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High intakes of Cr, Ni, and Zn in clinker Part I. Influence on burning process and formation of phases

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Abstract

The influence of high intakes of Cr, Ni, and Zn on the burning process and the formation of clinker phases is described. Three different raw meals were used and were burned with the metal oxides in four concentrations from 200 to 25,000 ppm. The resulting clinker was analysed for the content of free lime and X-ray diffraction analysis was done. Some of the clinker material was crushed and polished, and quantitative point counting was performed to provide the content of the different clinker phases. These samples were also analysed by scanning electron microscope connected with an energy-dispersive X-ray-spectrometer to detect the composition of the clinker phase. The results show that only very high intakes of heavy metals have measurable effects on the formation and composition of the clinker.

Keywords: Chromium; Clinker; Heavy metals; Zinc; Nickel

1. Introduction

The content of the main phases alite, belite, aluminate, and ferrite phase in a Portland cement depends on the concentration of the main components CaO, SiO_2, Al_2O_3, and Fe_2O_3. Minor components like MgO, SO_3, and alkalis also influence the clinker formation during the burning process and the hydration process of the cement.

Cement also contains heavy metals in the form of trace elements from the natural sources of the raw material. Volatile components, such as compounds of Hg, Pb, and Tl, can evaporate during the burning process and precipitate in the cooler parts of the kiln. They can be found in the kiln dust. Less volatile compounds are incorporated in the clinker phases during the burning process [1]. Normally, these trace elements have no influence on the burning or hydration process because their concentration is very low. However, with more frequent use of alternative fuels and secondary raw materials and due to geologically caused variations of the concentration of trace elements, their concentration can possibly rise within the typical range of the clinker and its products.

To estimate the influence of these heavy metals on the formation of clinker and the hydration of cements, tests were made with clinker composed of different raw meals mixed with different concentrations of heavy metals.

2. Methods

2.1. Raw materials

For the experiments three types of raw meal with different compositions were chosen: raw meal for ordinary Portland cement (PC), sulphate-resisting Portland cement (SRPC), and white Portland cement (WPC). The samples were taken from the industrial production process of three cement plants. To prepare clinker with higher concentrations of heavy metals, Cr_2O_3, NiO, and ZnO were added to the raw meal to give a metal concentration of approximately 0.02, 0.10, 0.50, or 2.50 wt.% (=200, 1,000, 5,000, or 25,000 ppm), respectively. The composition of the main and minor components as well as the relevant heavy metals in the used raw meal is given in Table 1, which also shows the specific surface of the raw meal. In this work all given concentrations refer to the metals and not to the oxides.

2.2. Sample preparation and methods of investigation

The heavy metal oxides were intensively mixed with 800 g of raw meal and then pellets were made (diameter > 20 mm) to give a regular burnability of the clinker. The clinker was burned in platinum crucibles in an electrically heated

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Table 1
Composition of the raw meal and fineness

Oxide	PC	SRPC	WPC
SiO_2 (wt.%)	14.1	13.0	14.4
Al_2O_3 (wt.%)	3.5	2.5	2.7
Fe_2O_3 (wt.%)	2.2	4.9	0.1
CaO (wt.%)	41.3	42.2	44.7
MgO (wt.%)	1.7	1.2	0.3
K_2O (wt.%)	1.1	0.4	0.2
SO_3 (wt.%)	0.6	0.1	0.7
Cr (ppm)	51	46	12
Ni (ppm)	15	15	5
Zn (ppm)	88	111	48
Specific surface (m^2/cm^3)	1.71	2.06	3.19

furnace. The burning time and temperature depended on the composition of the raw meal and was determined by burning pellets of the pure raw meal until the content of free lime was between 1.0 and 1.3 wt.%. The burning conditions for the three raw meals are given in Table 2. After burning, the clinker was cooled very quickly to prevent decomposition of alite.

For the phase analysis by light microscopy and scanning electron microscopy (SEM), the clinker was crushed (<2 mm) with a jaw crusher and then a fraction was embedded in epoxy resin. The samples were ground with SiC paper and then polished. For the quantitative phase analysis via point counting, the samples were etched with hydrofluoric acid vapour. After completion of the light microscopy, the same samples were coated with carbon to give good images with SEM. The pore size distribution of some of the crushed samples was analysed by means of mercury intrusion porosimetry.

