



Chloride influence on the incorporation of Cr_2O_3 and NiO in clinker: a laboratory evaluation

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Abstract

Co-incinerating wastes in cement rotary kilns may introduce elements not usually found in the raw material into the process or even increase the quantity of some minor elements. Chromium and nickel are present in some electroplating sludges. These wastes are hazardous and must be treated and disposed of in a controlled landfill. The objective of this work was to study the incorporation of chromium and nickel oxides when they were added to clinker raw meal. The clinker raw meal used in this study was prepared by mixing pure compounds in the ratio that made it possible to obtain the same phases of an industrial Portland clinker at the end of the heating process. Twelve samples were prepared by adding 0.05, 0.1, 0.3, 0.5, 0.8 and 1.0 wt.% of Cr_2O_3 and 0.05, 0.1, 0.3, 0.5, 0.8 and 1.0 wt.% of NiO to the base charge. Also, four more samples were prepared with additions of 0.6% Cr_2O_3 and 0.1% NaCl, 0.7% Cr_2O_3 and 0.1% KCl, 0.8% NiO and 0.1% NaCl and 0.8% NiO and 0.1% KCl. In order to study the Cr and Ni incorporation, thermogravimetric (TG) tests were performed, as well as tests in an assembled experimental device. The products were characterized by X-ray fluorescence chemical analysis, microprobe analyses by energy disperse scanning (EDS) and leaching tests. The results showed that the chromium and nickel added were incorporated into the clinker, even when chlorides were present. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Waste co-incineration in cement rotary kilns is generally classified as a treatment process similar to incineration [1,2]. This fact is due largely to the high temperature of the clinker production process and to the reactor length, which leads to a longer residence

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time of the charge when compared to standard incinerators. Nevertheless, the metal incorporation makes the co-incineration in cement rotary kilns different from the incineration process.

Galvanic sludge is the waste generated in the electroplating process. This sludge is considered hazardous waste due to its heavy metal content. Therefore, galvanic sludges must be treated or disposed of in controlled landfills. As a result of the process that generates the sludge, the heavy metals are generally in the form of hydroxides [3]. These hydroxides, when heated, decompose to oxides. Chromium and nickel are frequently found in galvanic sludges.

During waste co-incineration in cement kilns, a fraction of the hazardous metal is incorporated into the clinker, while another fraction is liberated into cement kiln dust (CKD). Mantus [4] summarized the emissions from cement kilns using conventional fuel and using waste as a secondary fuel source and showed that metal emissions did not differ significantly in these two situations.

The main problem of the conventional approach is the monitoring of the emissions produced by waste additions on an industrial scale. In many cases, the amount of waste added to the raw meal increases only slightly the metal content in charge, maintaining the metal concentration within its natural concentration range. Fuel and cement raw meal have some elements that tend to become concentrated in CKD. This behavior makes the detection of the evaporation mechanism of these elements practically impossible; and, therefore, the understanding of the process reactions is not effectively complete.

This work presents a new approach to understand the process of metals incorporation during the clinkering process. The conditions during the process of Portland cement clinker production were simulated in a laboratory reactor, which allows a better understanding of the character of the reactions taking place in the co-incineration process.

This work studies the incorporation of chromium and nickel oxides in synthetic cement clinker, as well as the influence of chloride additions upon the incorporation of these oxides. The chloride additions were studied because of one characteristic of clinker raw materials and galvanic sludges, which is they contain chlorine [5,6]. Chromium and nickel oxides were added individually to the clinker raw meal.

On a regular basis, chlorine is added to cement kilns through raw materials such as clay (15–450 ppm) and limestone (50–240 ppm). In these raw materials, the chlorine is usually in the form of sodium chloride, mainly if they come from seaside areas. The primary and secondary fuels can also bring chlorine into cement kilns; the fuels can contain up to 1100 ppm of chlorine [7,8].

The presence of alkalis, Na_2O and K_2O , is common in cement kilns. These compounds are also found in the raw materials. Portland cement should contain between 0.5 and 1.3% of $\text{K}_2\text{O} + \text{Na}_2\text{O}$. The incorporation ratio of these oxides is nearly 50% [9]. Sodium and potassium oxides are volatile compounds: under the clinkering temperature they volatilize and condense in regions of the cement kiln system which are below 700 °C, forming rings of condensed material that can compromise the kiln [10,11,13].

