

## Evaluation of the incorporation ratio of ZnO, PbO and CdO into cement clinker

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### Abstract

Zinc, lead, and cadmium are minor elements that might be brought by wastes to the cement kilns. This work studies the incorporation ratio of ZnO, PbO, and CdO when they are added to the clinker raw material. The cement raw material used in this work was prepared by mixing pure compounds, this choice was made to avoid the effect of other elements and provide a better understanding of the behavior of these metals during the clinkering process. The samples contained additions of 0.05, 0.10, 0.30, 0.50, 0.80 and 1.00 wt.% of a specific oxide (ZnO, PbO, or CdO) to the clinker raw-meal. The chlorine influence in the ZnO incorporation ratio was also evaluated. A device to simulate the thermal cycle imposed on the charge during the clinker production was used to evaluate the incorporation ratio of these oxides as well as thermogravimetric tests. The products of the tests in the simulator device were submitted to X-ray fluorescence chemical analysis or energy disperse scanning (EDS) microprobe analysis. The results led to the conclusions that the evaporation of Zn in cements kilns is due to the chlorine content and the Pb and Cd incorporation ratio stands around 50 wt.%.

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### 1. Introduction

This work studies the incorporation ratio of ZnO, PbO and CdO when they are added to the clinker raw-mixture. The clinker raw-mixture was made of pure compounds and calculated to have the same proportion of main phases as a Portland cement clinker at the end of the clinkering process. Since chlorine is commonly found in real cement clinker raw-mixture [1–3], the chlorine influence in the incorporation ratio of ZnO was evaluated.

The added compounds are volatile and can be introduced into the cement kiln by wastes. The study of their incorporation ratio in a cement raw-mixture made of pure compounds was chosen in order to avoid the effect of other elements and to gain a better understanding about what happens to these heavy metals during clinker production.

Zinc can be brought to cement kilns through lime (22–24 ppm of zinc), clay (59–115 ppm of zinc) and fuels (16–200 ppm of zinc) [4]. Nevertheless, waste

co-incineration can introduce materials containing a higher content of zinc, such as oil, which can contain up to 3000 ppm of zinc, and tires, which can contain 10 000 ppm of zinc [5].

Between 80 and 90 wt.% of the zinc introduced into the cement kiln is incorporated in the clinker [4]. ZnO reduces the temperature of the liquid phase formation by about 50–100 °C, which helps the clinkering reaction kinetic [1,6,7].

Lead is introduced into the cement kiln largely by conventional fuels or by wastes used as fuel [4,5]. Generally, 0.001–0.02 wt.% of PbO is introduced into the kiln, but with the use of wastes this amount can increase to 0.02–0.04 wt.% [8].

Even though Pb compounds are volatile, Sprung found an incorporation ratio of 54 wt.% for PbO. This compound evaporates and joins the cement kiln dust (CKD). The CKD is reintroduced into the kiln; this recirculation enhances the PbO residence time inside the kiln and makes possible a higher incorporation ratio. The presence of chlorides decreases the PbO incorporation ratio to less than 4 wt.% [4].

Cement clinker raw materials contain very low amounts of Cd. However, many wastes have high Cd content, which

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can considerably increase the quantity of this metal in the process if these wastes were co-incinerated [4,5].

CdO is a volatile compound, but its introduction into the cement kiln does not lead to an increase in dust emission [4]. Sprung [4] found a CdO incorporation ratio of 51 wt.% in cement kilns, when the addition of Cd was 0.167 mg of Cd per kilogram of clinker. This incorporation ratio can be achieved only under low chlorine concentration; otherwise there is the formation of CdCl<sub>2</sub> that has a lower evaporation temperature. The condensation temperature of the CdCl<sub>2</sub> is lower than the cyclones and pre-heater systems temperature [5].