Some of the clinker was finely ground (<63 μm) and then analysed for the content of free lime by Franke's method [2]. These samples were also analysed by means of X-ray powder diffraction (XRD). After dissolution of samples in a mixture of nitric acid, hydrofluoric acid, and boric acid, the content of heavy metals was analysed by means of graphite furnace atomic absorption spectrometry (AAS).

3. Results and discussion

3.1. Content of heavy metals

The concentration of Cr, Ni, and Zn in the clinker was analysed by AAS. The results show that the concentration in the analysed clinker did not differ much from the amount predicted by theoretical calculations based on the concentration in the raw meal and the ignition loss. In some cases, however, the measured metal concentration was below the expected concentration. This loss cannot be attributed to normal evaporation, since another study [1] shows that no loss of Cr or Ni occurs when they are added to pure C_3S; however, a loss of about 25 wt.% of Zn is due to a higher temperature (1550°C) and longer time (12 h) for the clinkering process. Compared to pure clinker phases like C_3S, the heavy metals possibly behave differently in the more complex mixture of the raw meal because reactions might also occur with the minor elements. Chlorides in particular might form new compounds with the heavy metals that are more volatile and can evaporate more easily during the clinkering process. The results from other publications [3–5] show that the evaporation of heavy metals depends on the composition of the raw meal, burning conditions, and atmosphere (reducing or oxidising) during the burning process.

Table 2
Burning conditions for the raw meal

Sample	Temperature (°C)	Time (min)
PC	1400	60
SRPC	1450	70
WPC	1550	180

3.2. Content of free lime

The content of free lime in the clinker is a good indicator of the degree of burning. Other than the concentration of the heavy metal in the raw meal, all conditions for the burning were constant. Hence it follows that a decrease in free lime means an improvement in the burnability by the addition of the metal in the specific concentration. In contrast a rise in the free lime means a deterioration in the burnability. The content of free lime can also change when CaO takes place in a reaction that leads to a new compound. The analysed content of free lime in the clinker is shown in Fig. 1.

The PC with Ni and Zn shows a permanent decrease in the free lime. The sample containing Cr shows a different behaviour. Up to a concentration of 0.5 wt.%, Cr has a positive effect on the burnability of the clinker. Between 0.5 and 2.5 wt.%, the doping with Cr leads to a higher concentration of free lime resulting from the decomposition of alite (see Table 3). The SRPC does not show this strong decrease in free lime with increasing content of heavy metal, but the free lime in the sample with 2.5 wt.% of Cr is very high.

The content of free lime in the corresponding sample of the WPC clinker is even higher, but the free lime in the sample with 0.5 wt.% of Cr is the lowest of all the clinkers. In this clinker, Zn does not change the content of free lime and the influence of Ni is equal to that of SRPC.

Some effects of the Cr on the content of free lime in C_3S or clinker were described by other authors, but the results often differ. Odler et al. [6], for example, found the highest content of free lime in the sample with 0.3 wt.% of Cr (according to the raw meal), and then the content of free lime decreased (up to 2.1 wt.%). Malozhon et al. [7] found similar results to those shown in Fig. 1. A clinker with a high lime standard showed less free lime when doped with Cr, but above a concentration of 1.5 wt.% of Cr_2O_3, the content of free lime rose extremely. Using clinker rich in belite, there was only a small increase in free lime. This was also found by Butt et al. [8]. Imlach [9] assessed the role of Cr in the manufacture of Portland cement and found Cr to be a mineraliser.