The chlorine in the fuels and raw materials occurs in the ionic form or compound form [2]. During the combustion, the chlorine forms chlorine gas (Cl_2) or HCl and under the temperature and turbulence within the kiln, these gases convert all Na_2O and K_2O to NaCl and KCl [8,9,11]. Sodium and potassium chlorides are more volatile than their oxides;

calcium chloride additions can be used to eliminate the alkalis in the cement production process [9]. Therefore, one can conclude that within the cement kiln, chlorine takes the form of NaCl and KCl.

Sodium and potassium chlorides also condense in the colder regions of the cement kiln system, besides the fact that they have a longer residence time inside the kiln. In the cement kiln, the maximum chloride content admitted in the charge is 0.02% [10].

In the case of systems that have preheaters and precalciner kilns, chlorides exit the system before entering the cement kiln itself [8,11], hence there is no risk of condensed material formation and higher chloride content is admitted in the charge. Nevertheless, the maximum content of chlorides becomes a function of the dust control system efficiency [8].

1.1. Objectives

The objective of this work was to study the incorporation of chromium and nickel oxides when they were added to clinker raw meal. Another objective was to verify the influence of chloride additions on the incorporation ratio of chromium and nickel.

2. Materials and methods

In this paper, the cement industry nomenclature is used to name the clinker main phases. This shorthand is C = CaO, S = SiO₂, A = Al₂O₃ and F = Fe₂O₃. Thus, the main clinker phases are written as follows:

- C₃S: tricalcium silicate (alite);
- C₂S: dicalcium silicate (belite);
- C₃A: tricalcium aluminate;
- C₄AF: tetracalcium aluminoferrite (ferrite).

Portland cement clinker consists essentially of C₃S, C₂S, C₃A, C₄AF, MgO and CaO. Gypsum is added during the clinker grinding in order to control the setting time of the cement. Knowing the composition and proportion of the raw materials, it is possible to calculate the potential phase composition of the clinker. This calculation is known as Bogue calculation [12].

2.1. Mixtures preparation

All the compounds used in this work were 99.999% pure. The composition of the clinker raw meal, henceforth called base mixture, was calculated to provide the same phases as the main phases of a real Portland clinker. Using the Bogue calculation, the base mixture was calculated to have 65% C₃S; 15% C₂S; 10% C₃A and 10% C₄AF after the heating process. Table 1 shows the base mixture composition using the Bogue calculation. The mixtures were prepared following the equation:

$$\%O = \frac{OM}{(BM(1 - LI)) + OM},$$

Table 1
Base mixture calculated through the Bogue calculation

Compound	Non-calcined base mixture (%)	Calcined base mixture (%)
CaCO ₃	79.52	68.51
SiO ₂	14.52	22.33
Al ₂ O ₃	3.82	5.87
Fe ₂ O ₃	2.14	3.29
CaO		68.51

where %O is the percentage of chromium or nickel oxide, OM the chromium or nickel oxide mass, BM the base mixture mass, and LI the loss on ignition. The calcium carbonate calcination corresponds to a loss on ignition of 35 wt.%. This behavior was confirmed in the thermogravimetric (TG) tests.

Mixtures were prepared to have, after calcination, the following quantities of chromium or nickel oxides: 0.05, 0.10, 0.30, 0.50, 0.80 and 1.00%. The oxides were placed into a ceramic pot with corundum balls; the ceramic pot was closed and placed on rotating cylinders for 4 h to homogenize the mixture. Four more mixtures were prepared with the addition of chlorides. Table 2 shows the prepared mixtures used as charges.