## 2. Methods and materials

The clinker raw-mixture used in this work will be denominated “base mixture” and was prepared by mixing 99.999% pure compounds. The Bogue calculation was used to determine the composition of the base mixture. The base mixture was calculated to provide a clinker which contains 65% C<sub>3</sub>S; 15% C<sub>2</sub>S; 10% C<sub>3</sub>A and 10% C<sub>4</sub>AF after the burning process.

Samples were prepared by mixing a determined amount of a minor element oxide (ZnO, PbO or CdO) to the base mixture. These samples were subjected to thermogravimetric analysis and tests in a laboratory apparatus to evaluate the incorporation ratio of these minor element oxides.

### 2.1. Sampling strategy

The mixtures used as charge were made by adding ZnO, PbO and CdO to the base mixture in such a way that after the burning process, the produced clinker would have the desired amount of these oxides. Table 1 shows the 20 mixtures prepared. The mixtures were prepared following the equation:

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

Table 1  
Mixtures used as charge

Minor element oxide added	Amount of the minor elements oxides after the clinkering process (wt.%)					
	0.05	0.10	0.30	0.50	0.80	1.00
ZnO	Z05	Z10	Z30	Z50	Z80	Z100
ZnO + 0.10 wt.% of NaCl					ZNa	
ZnO + 0.10 wt.% of KCl					ZK	
PbO	P05	P10	P30	P50	P80	P100
CdO	C05	C10	C30	C50	C80	C100

The name of the mixture can be found in the intersection of the row indicating the compounds added to the base mixture and the column that indicates the amount of the minor element oxide after the clinkering process.

where %O is the percentage of ZnO, PbO or CdO; OM the ZnO, PbO or CdO mass; BM the base mixture mass; and LI the loss on ignition.

### 2.2. Thermogravimetric tests

Thermogravimetric tests were performed on all mixtures in a Netzsch STA 409C piece of equipment. The samples were heated at 10 °C/min up to 1450 °C, and then they were held at this temperature for 20 min. The gas flow was 10 mL/min of synthetic air (80% N<sub>2</sub> and 20% O<sub>2</sub>). A platinum crucible was used to hold the sample.

### 2.3. Experiences in the simulator device

A laboratory device was assembled to simulate the thermal cycle imposed on the charge during Portland clinker production. This device is composed of an electrical furnace, which can heat up to 1700 °C and a corundum tube used as chamber. On one end of the chamber is placed a valve that allows the chosen gas to enter the chamber; on the other end a condenser is placed. The condenser is composed of a stainless steel stem with a copper water-refrigerated end. A detailed description of this device can be found elsewhere [2,9].

Briquettes of all mixtures were prepared using a manual press with a 25 mm diameter tool steel matrix. Three briquettes were used in each test. The heating rate adopted was 15 °C/min up to 1450 °C and the gas flow was 10 cm<sup>3</sup>/min of synthetic air.

Each test can produce two kinds of samples: briquettes and condensed material. Generally the amount of condensed material was either too small or non-existent, so they were submitted to energy disperse scanning (EDS) microprobe analysis. The briquettes were submitted to X-ray fluorescence chemical analysis.

## 3. Results and discussion

### 3.1. ZnO additions

All thermogravimetric curves of the base mixture with additions of ZnO showed only the mass loss regarding the CaCO<sub>3</sub> decomposition. This fact indicates that all added ZnO was incorporated into the clinker structure and did not evaporate.

In order to verify the ZnO total incorporation, tests in a larger scale were performed in the simulator device. Table 2 shows the chemical analysis results of the briquettes from the tests in the simulator device. There was no condensed material in this set of tests.