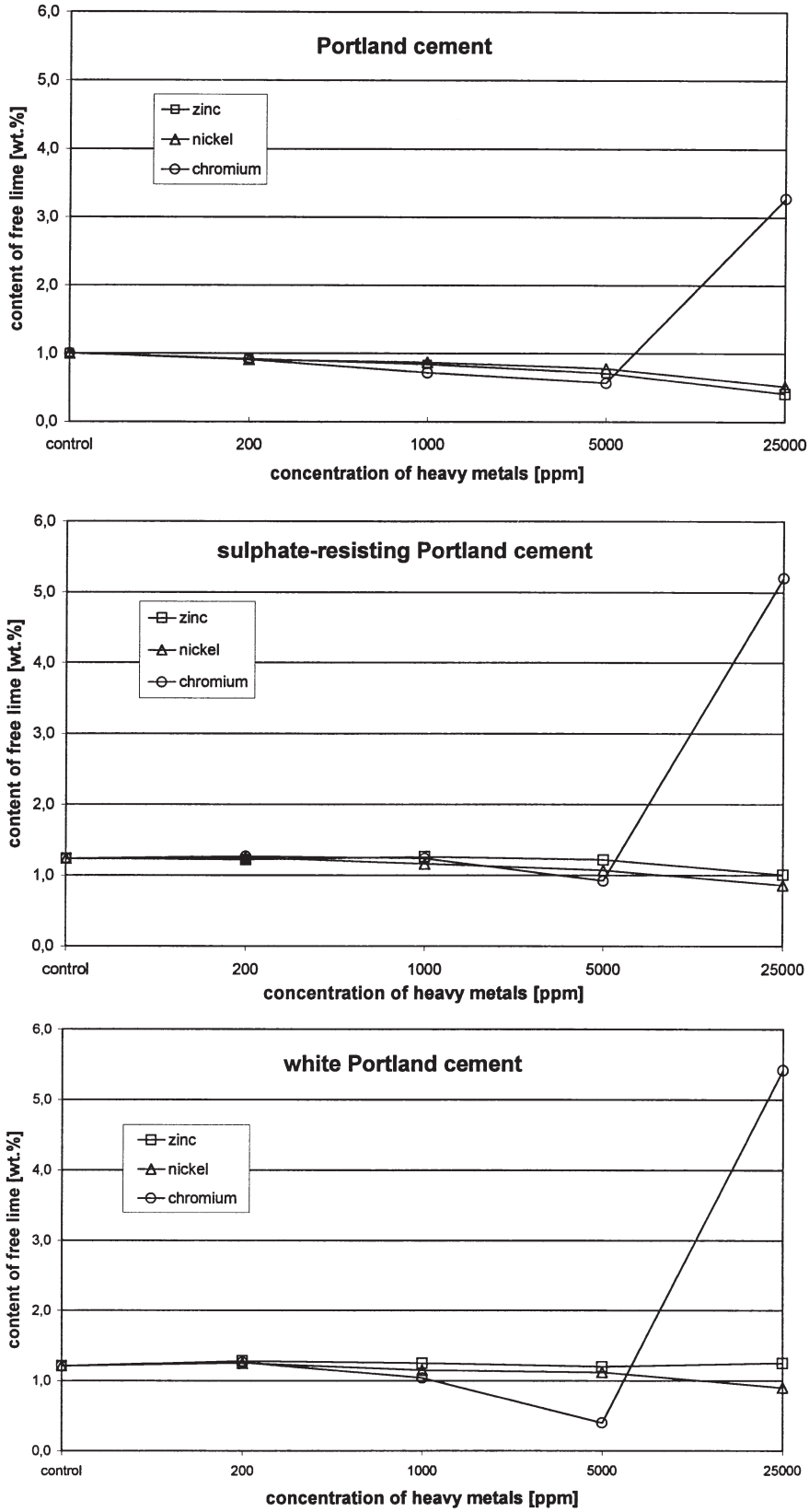

Fig. 1. Content of free lime in the doped clinker and control sample.

Table 3
Phase content of clinker determined by means of point counting (wt.%)

Cement	Element	Concentration (ppm)	Alite	Belite	Aluminate	Ferrite
PC	0		64.4	16.4	4.3	13.9
PC	Zn	1,000	67.1	15.4	4.4	13.0
PC	Zn	25,000	69.4	10.9	4.5	15.2
PC	Ni	1,000	66.5	14.3	4.3	14.9
PC	Ni	25,000	64.4	16.8	6.8	11.9
PC	Cr	1,000	66.3	16.9	4.2	12.9
PC	Cr	25,000	21.9	61.6	3.6	12.8
SRPC	0		72.5	5.2	1.3	21.0
SRPC	Zn	1,000	71.9	5.2	2.0	20.9
SRPC	Zn	25,000	75.1	3.1	1.8	19.9
SRPC	Ni	1,000	73.1	5.4	1.3	20.3
SRPC	Ni	25,000	74.3	2.8	0.8	22.1
SRPC	Cr	1,000	73.0	4.9	1.5	20.5
SRPC	Cr	25,000	21.8	53.7	0.7	23.8
WPC	0		89.7	1.2	9.1	–
WPC	Zn	1,000	86.5	2.7	10.8	–
WPC	Zn	25,000	89.3	1.1	9.5	–
WPC	Ni	1,000	89.4	1.2	9.5	–
WPC	Ni	25,000	87.0	1.1	11.9	–
WPC	Cr	1,000	88.6	3.3	8.1	–
WPC	Cr	25,000	45.2	48.3	6.5	–

As in our investigations, other authors found similar effects of Zn on the content of free lime in the clinker. Odler et al. [6,10] as well as Bordoloi et al. [11] and Knöfel [12] found a better burnability of clinkers containing Zn, but the efficiency of the mineralising effect of the metal decreases with rising temperature. The same effect can be seen in Fig. 1. The biggest change in the content of free lime is found in the PC, a smaller influence is found in the SRPC, and nearly no effect is found in the WPC. In the same order, the temperature of the burning process increases (see Table 2).