2.2. Thermogravimetric tests

TG tests were performed on all mixtures in a Netzsch STA 409C piece of equipment. The tests parameters were as follows:

- heat rate: 10 °C/min up to 1450 °C;
- residence time at 1450 °C: 20 min;

Table 2
Prepared mixtures

Mixture	Cr ₂ O ₃ (%)	NiO (%)	NaCl (%)	KCl (%)
C05	0.05	–	–	–
C10	0.10	–	–	–
C30	0.30	–	–	–
C50	0.50	–	–	–
C80	0.80	–	–	–
C100	1.00	–	–	–
Ni05	–	0.05	–	–
Ni10	–	0.10	–	–
Ni30	–	0.30	–	–
Ni50	–	0.50	–	–
Ni80	–	0.80	–	–
Ni100	–	1.00	–	–
CrNa	0.60	–	0.10	–
CrK	0.70	–	–	0.10
NiNa	–	0.80	0.10	–
NiK	–	0.80	–	0.10

- cooling rate: 10 °C/min up to 900 °C;
- gas flow: 10 cm³/min of synthetic air (80% N₂ and 20% O₂);
- platinum crucible;
- reference: alumina.

2.3. Experiences in the set-up apparatus

A laboratory device was assembled to simulate the thermal cycle imposed on the charge during Portland clinker production. This device is composed of an electric furnace that can heat up to 1700 °C, a corundum tube retort and a system to condense the vapors formed during the heating process. This condensation system is, basically, a water-refrigerated stainless steel stem with a copper extremity. A more detailed description of this device can be found elsewhere [13].

Briquettes were made using all mixtures shown in Table 2. The briquettes were prepared using a manual press with a 25 mm diameter tool steel matrix. Three briquettes were placed in a corundum crucible and then the crucible was positioned in the middle of the retort. The heating rate adopted was 15 °C/min up to 1450 °C and the gas flow was 10 cm³/min of synthetic air.

Two kinds of samples could be collected in each test: briquettes and condensed material. The samples were characterized by X-ray fluorescence chemical analysis or microprobe analyses by energy disperse scanning (EDS). Samples of the produced briquettes went through leaching tests in order to verify the effective incorporation of the metals in the clinker matrix.

3. Results and discussion

3.1. Cr₂O₃ additions

TG tests were carried out with samples of the mixtures containing 0.05, 0.10, 0.30, 0.50, 0.80 and 1.00% of Cr₂O₃. The resulting curves did not show any mass loss after the CaCO₃ decomposition. This fact indicates that the chromium remained in the mixture, not being released to the furnace atmosphere; hence all Cr₂O₃ was incorporated into the mixture.

In order to confirm these results on a larger scale, tests were performed with the same mixtures in the simulator device. After the heating cycle, the briquettes were rapidly cooled in alcohol to avoid the C₃S decomposition. The composition of the briquettes was analyzed by X-ray fluorescence chemical analysis. The results of the chemical analyses are shown in Table 3.

The results presented in Table 3 show that the Cr₂O₃ is totally incorporated into the charge when added to clinker raw meal. This result agrees with Sprung's [11] results, which show 93% of Cr incorporation in cement furnaces. This result also agrees with Espinosa and Tenório [13], who studied additions of galvanic sludge, containing only Cr as restriction metal, to Portland cement raw meal. Espinosa and Tenório reported a ratio of Cr incorporation over 99% for additions of up to 3 wt.% of galvanic sludge, while the studied galvanic sludge contained 4 wt.% of Cr.

Table 3

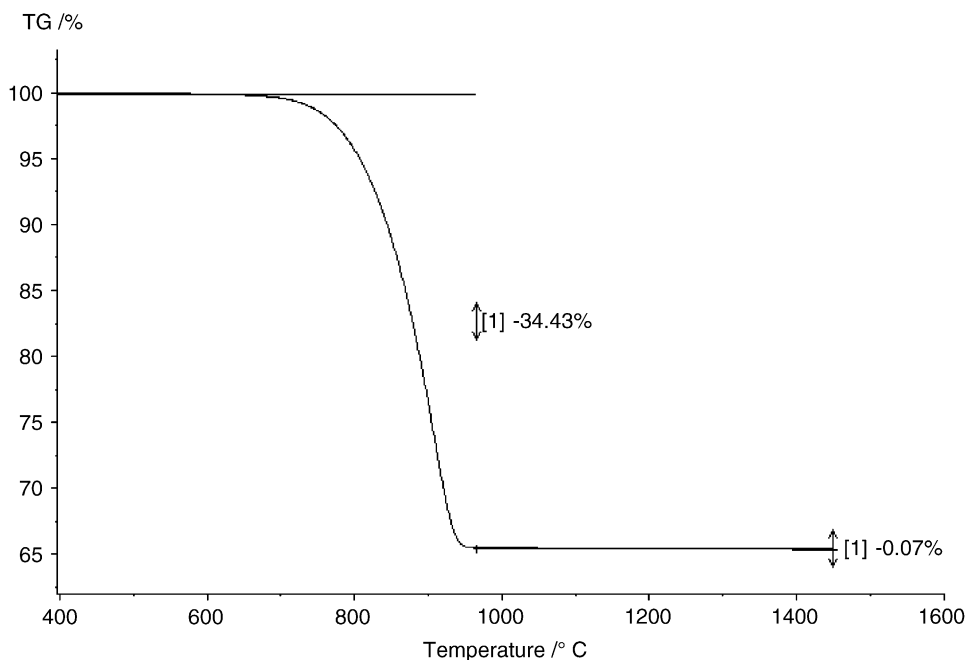
Chemical analyses results of the briquettes with Cr_2O_3 additions after treatment in the simulator device