The results indicate that all ZnO incorporates into the clinker. Sprung [4] studied various metals' incorporation ratios in cement kilns, finding a Zn incorporation ratio higher than 90%. On the other hand, Caponero and Tenorio [3]

Table 2  
Chemical analysis results of the briquettes with ZnO additions from the tests in the simulator device

	Z05 (wt.%)	Z10 (wt.%)	Z30 (wt.%)	Z50 (wt.%)	Z80 (wt.%)	Z100 (wt.%)
Al <sub>2</sub> O <sub>3</sub>	4.79	4.77	4.65	4.76	4.68	4.56
SiO <sub>2</sub>	19.71	19.50	19.4	19.40	19.7	18.90
CaO	72.10	72.20	72.2	71.50	71.4	71.00
Fe <sub>2</sub> O <sub>3</sub>	3.36	3.43	3.45	3.87	3.38	4.57
ZnO	0.04	0.10	0.30	0.47	0.84	0.97

found a Zn incorporation ratio of 75%, when performing a laboratory study of phosphate coating sludge additions to Portland cement clinker raw-mixture. These different incorporation ratios could have been caused by the chlorine presence in real cement clinker raw-mixtures. Sprung's results are higher than the results of Caponero and Tenorio mainly because Sprung studied the incorporation ratio in a cement kiln that had CKD recirculation, which enhanced the Zn residence time so the incorporation became higher.

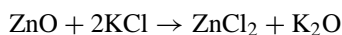
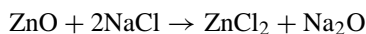
In order to study the chlorine effect on the Zn incorporation ratio, thermogravimetric tests and tests in the simulator device were performed with additions of ZnO and NaCl or KCl to the base mixture.

Figs. 1 and 2 show the TG curves of the samples with additions of 0.8 wt.% of ZnO and 0.1 wt.% NaCl to the base mixture (ZNa) and 0.8 wt.% of ZnO and 0.1 wt.% of KCl to the base mixture (ZK), respectively.

The mass loss equivalent to the final calcined sample mass loss was calculated for both thermogravimetric tests and the mass loss was 0.15 wt.% ZnO for the mixture containing NaCl and 0.28 wt.% for the mixture containing KCl.

Tests in the simulator device were carried out with the same samples: ZNa and ZK. The chemical analysis results of the briquettes from the tests on the simulator device appear in Table 3. The ZnO content in the briquette from the sample ZNa was 0.61 wt.% and in the briquette from the sample ZK was 0.62 wt.%.

The chemical analysis results indicate that the Zn evaporates in the chloride form, as shown in the following reactions:



The ZnCl<sub>2</sub> evaporation was verified by EDS microanalysis of the condensed material collected in the tests in the simulator device. Peaks of Cl and Zn were identified in the condensed material samples of both tests.

The ZnO retention ratio was roughly 76 wt.%. This result agrees with the results of Caponero and Tenorio [3].

### 3.2. PbO additions

Fig. 3(A) depicts the part of the TG curves of the mixtures containing PbO additions relating to the PbO evaporation. The PbO evaporation occurs in two steps, as can be seen in the DTG curve of the sample containing 1 wt.% PbO—Fig. 3(B). One step was characterized by a higher evaporation rate up to 1319 °C and the other by a lower evaporation rate after 1319 °C. The decrease in the evaporation rate was associated with the beginning of the clinkering reactions and with C<sub>2</sub>S formation. C<sub>2</sub>S is the phase most affected by Pb. Table 4 summarizes the mass loss results.