3.3 Phase content of doped clinker

The phase content of all clinker with 1.0 and 2.5 wt.% of heavy metal and the control sample were determined by means of point counting under a light microscope. At least 4,000 points were counted. Table 3 shows the concentration of the main phases of clinker. The detection of the phases in clinkers with 2.5 wt.% of Cr or Ni were complicated because of new phases. The clinkers were always cooled very quickly; therefore, crystallisation of the aluminate and ferrite was not very good. Hence the differentiation of the two phases was more difficult, which affects the accuracy of the results of the point counting. Also counted were free lime, periclase, and new phases, but the contents were too low to receive statistically correct results.

All samples with 1.0 wt.% of heavy metal and the samples with 2.5 wt.% of Ni showed no significant change in the phase composition compared to the control sample. As was expected from the analysis of the free lime, the composition of the phases in clinker with 2.5 wt.% of Cr was much different than the control sample. The content of belite was always higher than that of alite. Cr inhibits the reaction from belite and CaO to form alite. Either alite is destabilised in the presence of Cr so that it is hard to form, or belite is stabilised by Cr so that a further reaction is more difficult. Malozhon et al. [7] also found a lower content of alite in clinker with a high lime factor when doped with Cr. The phase composition of clinker rich in belite was not influenced.

The PC and the SRPC with 2.5 wt.% of Zn showed a small increase of alite and a corresponding decrease of belite. Odler et al. [10] interpreted this increase of alite as due to a substitution of Zn for Ca. This free lime can react with belite to give more alite. Investigations by Knöfel [12] with up to 4.0 wt.% of ZnO did not show a shift from belite to

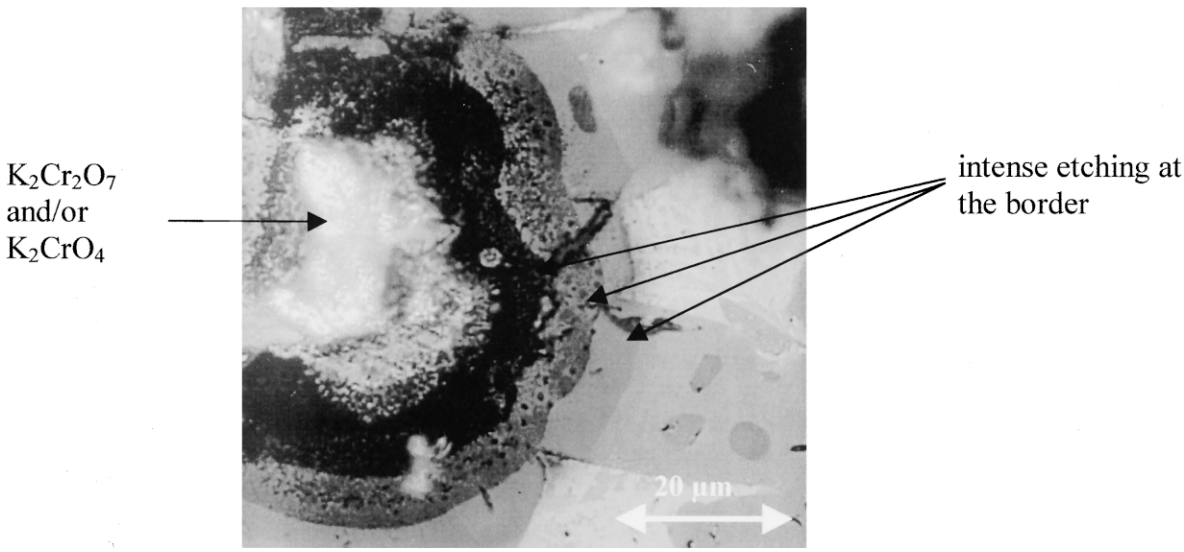

Fig. 2. Typical inclusion of $K_2Cr_2O_4$ and/or $K_2Cr_2O_7$ in PC with 25,000 ppm of Cr: intense etching at the border.