	Cr_2O_3 (%)					
	0.05	0.10	0.30	0.50	0.80	1.00
Al_2O_3 (%)	4.73	4.61	4.82	4.91	4.76	4.65
SiO_2 (%)	19.50	19.60	19.30	19.60	19.40	19.30
CaO (%)	72.22	72.23	71.90	71.74	71.60	71.70
Fe_2O_3 (%)	3.49	3.44	3.65	3.29	3.46	3.36
Cr_2O_3 (%)	0.06	0.12	0.33	0.46	0.78	0.99

3.2. Cr_2O_3 and chloride additions

TG tests were carried out for the samples containing additions of 0.60% Cr_2O_3 and 0.10% NaCl to the base mixture (CrNa) and containing additions of 0.70% Cr_2O_3 and 0.10% KCl to the base mixture (CrK). The curve for the test with the sample CrNa is shown in Fig. 1 and for the test with the sample CrK can be seen in Fig. 2. One can notice that after the CaCO_3 decomposition there is a mass loss of 0.07%. This mass loss would correspond exactly to the 0.10% of chloride addition, which completely evaporates.

Tests in the simulator device were also performed; the results of the chemical analyses of the briquettes after the treatment appear in Table 4. These results indicate that there is

Fig. 1. TG curve of the sample CrNa (0.60% Cr_2O_3 + 0.10% NaCl).

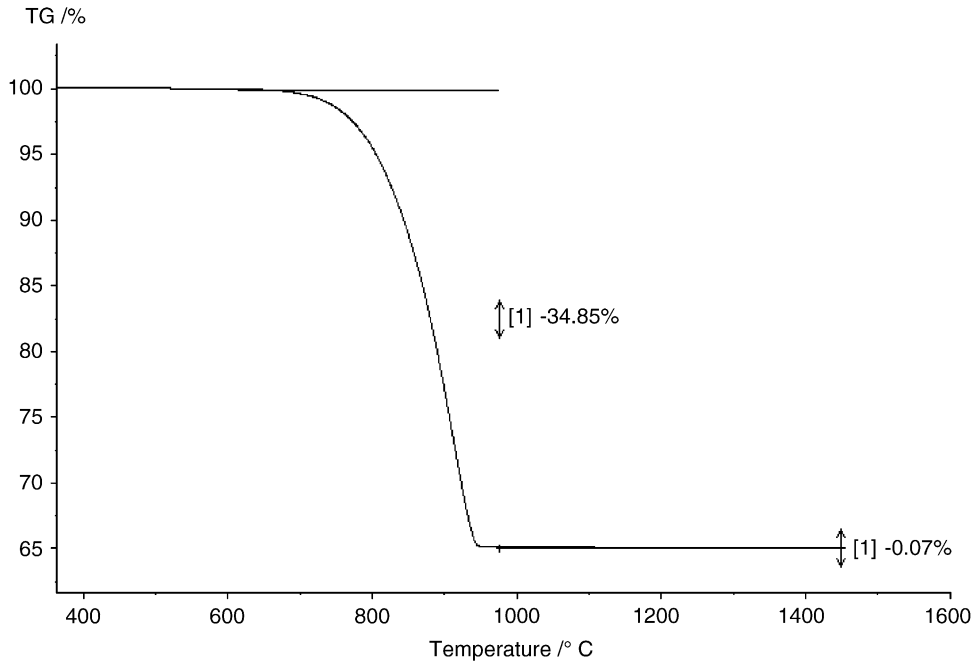


Fig. 2. TG curve of the sample CrK (0.70% Cr₂O₃ + 0.10% KCl).

no presence of NaCl or KCl in the briquettes after the test and the final composition of the briquettes was not modified by the chloride presence.