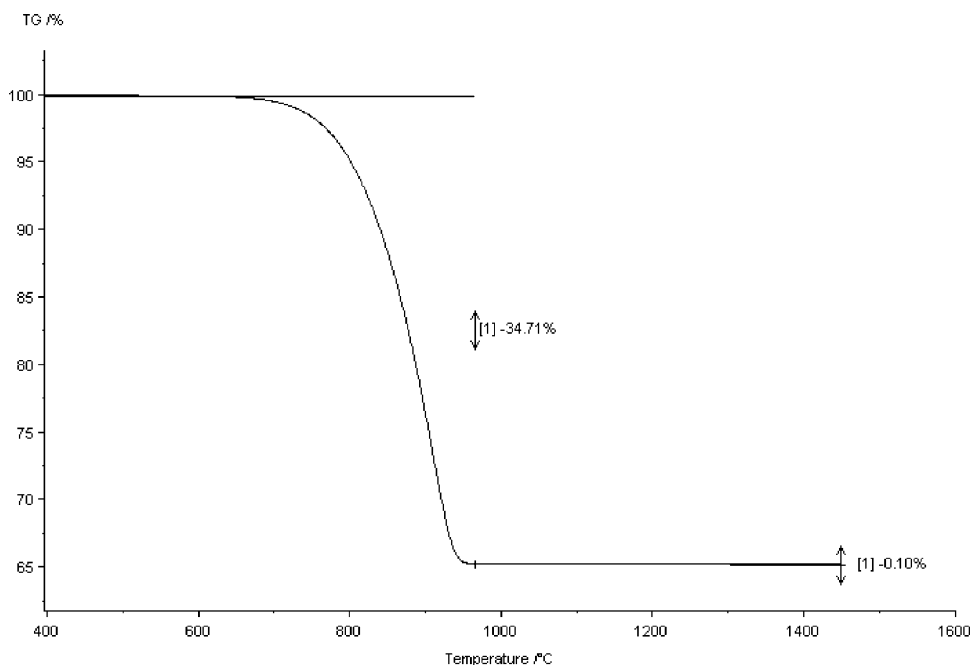


Fig. 1. TG curve of the sample ZNa.

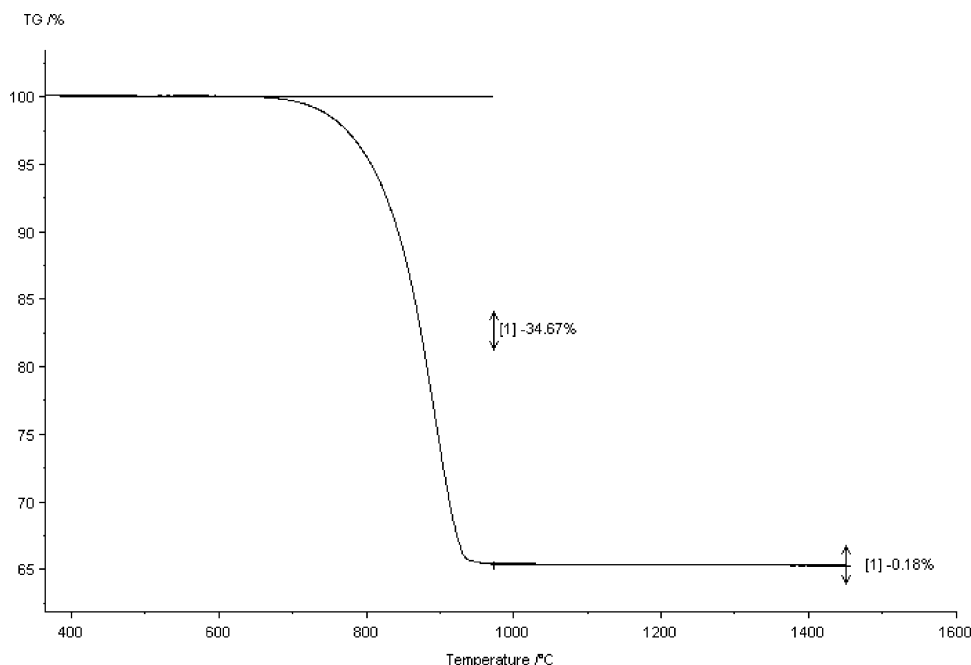


Fig. 2. TG curve of the sample ZK.

The chemical analysis results of the briquettes obtained from the tests in the simulator device appear in Table 5. These results show that for addition of 0.05 wt.% of PbO, the PbO was entirely incorporated. However, the incorporation ratio decreases with the increase in PbO addition, becoming stable at roughly 50 wt.% for addition higher than 0.5 wt.% of PbO. The retention ratio was calculated for all mixtures that contained PbO and Fig. 4 shows the results.

The condensed material was characterized by EDS microanalysis and peaks of only Pb and O were identified.

