Thermodynamic analysis of cement clinker formation using low temperature plasma

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Abstract. The paper deals with the synthesis of cement clinker using the highly-concentrated thermal flux. The thermodynamic analysis shows that during this synthesis, the temperature increase up to 2727°C (3000 K) is accompanied by the change in the probability of C₃S, C₂S, C₃S₂, CS formation. Starting from 1907°C (2180 K), the most stable compound is found to be C₃S which is not feasible by applying the traditional technology.

1. Introduction
Plasma-chemical synthesis of cement clinker is one of the innovative methods of the cement production process [1–4]. It differs from traditional cement production by the intensity, one-step process, and complete physico-chemical processes in the liquid phase. These factors determine the relevance of investigations in this field. At the same time, a study and the analysis of the combined complex phenomena, which occur during chemical reactions and phase formations in clinker minerals may provide valuable information concerning methods of directed chemical reactions, ways of rational industrial process control, and the improvement of the cement production technology. The principles of chemical thermodynamics allow making extrapolating calculations of the Gibbs potential which contributes to the assessment of energy reactions observed in the cement clinker formation using the low-temperature plasma, concurrent reaction direction and enthalpy changes, stability of obtained compounds, and a choice of the optimum temperature conditions for the cement clinker synthesis.

This work aims at the thermodynamic analysis of the formation of the main clinker minerals (C₃S, C₂S,CS, C₃S₂, C₄AF, CA, C₃A) during the cement clinker synthesis using the highly-concentrated thermal flux. The Gibbs energy (ΔG) is calculated at a temperature not over 3000 K.

2. Thermodynamic analysis
The Gibbs-Helmholtz equation is used for the thermodynamic analysis. The calculations are based on the initial reference data for the substances and compounds involved in the chemical reactions [5–7]. The chemical reactions observed during the cement clinker synthesis are gathered in table 1.

The values of the Gibbs energy in the temperature range of 298–1160 K are calculated for reactions involving CaCO₃. When the temperature is higher than 1160 K due to a completion of the decarbonization process, CaO is involved in the cement clinker synthesis. In this connection, we use the initial data on the new component for further calculations. We therefore recalculate the Gibbs energy
$\Delta G$ of the substances which undergo phase and polymorphic transformations within the indicated temperature range, with regard to the new component.

Table 1. Chemical reactions in the synthesis of cement clinker.

| №  | Chemical reactions                                      | №  | Chemical reactions                                      |
|----|---------------------------------------------------------|----|---------------------------------------------------------|
| 1  | $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaO} \cdot \text{SiO}_2 + \text{CO}_2$ | 4  | $\beta$-2CaO$\cdot$SiO$_2$ + CaO $\rightarrow$ 3CaO$\cdot$SiO$_2$ |
| 2  | $3\text{CaCO}_3 + 2\text{SiO}_2 \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 + 3\text{CO}_2$ | 5  | $\text{CaCO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{CO}_2$ |
| 3  | $2\text{CaCO}_3 + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2 + 2\text{CO}_2$ | 6  | $3\text{CaCO}_3 + \text{Al}_2\text{O}_3 \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CO}_2$ |

Based on the proposed calculation algorithm and the initial data on all the chemical reactions (see Table 1), we derive the equations of the Gibbs energy depending on the temperature of the raw mixes comprising 83.90 wt.% marble, 11.70% fly ash from thermal power plant, 1.55 wt.% quartzites, 2.85 wt.% purple ores from OAO “Angarsktsement” (Angarsk, Russia) and industrial wastes of Kuzbass [8]. The latter includes 83.57 wt.% dolomitic limestone grinding waste, 11.90 wt.% flotation waste, 4.53 wt.% limestone. The composition of these substances is calculated by formulas suggested by V. A. Kind. The optimum chemical composition and values of the silicate and alumina moduli of the raw mixes are presented in Table 2.

