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Effect of Cr_2O_3 and NiO additions on the phase transformations at high temperature in Portland cement

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Abstract

Although there exists much work to characterize the effect of minor elements on the properties of Portland cement, the same is not valid for the knowledge about their impact on the clinkering process. The goal of this work is to study the effects of chromium and nickel oxide additions on the transformations during the production of Portland cement clinker. The experiments were carried out using a differential thermal analysis (DTA) piece of equipment to obtain the heating and cooling transitions. Samples were prepared using high-purity reactants. The achieved results showed that the Cr_2O_3 additions to cement raw meal act as an inhibitor of C_2S formation and increase the amount of liquid phase. On the other hand, NiO has very little effect on the clinkering reactions, but NiO does cause a small increase in the temperature of C_2S formation and an opposite effect on the temperatures of liquid and the polymorphic transformation of C_2S.

Keywords: Thermal analysis; Chromium; Nickel; Portland cement; Clinker

1. Introduction

The production of Portland cement clinker in rotary cement kilns uses many sources of calcium, aluminum, silicon and iron oxides in the raw meal; although, not an essential element, chromium is always present in the charge. On average, 16 ppm of chromium are found in limestone and 100 ppm are found in clay. About 80 ppm of chromium are found in char and 50 ppm are found in oils [1], which are fuels used in rotary cement kilns. Another source of chromium is the contamination from abrasive wear that happens on the cast iron balls during the milling of the raw meal in ball mills. The use of bauxite as a source alumina may also increase the amount of chromium in the final product [2].

In the clinker production process, around 93% of the total chromium fed to the kiln is transferred to the clinker [1]. The incorporated chromium is described as Cr_2O_3, and this compound reduces the viscosity of liquid during the process of clinker formation [3].

The chromium distributes in belite, ferrite, alite and in the calcium aluminate according to the data shown in Table 1 [4].

Indeed, the most important effect of chromium additions on the Portland cement is the inhibition of the C_3S formation [5]. It was also observed that for Cr_2O_3 concentrations above 0.5 wt.%, there occurs an increase in free CaO [5].

The hydration behavior depends directly on the concentration of crystalline imperfections in the phases. Chromium promotes distortions of the crystalline structure; also, Cr–O bonds are weaker than Ca–O bonds; thus, this explains the observed increase in the hydrating heat and cure time when chromium is present in the cement [6].

Chromium is considered to be present in the cement as Cr^{3+}, but under oxidizing atmospheres, it exists as Cr^{4+}, $Cr^{4.6+}$ and Cr^{5+}. In such valences, chromium may occupy the Si^{4+} places in the C_2S crystalline structure [2]. Cr^{6+} may be present in belite and alite, and it promotes the stabilization of β-C_2S [2].

The main sources of nickel in the production of Portland cement are limestone (1.5–7.5 ppm), clay (61–71 ppm), coal (20–80 ppm), oil (3–30 ppm) and coke (208 ppm) [1]. Ninety-seven percent of nickel fed into the rotary cement kiln is transferred to the clinker [1]. The NiO concentrates in the ferrite, but NiO is also present in the alite and belite. When NiO is present from 0.5% to 1.0%, it stabilizes the alite, where the NiO replaces the CaO in the crystalline

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Table 1
Chromium distribution in a clinker where 0.55 wt.% Cr was fed in the charge [4]

Phase	Cr (wt.%)
C_2S	0.87
C_4AF	0.55
C_3S	0.39
C_3A	0.04

Table 2
Raw meal composition

Charge before calcination (%)		Calcinated burden (%)	
$CaCO_3$	79.52	CaO	68.51
SiO_2	14.52	SiO_2	22.33
Al_2O_3	3.82	Al_2O_3	5.87
Fe_2O_3	2.14	Fe_2O_3	3.29

structure. The NiO stabilizes the alite in the monoclinic structure [2].

2. Objective

The aim of the present work is to study the effects of chromium oxide and nickel oxide additions on the phase transformations that occurs in the clinkering process.