In the tests carried out in the simulator device with the briquettes of the mixtures CrNa and CrK, some material could be collected from the condensation system, but the condensed material amount was not enough to use for X-ray fluorescence chemical analysis, so microprobe analysis by EDS coupled to an scanning electronic microscope (SEM) was performed. The result spectra for both tests are shown in Fig. 3. It can be seen that only Na and Cl were identified on the condensed material from the test made with the mixture CrNa and only K and Cl were identified on the condensed material from the test made with the mixture CrK.

The results shown in this section demonstrate that NaCl and KCl presence in the cement raw meal does not affect the Cr₂O₃ incorporation ratio. This result agrees with the data found

Table 4

Chemical analyses results of the CrNa (0.60% Cr₂O₃ + 0.10% NaCl) and CrK (0.70% Cr₂O₃ + 0.10% KCl) briquettes after treatment in the simulator device

	CrNa (%)	CrK (%)
Al ₂ O ₃	4.81	4.79
SiO ₂	19.80	19.70
CaO	71.30	71.50
Fe ₂ O ₃	3.49	3.34
Cr ₂ O ₃	0.60	0.67

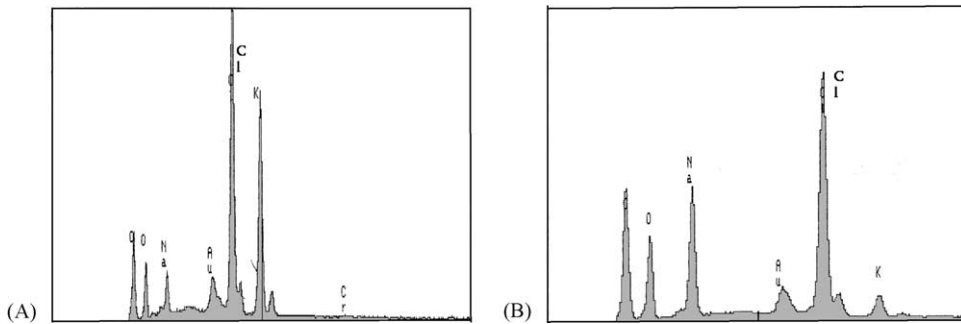


Fig. 3. EDS spectra of the condensed material in the tests performed in the simulator device with the mixtures CrNa (A) and CrK (B).

in the literature. Some [14–16] studied the influence of chlorides on the Cr_2O_3 evaporation ratio and verified that the Cr_2O_3 evaporation ratio was negligible.

3.3. NiO additions

The same tests performed for the Cr_2O_3 additions were done for the NiO additions, and TG tests were carried out for the samples containing 0.05, 0.10, 0.30, 0.50, 0.80 and 1.00% of NiO. The only mass loss verified in these tests was the one related to the CaCO_3 decomposition. This result indicates that all NiO was incorporated into the clinker during the heating process.

Briquettes of all mixtures containing NiO additions were treated in the simulator device. Chemical analyses of the resulting material were performed. The chemical analyses results are shown in Table 5. It is seen from these results that all NiO was incorporated into the clinker. This result agrees with Sprung [11], who observed that 97% of the Ni inserted in the cement kiln is incorporated into the clinker.