Table 2. Optimum chemical composition and modules of the raw mixes.

| Code | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Ignition loss | Σ | Saturation factor | Silicate module | Alumina modulus |
|------|---------|-------------|-------------|-----|-----|--------------|---|------------------|----------------|-----------------|
| A-1  | 13.16   | 3.11        | 1.85        | 43.72 | 2.52 | 35.64        | 100 | 1.03            | 2.65           | 1.68            |
| B-1  | 10.35   | 2.60        | 1.31        | 34.74 | 11.23 | 39.78        | 100 | 1.03            | 2.65           | 1.98            |

It is interesting that all these raw mixes possess the uncommon, higher saturation factor (> 1) accepted according to the results of the mathematical design of the experiment. This value of the saturation factor provides the synthesis of the highly-active cement clinker [8]. The raw mixes are multi-component and characterized by the diverse chemical composition which complicates studying the chemical thermodynamics of the clinker formation. For simplification of the system, we exclude such impurity oxides as Na$_2$O, K$_2$O, MgO, P$_2$O$_5$, and some others. The C:S ratio in the raw mixes is assumed to be 3.32:1 and 3.36:1. Therefore, the difference in the Gibbs energy $\Delta G$ on the graphic image of the two systems is $\pm 10.5$ kJ·mol$^{-1}$. Figure 1 shows the temperature dependences of the Gibbs energy at C:S = 3.32:1.

Figure 1. Temperature dependences of the Gibbs energy: 1 – CS; 2 – C$_3$S$_2$; 3 – C$_3$S; 4 – C$_5$S; 5 – CA; 6 – C$_3$A; 7 – C$_4$AF. $\Delta G$, kJ·mol$^{-1}$. 
As can be seen from figure 1, the sequence of formation of calcium silicate in the system is as follows: the first compound is CS formed at about 600 K. This is indicated by the first crossing with the X-axis at 582 K (309°C). Then, the formation of C3A, C2S, C4AF and C3S2 is observed in the temperature range of 650–750 K (377–477°C). With the increasing temperature, the probability of cement clinker changes. At 708 K (435°C), the primary compound forming during the thermal treatment is C2S, the synthesis of which is based on CS. This privilege of C2S remains up to 2180 K (1907°C), and then C3S forms. This is indicated by crossings of these reaction curves and the following increase in the absolute values of the Gibbs energy. At 3000 K (2727°C), these values achieve 197.6 and 186.7 kJ·mol⁻¹ respectively for C3S and C2S. Thus, within 685–2180 K (412–1907°C), the formation of dicalcium silicate is highly possible. With the temperature increase over 2180 K, the only phase of tricalcium silicate can be formed. Its formation is possible due to such minerals as C4AF, CA, C3A, CS, C3S2 and CaCO3, CaO. It is also found that the synthesis of C3A from CA and CaO or CaCO3 is impossible, because there are no crossings between the ΔG value and these compounds. Thus, we can suppose that tricalcium aluminate results from the melt that correlates with Babushkin’s studies [9].

3. Results and discussion
The composition of the investigated raw mixes was obtained after the calculations. The mixes were prepared in several stages including the dosage of components, their grinding in a ball mill ShLM-5 up to 0.16 mm size, homogenization in a dry state and granulation in an R-009 granulating machine down to a 5 mm size. The thermal treatment of the granulated mix was conducted on the laboratory setup depicted in figure 2. It is a thermal generating unit comprising a plasma torch and a furnace with enclosed volume.

![Figure 2. Experimental laboratory setup for low-temperature plasma treatment: 1 – cathode; 2 – granulated raw mix, partial melt; 3 – arc plasma; 4 – power supply; 5 – furnace; 6 – anode.](image-url)

The laboratory setup for the low-temperature plasma treatment comprises cathode (plasma torch) which moves along the vertical axis; graphite anode mounted to the bottom of the furnace; the gas distribution system which provides the plasma gas (air) supply at a rate of 2.0–7.0 m³·h⁻¹; and the water cooling system for cooling the plasma-chemical reactor [10, 11].