3. Experimental procedures

To isolate the effect of chromium oxide and nickel oxide additions, a mixture of pure oxides that simulate a typical Portland cement composition, was prepared. The Bogue calculation [7] was also used to calculate the amounts of calcium carbonate, alumina, hematite and silica to obtain the following proportion of phases in the final product: 65% C_3S, 15% C_2S, 10% C_3A and 10% C_4AF. The reached composition is indicated in Table 2.

The size of particles of oxides was always less than 50 μm. The mixtures were homogenized in a ceramic ball mixer.

The samples were prepared to reach the specified Cr_2O_3 final concentrations: 0.05%, 0.10%, 0.30%, 0.50%, 0.80% and 1.00%. Analogously, in the second set of tests, NiO was used using the same concentrations as the chromium oxide ones.

Eq. (1) was used to evaluate the additions:

$$\%C = \frac{MC}{(MM \times (1 - PF)) + MC} \tag{1}$$

where: %C is Cr_2O_3 (or NiO) concentration; MC is the mass of Cr_2O_3 or (NiO); MM is the mass of raw meal and PF is the calcining loss.

The mixtures were chemically analyzed prior to and after calcining, using an atomic absorption spectrophotometer to confirm the calculated composition and also to check some chemical modification.

A simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TG) NETZSCH STA-409C piece of equipment was used to determine the reaction temperatures involved in the clinkering process and mass losses during the heating and cooling cycle.

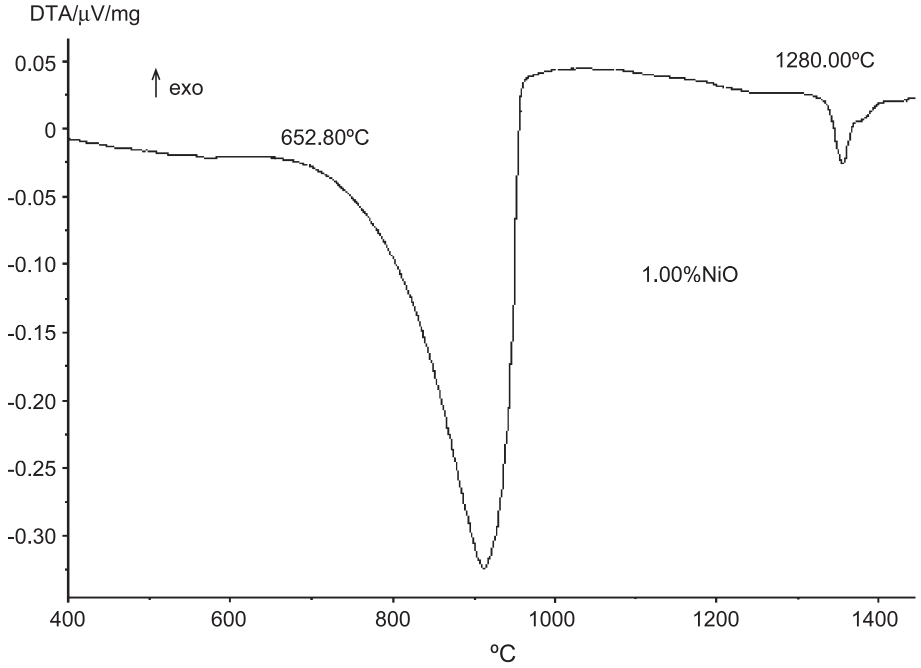

Fig. 1. DTA curve for the 1.0% NiO test showing the decomposition of $CaCO_3$ and the clinkering reactions.