Table 3

Chemical analysis results of the briquettes produced in the simulator device from the samples ZNa and ZK

	ZNa (wt.%)	ZK (wt.%)
Al <sub>2</sub> O <sub>3</sub>	4.88	4.74
SiO <sub>2</sub>	20.60	20.10
CaO	70.40	71.20
Fe <sub>2</sub> O <sub>3</sub>	3.51	3.34
ZnO	0.61	0.62

Table 4

Mass loss identified in the TG curves for all samples with PbO additions to the base mixture

PbO additions (wt.%)	Mass loss (wt.%)	
	Until 1319 °C	From 1319 until 1450 °C
0.1	0.03	0.03
0.3	0.20	0.06
0.5	0.27	0.13
0.8	0.45	0.15
1.0	0.47	0.23

There is a difference between the incorporation results of the TG tests and the tests carried out in the simulator device. A continuous PbO evaporation was observed in the TG tests, and the PbO amount that remained in the TG tests samples was lower than the PbO amount that remained in the briquettes. These differences appear in Table 6.

The aforementioned reduction of the PbO evaporation rate at temperatures higher than 1319 °C was associated with the

Table 5

Chemical analysis results of the briquettes produced in the tests in the simulator device for all samples containing PbO

	P05 (wt.%)	P10 (wt.%)	P30 (wt.%)	P50 (wt.%)	P80 (wt.%)	P100 (wt.%)
Al <sub>2</sub> O <sub>3</sub>	4.73	4.68	4.75	4.64	4.78	4.68
SiO <sub>2</sub>	19.60	19.40	19.80	19.40	19.40	19.30
CaO	72.20	72.30	71.90	72.20	71.90	71.90
Fe <sub>2</sub> O <sub>3</sub>	3.42	3.54	3.36	3.51	3.50	3.56
PbO	0.05	0.08	0.19	0.25	0.42	0.56

Table 6

PbO content in the briquettes and the PbO content calculated to the TG samples up to 1319 °C and at the end of the test

PbO added (wt.%)	PbO in the briquettes (wt.%)	PbO retained up to 1319 °C (wt.%) (by the TG tests)	PbO retained at the end of the thermal cycle (wt.%) (by TG tests)
0.05	0.05	0.05	0.05
0.10	0.08	0.07	0.04
0.30	0.19	0.10	0.04
0.50	0.25	0.23	0.10
0.80	0.42	0.35	0.20
1.00	0.56	0.53	0.30