3.4. NiO and chloride additions

Since chlorine is an element commonly found in galvanic sludges, two mixtures containing NiO and chloride were made in order to investigate the effect of chlorides in the NiO

Table 5
Chemical analyses results of the briquettes with NiO additions after treatment in the simulator device

	NiO (%)					
	0.05	0.10	0.30	0.50	0.80	1.00
Al_2O_3 (%)	4.63	4.67	4.71	4.61	4.79	4.84
SiO_2 (%)	19.60	20.40	19.66	20.10	19.80	19.33
CaO (%)	72.22	71.60	71.50	71.50	71.25	71.46
Fe_2O_3 (%)	3.50	3.25	3.83	3.33	3.37	3.39
NiO (%)	0.05	0.08	0.30	0.46	0.79	0.98

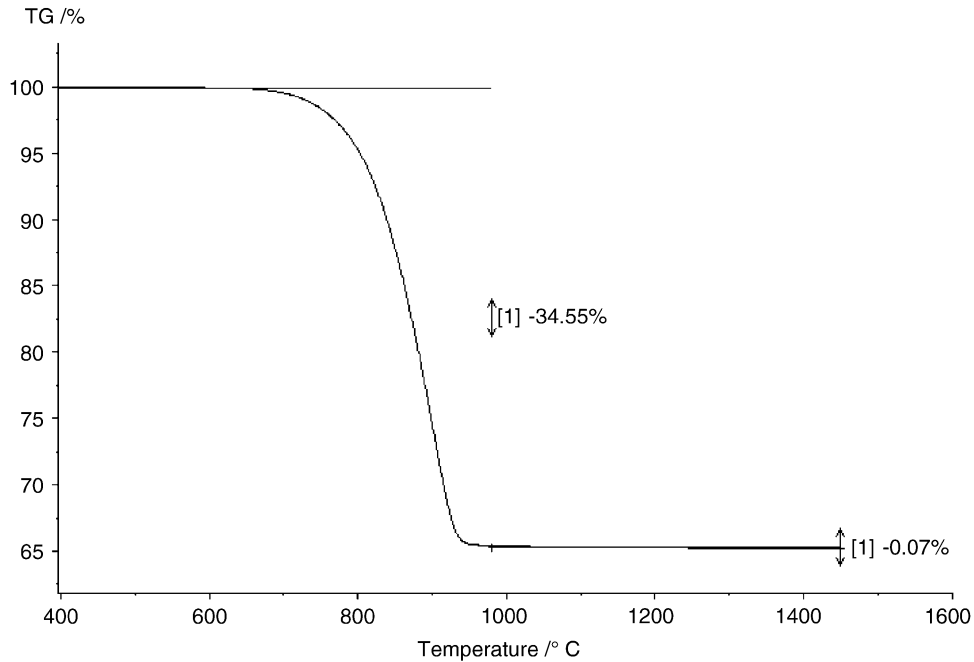


Fig. 4. TG curve of the sample NiNa (0.8% NiO + 0.1% NaCl).

incorporation ratio. These two mixtures were additions of 0.8% NiO and 0.1% NaCl to the base mixture (NiNa) and additions of 0.8% NiO and 0.1% KCl to the base mixture (NiK).

Fig. 4 shows the TG curve obtained in the TG test with a sample of the mixture NiNa. Fig. 5 shows the TG curve for the mixture NiK. Both curves have the CaCO_3 decomposition mass loss followed by a 0.07% loss of the total mass. This mass loss of 0.07% corresponds numerically to the 0.1% of chloride added, since the chloride was added to have 0.1% of the mixture's mass after calcination. Hence, these results indicate that just the chloride evaporated.

To confirm this theory, tests with these two mixtures (NiNa and NiK) were carried out in the simulation device. X-ray chemical analyses were performed on samples of the briquettes after the treatment. The chemical analyses results are presented in Table 6. The chemical

Table 6

Chemical analyses results of the NiNa (0.8% NiO + 0.10% NaCl) and NiK (0.8% NiO + 0.1% KCl) briquettes after treatment in the simulator device

	NiNa (%)	NiK (%)
Al_2O_3	4.47	4.65
SiO_2	19.50	19.50
CaO	71.80	71.50
Fe_2O_3	3.44	3.55
NiO	0.79	0.80