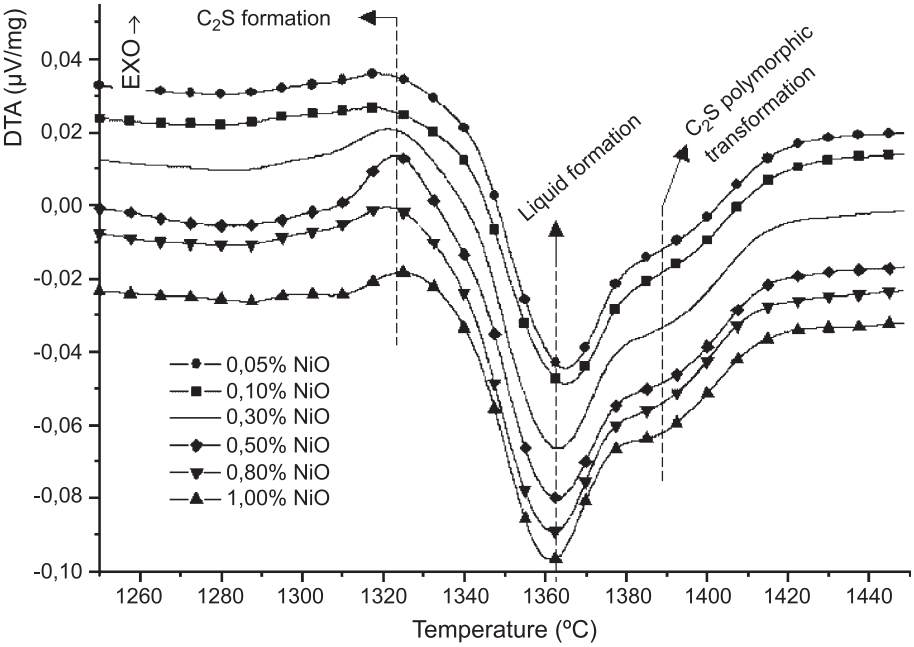

Fig. 2. Detailed curves showing the clinkering reactions for the samples containing NiO.

The parameters were set as follows:

Heating rate: 10 °C/min,
Hold temperature: 1450 °C,
Hold time: 20 min,
Cooling rate: 10 °C/min,
Gas: synthetic air (10 ml/min),
Mass of sample: 140–150 mg,
Crucible: platinum, and
Reference: alumina.

4. Results and discussion

4.1. Influence of NiO

During the heating up cycle, the DTA curves presented only the decomposition of $CaCO_3$ and the clinkering reactions. Fig. 1 presents a typical whole curve for these tests. Fig. 2 shows detailed curves for the region where the clinkering reaction occurs. The clinkering reactions were identified in Fig. 2 [7–12].

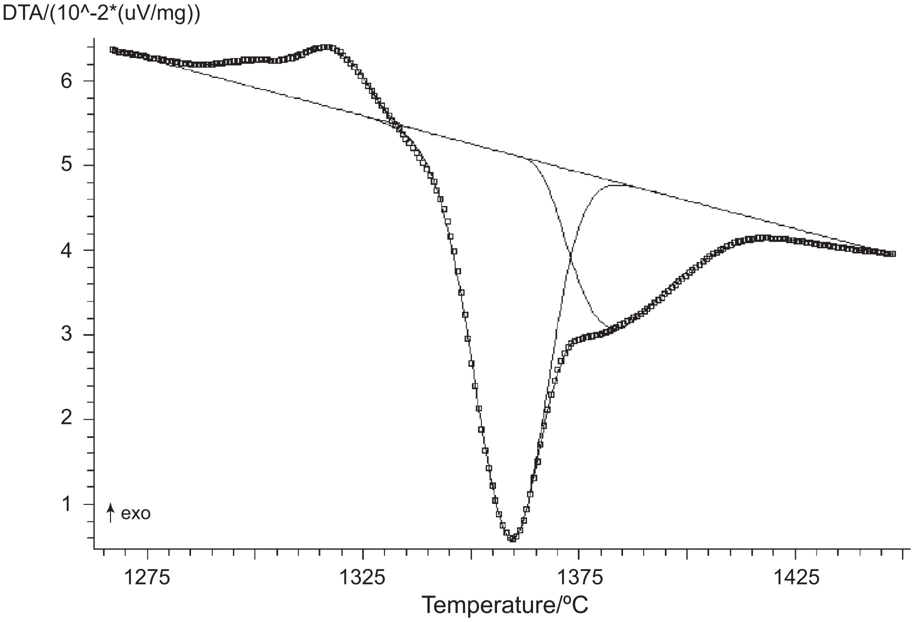

Fig. 3. Curve illustrating the peak separation method.

