinite clinker is stated to be 1050–1100° C. The over-all saving in energy in the production of such clinkers is about 1250 kJ/kg [68]. The clinkers are more appreciably easily grindable, so the electrical energy consumption for cement grinding is lower. The overall saving in fuel and electrical energy is up to 30% and a reduction in the cost of production of 10–12% in comparison to OPC is claimed. So far the production process is concerned even at such a low burning temperature the chloride already vaporises considerably and gives rise to the chloride cycle which may upset the kiln and the production.

Structure of Alinite:

The crystal structure of alinite as determined by various authors differs from each other. The crystal structure was determined by Ilyukin et al. [57, 58] and according to them the composition should be $Ca_{11}[(SiO_4)_3\ (AlO_4]O_2Cl$ with Si an Al statistically distributed in the XO_4 tetrahedra. But it is not possible to synthesise a mineral having the above composition without the addition of MgO [64, 65]. It is obvious from the industrial alinite that MgO is present as a minor oxide [66]. So all the XO_4 tetrahedra in the crystal structure are occupied by Si and Al and gets the formula [64, 65] $Ca_{9.9}\ Mg_{0.80}\ [Si_{3.4}\ Al_{0.6}O_{16}]O_{1.9}Cl_{0.9}$.According to Noudelman et al. [67] four modifications of alinite exists, they are , β, α', α, where the hight temperature forms have cubic syngonia. The alinite mineral is characterized by a considerable number of defective centers, namely oxygen vacancies and their association with other atom vacancies.

The presence of chloride atom in the structure of alinite has a number of advantages over OPC e.g. low formation temperature (1050–1100° C) and having high degree of grindability, dissolution of mixed and modifying elements, and high ability of interaction with water.

Phase Composition and Hydration

The phase composition of a typical alinite clinkers is as follows, alinite = 60–80%, belite = 10–30%, Calcium aluminochloride = 5–10%, Calcium aluminoferrite = 2–10%. The main hydrated product of alinite cement is C-S-H besides the calcium chloride. The SEM observation shows that the C-S-H formed in the case of alinite has a different morphology than that of OPC. The C-S-H produced from alinite is mostly having a spongy morphology [69]. The presence of calcium chloride favours the dissociation of ettringite to form the secondary gypsum. The rate of hydration of alinite is higher than that of aline and the amount of liberated $Ca(OH)_2$ is relatively lower.

Performance and Durability: The strength development of alinite cement is not significantly affected up to 90 days by the quantities of the added gypsum (4–8% of SO_3). The water to cement ratio affects the strength development remarkably. The standard consistency meaurement shows that alinite cement requires lower W/C ratio than Portland cement. Even at low chloride content the stength of alinite cement is comparable to that of OPC.

The utilization of such cement in the steel reinforced concrete is questionable for the reason of release of chloride ions during the hydration process and which accelerates the corrosion process. The investigation of the corrosion process of alinite cement shows that steel bars embedded axially in 4x4x16 cm mortar prism are completely corroded at the surface after 5 years of storage in open air [68]. But the chloride content of the alinite clinkers can be reduced after the burning process by exposing the clinker to the action of a gas-vapour-air mixture to less than 1%.

10. CLINKERS IN THE SYSTEM C-A-S-F-$CaBr_2$

The synonymous of chloride alinite has been prepared on the basis of bromide [70, 71] having the chemical compositions

$3[(CaO)_{0.875}(MgO)_{0.07}(CaCl_2)_{0.055}]$
$[(SiO_2)_{0.865}(Al_2O_3)_{0.115}]$

$3[(CaO)_{0.89}(MgO)_{0.055}(CaCl_2)_{0.055}]$
$[(SiO_2)_{0.88}(Al_2O_3)_{0.115}(Fe_2O_3)_{0.07}]$

and

$3[(CaO)_{0.89}(MgO)_{0.055}(CaBr_2)_{0.055}]$
$[(SiO_2)_{0.88}(Al_2O_3)_{0.5}(Fe_2O_3)_{0.07}]$

These compounds having hydraulic properties. Clinkers on the basis of the above system can very well be prepared.

CONCLUSION

The main idea behind the development of different kinds of low energy clinkers described in this article is to substitute the high lime containing C_3S phase by a suitable alternative low-lime containing phase i.e. C_4A_3S, $C_{11}A_7CaF_2$, $C_{11}A_7CaCl_2$ and active C_2S (β, α' C_2S) or an alinite phase, which could be synthesized at relatively lower temperature. The setting and hardening properties are mainly derived from main initial hydrated product ettringite except alinite and active belite cement. The ettringite formation leads to quick setting and hardening and in achieving low porosity, which enable these cements in special applications such a rusch repair work and sub-zero temperature applications. Besides these the main benefit in producing such clinkers are

- Energy Conservation
- Reduction in the production of polluting gases such as CO_2, SO_x, NO_x
- Industrial waste utilization
- Saving in natural raw material and utilization of low grade raw materials.

Considering these facts there is an urgent need to study the feasibility of different alternatives for mass production.

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