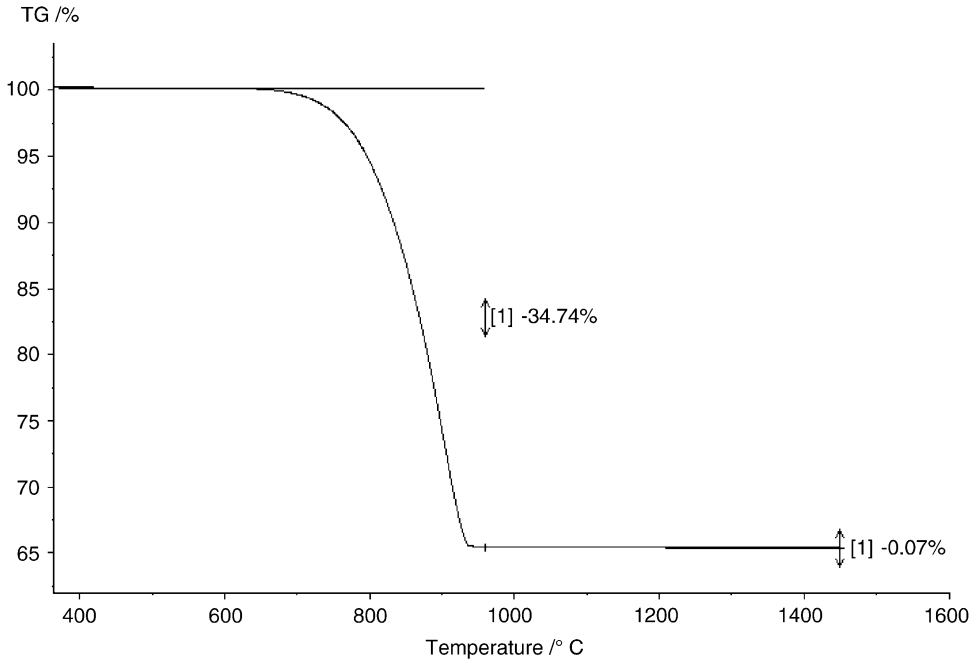


Fig. 5. TG curve of the sample NiK (0.8% NiO + 0.1% KCl).

composition of the briquettes shows that the presence of neither NaCl nor KCl affected the NiO incorporation ratio.

Some material could be collected from the condensation system, but its amount was not enough to use in X-ray fluorescence chemical analysis. Therefore, EDS analyses were performed on the condensed materials of both tests. The EDS spectra are shown in Fig. 6, which reveals that no Ni was identified in the condensed material.

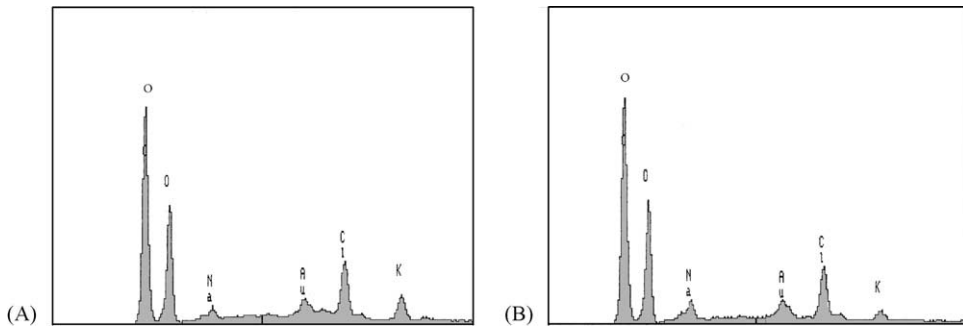


Fig. 6. EDS spectra of the condensed material in the tests performed in the simulator device with the mixtures NiK (A) and NiNa (B).

3.5. Leaching tests

Leaching tests were performed on three samples: C80, CrNa and Ni100. The results of the chemical analyses of the leaching solutions showed that Cr content in the solution was less than 0.55 mg/l and Ni content in the solution was 0.04 mg/l. These values are far below the legal limits.

4. Conclusions

The results presented in this work allow the following conclusions:

- Chromium and nickel oxides, when added to the clinker raw meal, do not evaporate during the burning process, and are thus incorporated into the clinker.
- NaCl and KCl additions do not interfere in the incorporation ratio of chromium and nickel oxides.
- NaCl and KCl added to the clinker raw meal evaporate entirely during the burning process.
- Additions of wastes containing chromium and nickel oxides in the clinker raw meal, up to 1% Cr₂O₃ and 1% NiO, would not affect the emission ratio of these metals, even if the wastes have chlorides. These oxides would be totally incorporated into the clinker.

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