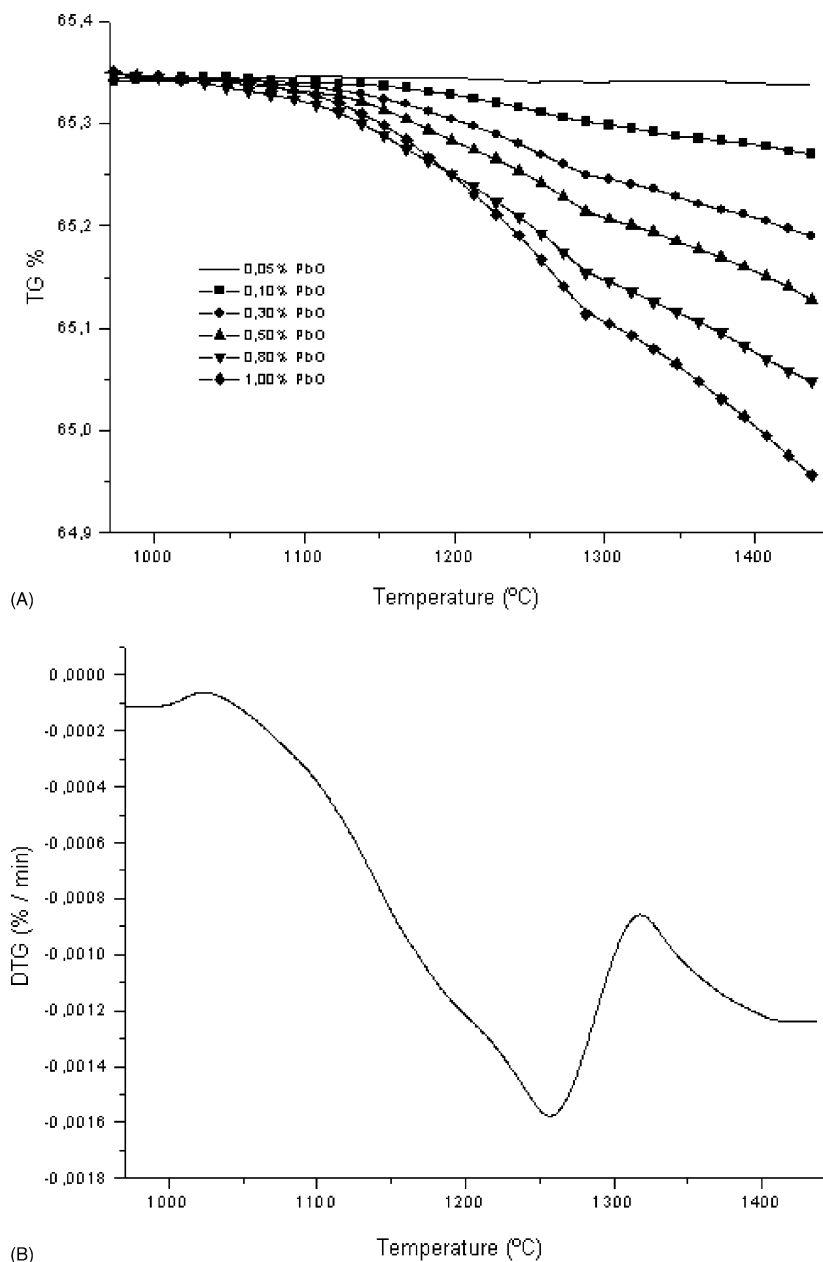


Fig. 3. (A) Part of TG curve of all mixtures containing PbO related to the PbO evaporation. (B) DTG curve of the mixture containing 1 wt.% of PbO.

beginning of the clinkering reactions. The clinkering process includes powder sintering and a liquid phase formation; making it difficult for the PbO vapor to leave the sample.

The sample amount used in the TG tests was much smaller than the amount used in the simulator device tests, so the PbO vapor found fewer barriers in the TG test samples to be released than in the briquettes. From these considerations, one can conclude that the PbO retention was higher in the briquettes because the PbO vapor was trapped inside the samples during the clinkering reactions.

Observing Table 6 results, one can verify that PbO evaporation occurred only below 1319 °C, since the PbO retained in the samples present similar figures for the briquettes and

for the TG tests below 1319 °C. Nodules between 3 and 25 mm form during the clinker production process [1,10]; making the conditions of the simulator device tests nearer the real process than the TG tests.

The PbO incorporation ratio found in this work was 50 wt.%, which agrees with Sprung's results. Sprung [4] found a PbO retention ratio of 54 wt.%, when studying a system with no chlorine.

### 3.3. CdO additions

Fig. 5 shows the TG curve of the samples with CdO additions after the CaCO<sub>3</sub> decomposition. Mass loss occurred

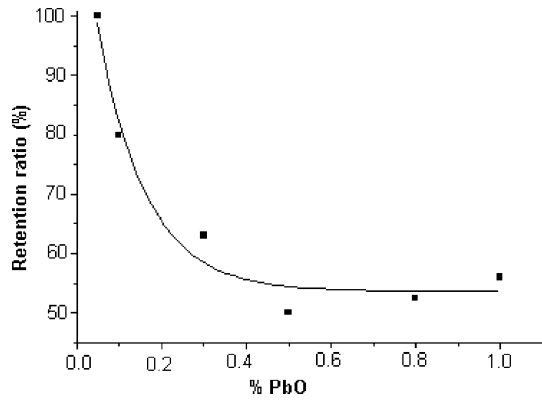


Fig. 4. Retention ratio of PbO as a function of the amount of PbO added to the base mixture.

for the samples with CdO contents higher than 0.3 wt.%. Mass loss was not observed for the samples containing 0.05 and 0.10 wt.% of CdO, which indicates that all CdO was incorporated.