The cement clinker formation was performed using the low-temperature plasma treatment of the granulated raw mix in the furnace. To create the required heating conditions, a pilot arc was preliminary stroke at 10–15 mm anode-cathode spacing. The cathode assembly was then raised to a distance of 90 mm for a stable operation of the plasma-chemical reactor and to achieve the required flux density of the primary arc stream. Its temperature ranged from 3000 to 3500°C. The raw mix was supplied in doses in the arc zone in the furnace of 250 cm³ volume. The heating of the granulated mixes of natural and man-made components was instantaneous. The initial raw mix melted in plasma and homogeneously distributed in the furnace. The time reading of the plasma treatment was started from the local melting
of the raw mix. In order to identify the optimum process conditions, the treatment time was different for each mix equaling 75, 90 and 120 seconds. The operation of the laboratory setup was cyclic. The cycle duration of one melting was determined by the time of the melt formation and its cooling. It is however, possible to organize a continuous run mode. In this case, the granulated mix feeding would be either continuous or dosing, while the melt of the cement clinker would be produced gradually.

The electrical specifications of the laboratory setup were varied within the following ranges: \( I = 340–380 \, \text{A} \), \( U = 120–140 \, \text{V} \). The power of the plasma-chemical reactor ranged between 40.8–53.2 kW. The surface temperature of the melt exposed to the highly-concentrated thermal flux was measured with the disappearing-filament optical pyrometer OPPR–017E and ranged from 3000 to 3500°C. The thermal process conditions of the raw mixes are given in table 3.

| Method                         | Temperature (°C) | Time (s)     | Electric current (A) | Voltage (V) |
|-------------------------------|------------------|--------------|----------------------|-------------|
| Plasma-chemical               | 3000–3500        | 75; 90;120   | 340–380              | 120–140     |
| Traditional (muffle furnace)  | 1450             | 7800         | 10–15                | 220–230     |

The similar raw mixes were burned in the laboratory muffle furnace at 1450 °C during 130 min by analogy with the traditional technique [12]. This time included a 40 min temperature rise up to 1450 °C and a 90 min isothermal aging with the subsequent gradual cooling of cement clinker.

The cooling procedure of cement clinker produced by different techniques includes two process conditions, namely quenching on air, at a temperature decrease from 3000 to 80°C during 20 min. The average quenching rate is 2.5°C·s\(^{-1}\). The second is a gradual cooling due to isothermal aging after the plasma treatment. The average cooling rate is 0.3°C·s\(^{-1}\) or a 3-hour cooling. The obtained cement clinker is then ground in a ball mill to produce the specific surface area of 3000–3100 \( \text{cm}^2 \cdot \text{g}^{-1} \). After sifting, the powder remained on a 0.08 mm x 0.08 mm sieve in the amount of not over than 5 %. Then physicochemical and physical-and-mechanical analyses are carried out for the obtained cement based on the different raw mixes.

It should be noted that the plasma-chemical reactor has a 70–85 % performance factor, a wide operational change of power and temperature. It is characterized by compactness and capable of generating the highly-concentrated thermal flux on a small scale. The use of the highly-concentrated thermal flux assists in the reduction in metal consumption for manufacturing the equipment and organization of mobile manufacture.

4. Conclusion

Based on the thermodynamic analysis of the synthesis of calcium silicates, aluminates and alucoferrites, it can be concluded that the use of the low-temperature plasma for the synthesis of the cement clinker is advisable for the raw mixes of interest and their C:S ratio. It is shown that in the traditional temperature range of 1000–1800 K, the formation of minerals and the sequence of reactions remains at C:S = 3.32:1 oxide content in the raw mixes and is as follows: C\(_2\)S, C\(_3\)S, C\(_3\)S\(_2\), CS. With the temperature increase up to 3000 K, this sequence changes: C\(_3\)S, C\(_2\)S, C\(_3\)S\(_2\), CS. Starting from 2180 K, the most stable compound formed is C\(_3\)S which is not feasible by applying the traditional technology (1673–1723 K). Thus, the use of the highly-concentrated thermal flux in cement production offers a unique opportunity for modifying the consistency of chemical reactions during the formation of clinker minerals and has a positive effect on the quality and properties of the obtained product.

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