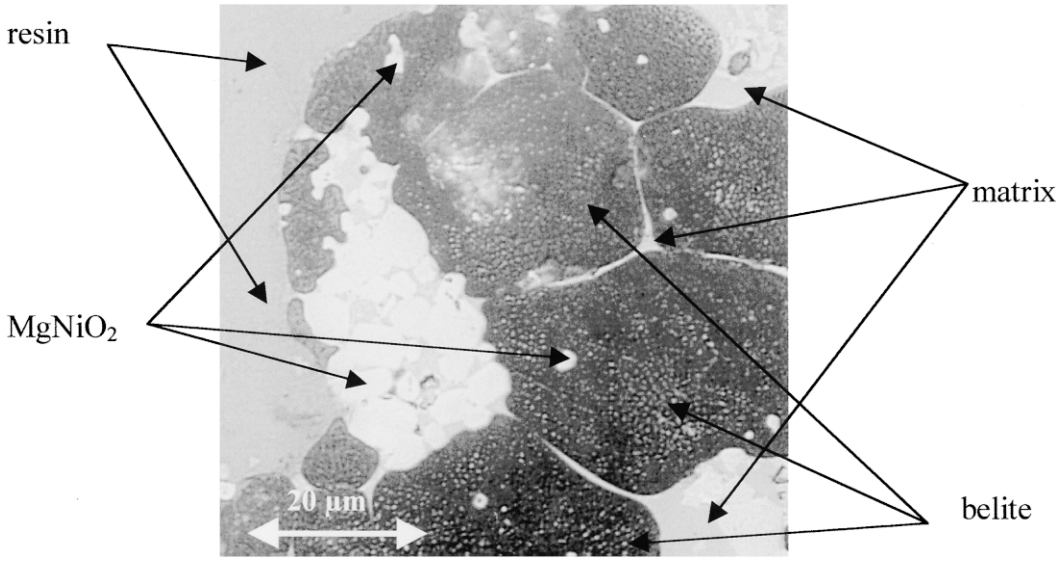

Fig. 3. $MgNiO_2$ in PC with 25,000 ppm of Ni: greater quantities in nests and inclusions in other phases.

alite, but showed an increase of the ferrite phase and a reduction of the aluminate.

Besides the quantitative results, the light microscopy gives information about the peculiarities of the clinker phases. Some of these peculiarities of the clinker, especially with high intakes of Ni or Cr, are shown in Figs. 2, 3, and 4. The composition of new phases was analysed with an energy-dispersive X-ray spectrometer (EDS). In the clinker containing Cr and high concentrations of K, K_2CrO_4 and/or $K_2Cr_2O_7$ was found. In clinker that contained high concentrations of Mg in addition to Ni, a new phase was found with the stoichiometric composition of $MgNiO_2$. In the WPC with a low concentration of Mg, no $MgNiO_2$ could be found, but a dentritic aluminate with a high concentration of Ni was detected.

3.4. Phase composition of doped clinker

A main aim of this work is to determine in which phase the heavy metals are enriched. A good instrument for this investigation is SEM connected with EDS. Samples with high intakes of heavy metals (2.5 wt.%) and the control samples were analysed.

The samples were examined with the backscattering electrons detector (BSE). The clinker phases could be differentiated by their shape and by the brightness of the scan. With the spot analysis of EDS, the composition of the