The first derivatives of all TG curves appear in Fig. 6. The CdO evaporation is a continuous process, unlike the PbO evaporation. The clinkering reactions triggered a reduction in the PbO evaporation rate, behavior not observed for CdO.

The chemical analysis results (Table 7) of the briquettes produced in the test carried out in the simulator device show that all CdO was incorporated into the clinker for additions up to 0.30 wt.% of CdO to the base mixture. Fig. 7 shows the CdO incorporation ratio of all samples obtained in the TG tests and tests in the simulator device. The incorporation

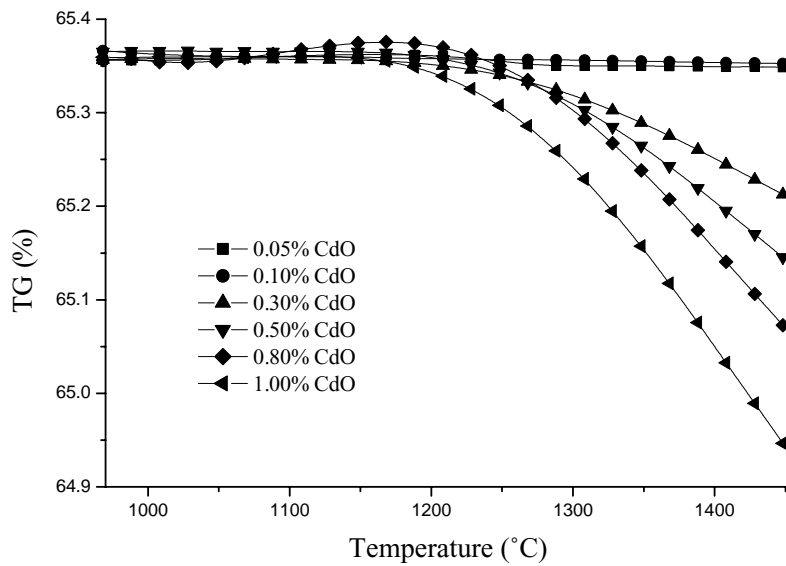


Fig. 5. TG curve of the mixtures containing CdO.

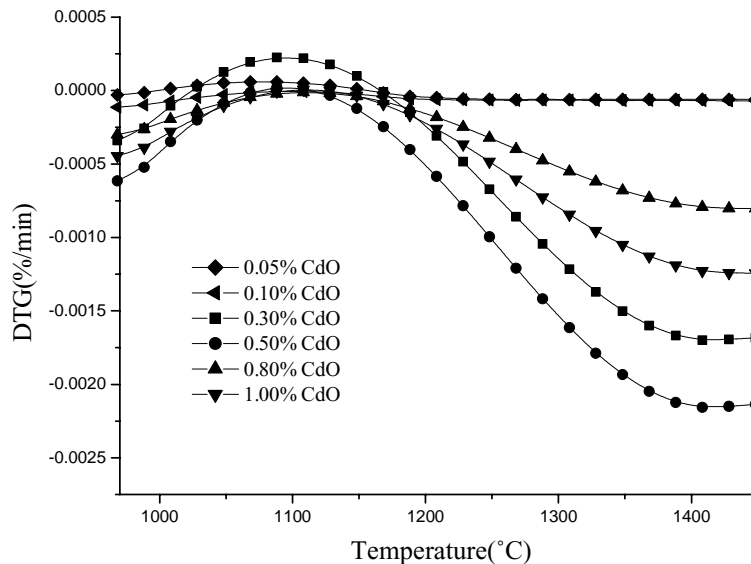


Fig. 6. First derivatives of the TG curves shown in Fig. 5.