Table 3
Enthalpy of clinkering reactions for the samples containing NiO (J/g)

NiO (%)	C_2S formation	Liquid formation	C_2S polymorphic transformation
0.00	0.56	1.92	0.89
0.05	0.59	2.07	0.90
0.10	0.51	2.10	0.85
0.30	0.68	2.01	0.98
0.50	0.44	2.05	0.92
0.80	0.66	2.11	0.92
1.00	0.50	1.93	0.87

All the NiO added to the charge was not lost during the processing; this behavior was also observed in a previous work using a larger amount of samples that allowed chemical analysis of the product [13].

The reaction enthalpies were calculated through the peak separation method. The use of this technique allows the separation of events that overlap in the clinkering process. Initially, the first derivative of the curve is drawn, which allows a better identification of the peaks. After identification of the onset and offset of each peak, the software graphically isolates the contribution of each peak to the overall curve, as illustrated in Fig. 3.

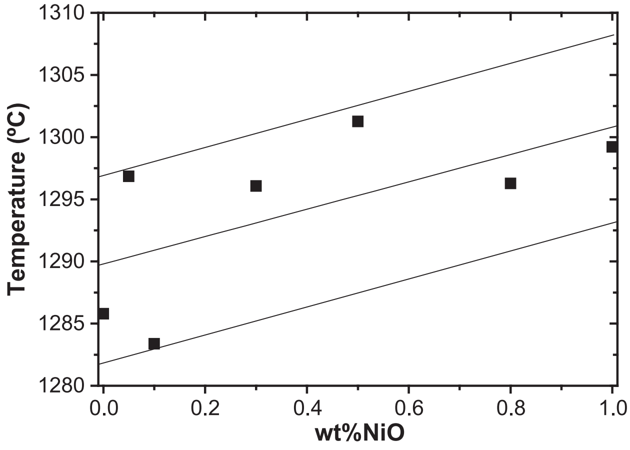

Fig. 4. Effect of NiO additions on temperatures of C_2S formation.

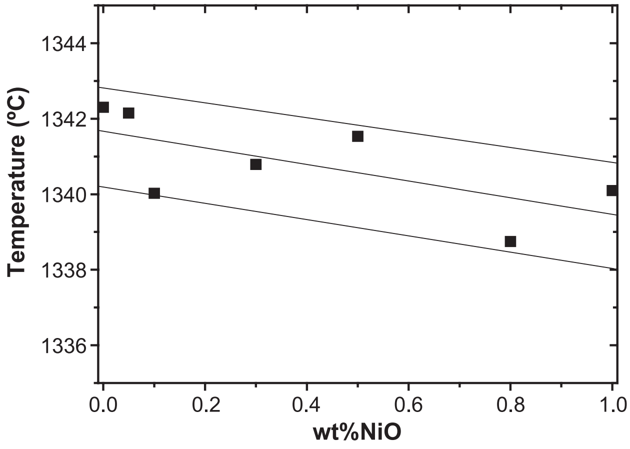

Fig. 5. Influence of NiO concentration in the temperatures of liquid formation.

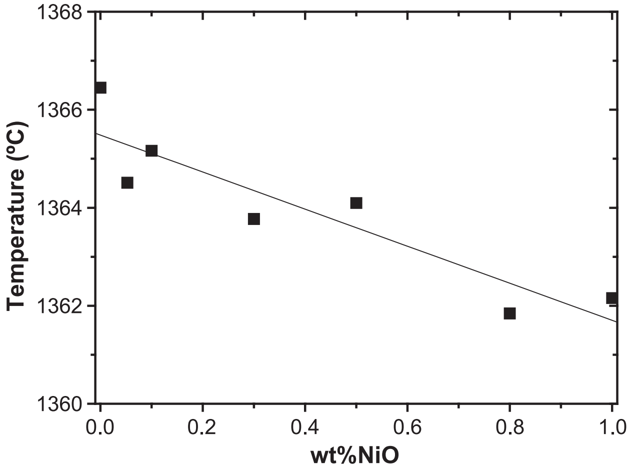

Fig. 6. Effect of NiO concentration on the C_2S polymorphic transformation.

The NiO additions exhibit little effect on the enthalpy of clinkering reactions as shown in Table 3. The same behavior was observed for the effect of NiO additions on the temperatures of clinkering reactions. Data from Fig. 2 were used to plot Figs. 4–7. Fig. 4 shows that the increase in the NiO content in the charge can cause a small increase in the temperature of C_2S formation. On the other hand, Figs. 5 and 6 show the opposite effect, respectively, in relation to temperatures of liquid formation and the polymorphic transformation of C_2S, $\alpha'_H \rightarrow \alpha$.

The reactions during the solidification are affected by the NiO additions as shown in Fig. 7. NiO goes preferentially to the C_4AF and to the C_3A [2] because these are the main phases in the liquid. Thus, the NiO incorporation to the clinker lowers the temperature of liquid crystallization.

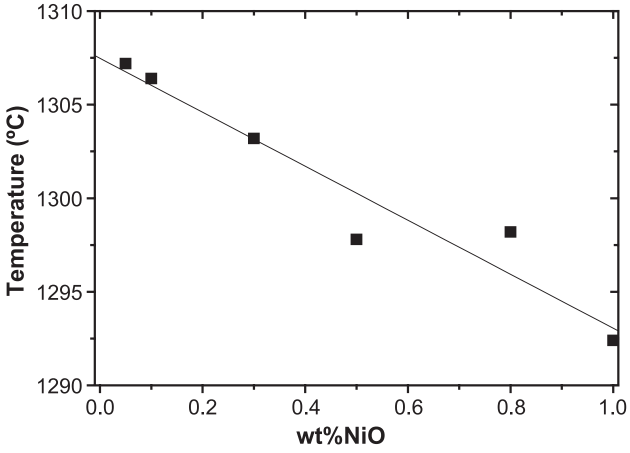

Fig. 7. Influence of NiO additions in the temperature of liquid decomposition.

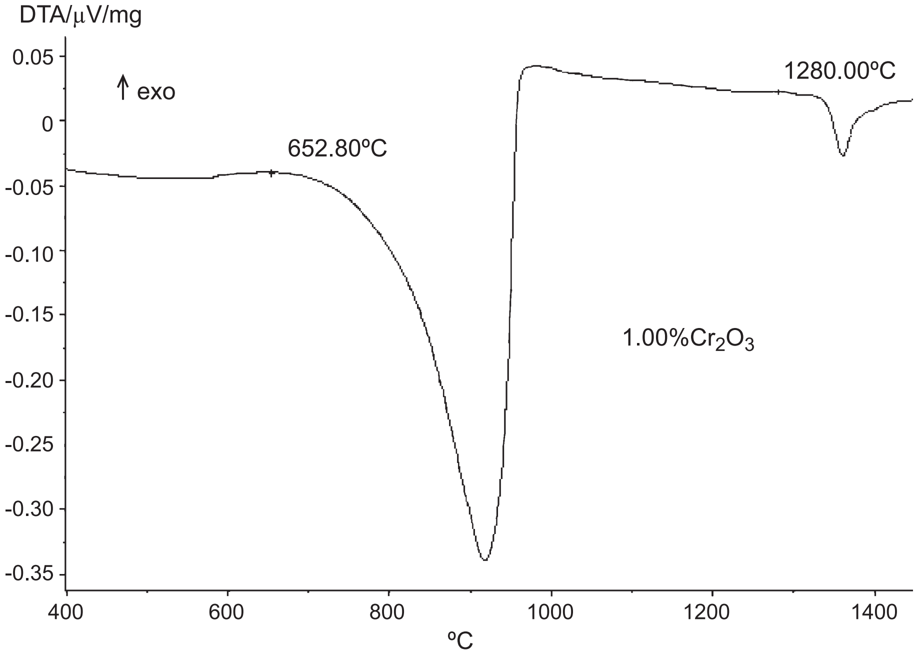

Fig. 8. DTA curve for the sample containing 1.0 wt.% Cr_2O_3.