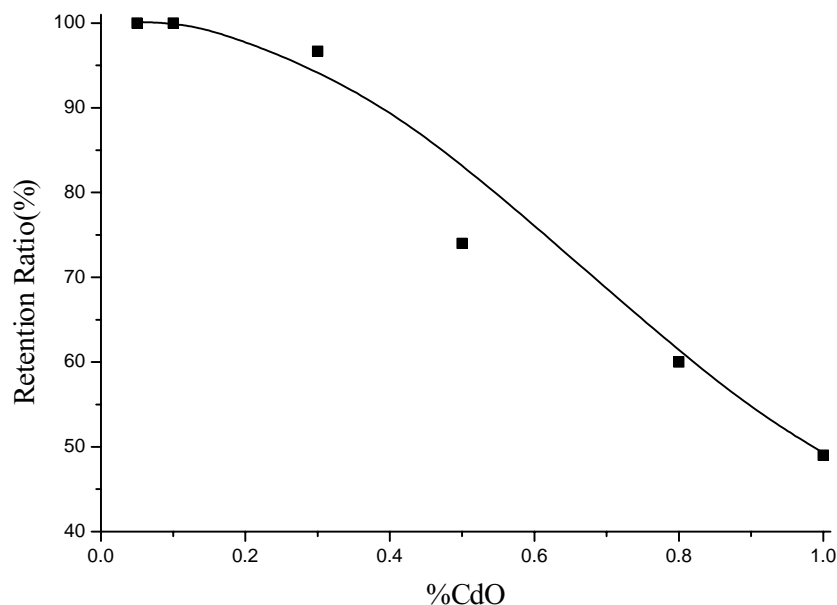


Fig. 7. CdO incorporation ratio based on the chemical analysis of the briquettes.

Table 7

Chemical analysis results of the briquettes from the tests in the simulator device of the samples containing CdO

	C05 (wt.%)	C10 (wt.%)	C30 (wt.%)	C50 (wt.%)	C80 (wt.%)	C100 (wt.%)
Al <sub>2</sub> O <sub>3</sub>	4.76	4.70	4.79	4.58	4.72	4.71
SiO <sub>2</sub>	19.40	19.50	19.30	19.40	20.10	19.50
CaO	72.20	71.90	72.10	72.00	71.5	71.60
Fe <sub>2</sub> O <sub>3</sub>	3.59	3.80	3.52	3.65	3.20	3.70
CdO	0.05	0.10	0.29	0.37	0.48	0.49

ratios found in the briquettes produced in the test in the simulator device were higher than the incorporation ratios found in the thermogravimetric tests. This difference in the incorporation ratio can be explained by the charge sintering during the clinkering process, which closes the pores of the charge trapping the CdO.

The condensed material was submitted to EDS microanalysis and peaks of only Cd and O were identified, suggesting that only CdO was evaporating during the burning process.

As observed in the tests with PbO additions, the conditions in the simulator device were closer to the real process than the thermogravimetric tests. The incorporation ratio found for the tests in the simulator device agrees with Sprung's [4] CdO incorporation results, which are roughly 51 wt.%.

#### 4. Conclusions

The results obtained in this research permit formulation of the following conclusions:

- All ZnO added to a clinker raw-meal made of pure compounds is incorporated into the charge during the burning

process. The presence of chlorine decreases the ZnO incorporation ratio to about 76 wt.%; the Zn evaporates in the form of ZnCl<sub>2</sub>.

- The incorporation ratio of the PbO is 100% for the addition of 0.05 wt.% of PbO to the base mixture. The incorporation ratio decreases with the increase of the amount of PbO added to the base mixture, stabilizing in roughly 50 wt.% for additions higher than 0.50 wt.% of PbO.
- The CdO was entirely incorporated into the charge during the burning process for additions up to 0.30 wt.%. The CdO incorporation ratio decreases gradually, achieving around 50 wt.% for the sample with 1.00 wt.% of PbO.
- The sintering of the charge during the clinkering process enhanced the incorporation of PbO and CdO.

#### Acknowledgements

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