4.2. Influence of Cr_2O_3

Analogous to thermogravimetric tests with NiO additions, the only mass loss event during the heating was the decomposition of calcium carbonate. All the Cr_2O_3 added to the charge was not lost during the processing; this behavior was also observed in previous works using bigger amounts of samples that allowed chemical analysis of the product [13,14].

The DTA curves present the temperature range for the clinkering reactions. The DTA curve for the addition of 1.0 wt.% Cr_2O_3, presented in Fig. 8, exhibits only the $CaCO_3$ decomposition and the clinkering reactions. The clinkering reactions were identified using the peak separation method and the temperatures for C_2S formation, liquid formation and polymorphic C_2S transformation were discriminated. Moreover, through this method, the enthalpies of each reaction were calculated.

Table 4
Enthalpies of clinkering reactions (J/g)

Cr_2O_3 (wt.%)	C_2S formation	Liquid formation	C_2S polymorphic transformation
0.00	0.56	1.92	0.89
0.05	0.42	1.37	1.03
0.10	0.32	1.50	0.88
0.30	0.26	1.71	0.78
0.50	0.15	1.94	0.70
0.80	0.11	2.08	0.58
1.00	0.09	2.11	0.43

The results indicate that chromium acts as an inhibitor of C_2S formation, and this is evidenced by the decrease in the C_2S exothermic peak. Moreover, the intensity of the last endothermic peak, which corresponds to $\alpha'_H \rightarrow \alpha$, also decreases with the increase of Cr_2O_3 concentration.

Table 4 presents the results of reaction enthalpies calculated through the peak separation method. Through the observation in Fig. 9, it is possible to realize the effect of Cr_2O_3 on the enthalpy of formation of C_2S; in Fig. 10, it is possible to observe the same effect for polymorphic transformation of C_2S.

In both cases, the reduction of the heat produced by the reaction indicates a reduction in C_2S formation as the Cr_2O_3

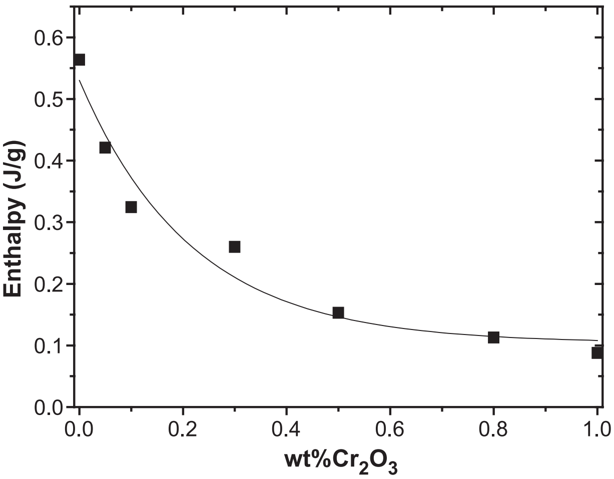

Fig. 9. C_2S formation enthalpy as a function of Cr_2O_3 concentration.

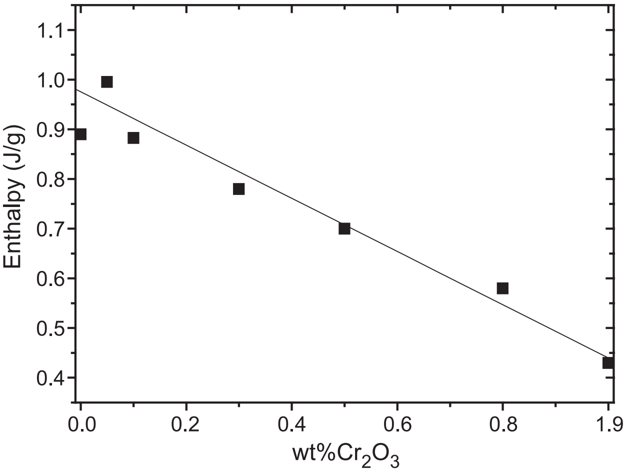

Fig. 10. Effect of Cr_2O_3 additions on the enthalpy of polymorphic transformation of C_2S.

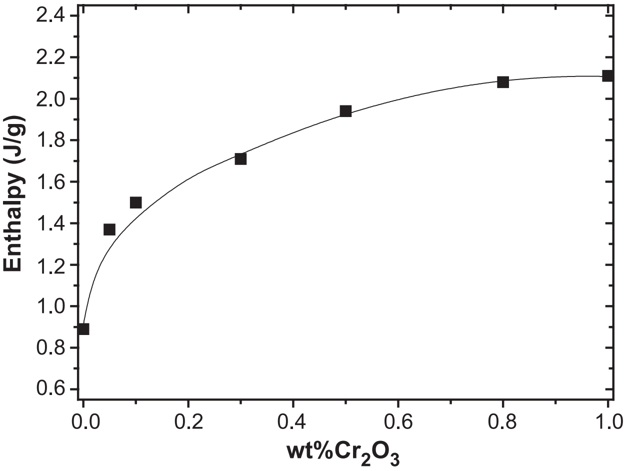

Fig. 11. The influence of the Cr_2O_3 concentration on the enthalpy of liquid formation.

concentration increases. These facts are further evidence of the effect of chromium on the inhibition of belite formation.

As C_2S formation is inhibited by the addition of Cr_2O_3, there is a greater amount of free CaO during the clinkering reactions. This promotes an increase in the enthalpy involved in the liquid formation because there exists more CaO available for the C_3S formation, as illustrated in Fig. 11.

Table 5
Temperatures of clinkering reactions (°C)

Cr_2O_3 (wt.%)	C_2S formation	Liquid formation	C_2S polymorphic transformation
0.00	1285	1342	1366
0.05	1288	1343	1365
0.10	1281	1343	1368
0.30	1280	1342	1366
0.50	1284	1342	1366
0.80	1272	1342	1364
1.00	1275	1341	1365

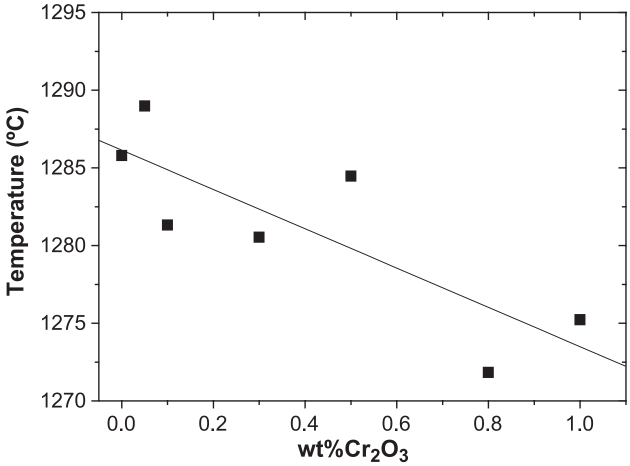

Fig. 12. Effect of concentration of Cr_2O_3 on the C_2S temperature of formation.

As Cr_2O_3 concentration increases, the reactions of temperatures for the liquid formation and polymorphic transformation of C_2S were not affected, as shown in Table 5. In Fig. 12, it is possible to verify a decrease of about 10 °C in the temperature of C_2S formation.

Although the initial temperatures of transformation, during the cooling cycle, remain the same, as shown in Table 6, there was a spread on the base of the peaks. The decrease in the amount of C_2S implies an increase in the quantity of C_3S and consequently favors the peritectic reaction where C_3A and C_4AF are formed.

5. Conclusions

1. Cr_2O_3 additions to cement raw meal act as inhibitors of C_2S formation.
2. Cr_2O_3 additions increase the amount of liquid phase, in spite of the fact that they do not affect the temperature of liquid phase formation.
3. NiO causes very little effect on the clinkering reactions, but NiO causes a small increase in the temperature of C_2S formation and an opposite effect on the temperatures of liquid and the polymorphic transformation.

Table 6
Enthalpies and transformation temperatures for the liquid phase

Cr_2O_3 (wt.%)	Enthalpy (J/g)	Transformation temperature (°C)
0.05	2.87	1302
0.10	3.23	1304
0.30	3.26	1305
0.50	3.18	1306
0.80	3.16	1306
1.00	3.11	1306

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