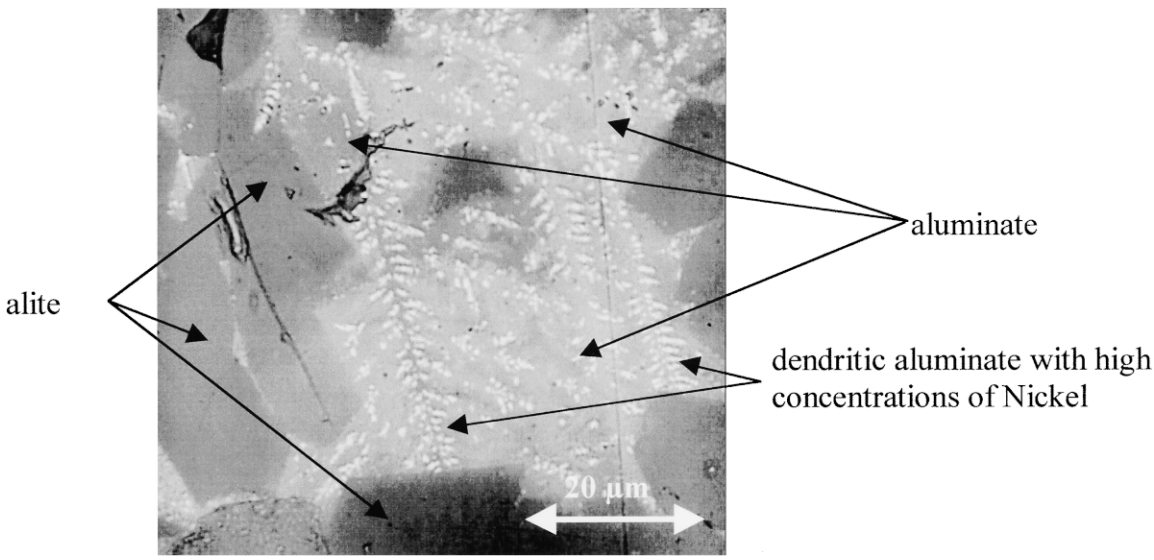

Fig. 4. Clinker phase rich in Ni in WPC with 25,000 ppm Ni: an aluminate with a high concentration of Ni is found in the matrix of aluminate; because of the low concentration of Mg, no $MgNiO_2$ was formed.

Table 4
Composition of the phases in the PC clinkers

Phase	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	MeO
Control							
Alite	69.8	26.5	1.2	0.5	1.5	0.5	
Belite	61.2	33.5	1.7	1.3	0.6	1.7	
Aluminate	35.2	6.1	30.8	11.4	9.2	3.6	
Ferrite	47.3	5.7	22.5	17.8	5.6	0.9	
Zn 25,000							ZnO
Alite	67.8	26.8	1.4	1.1	1.1	0.3	1.6
Belite	61.5	33.0	1.2	1.6	0.6	1.6	1.3
Aluminate	41.5	8.2	22.9	9.0	5.6	2.3	10.4
Ferrite	45.7	4.6	22.3	16.4	4.5	1.5	4.7
Ni 25,000							NiO
Alite	69.7	26.5	1.2	0.7	0.5	–	1.1
Belite	60.8	32.9	2.1	1.4	0.5	1.6	0.8
Aluminate	50.4	9.5	24.6	9.0	1.3	–	1.9
Ferrite	46.7	6.0	22.4	18.9	1.8	–	3.1
$MgNiO_2$	2.2	0.6	0.6	1.3	39.8	0.3	55.3
Cr 25,000							Cr_2O_3
Alite	70.4	23.9	1.5	1.2	1.0	0.4	1.7
Belite	61.5	27.3	2.5	1.5	0.7	1.5	5.2
Aluminate	55.8	9.2	21.6	8.3	2.3	1.5	1.9
Ferrite	49.1	5.2	20.1	20.1	3.6	0.1	1.8
$K_2Cr_2O_7/K_2CrO_4$	5.5	3.7	0.0	0.7	0.1	37.5	52.4

Table 6
Composition of the phases in the WPC clinker

Phase	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	MeO
Control							
Alite	69.4	26.5	1.4	0.5	0.5	0.3	
Belite	63.5	31.2	2.5	0.5	0.5	0.3	
Aluminate	53.0	6.1	35.2	1.7	2.4	0.2	
Zn 25,000							ZnO
Alite	69.3	26.3	1.3	0.4	0.4	0.3	1.9
Belite	63.0	32.7	2.1	0.3	0.5	0.3	1.0
Aluminate							
Dark	52.7	5.2	32.6	1.6	1.5	0.3	6.0
Bright	37.2	4.3	26.8	1.9	3.7	0.2	25.7
Very bright	28.3	3.1	19.5	1.3	5.0	0.3	42.5
Ni 25,000							NiO
Alite	69.8	26.7	0.9	0.4	0.4	0.2	1.5
Belite	62.3	33.0	2.1	0.5	0.6	0.2	1.2
Aluminate							
Dark	55.7	5.2	35.2	1.5	0.5	0.3	1.5
Bright	47.5	5.8	26.6	1.3	2.2	0.3	16.2
Very bright	23.4	3.5	13.2	1.2	6.2	0.2	52.3
Cr 25,000							Cr_2O_3
Alite	70.0	24.6	1.6	0.5	0.6	0.3	2.4
Belite	61.4	27.9	3.9	0.5	0.7	0.3	5.6
Aluminate	56.2	6.4	31.9	1.5	1.7	0.2	2.0

phases, including those newly formed, were analysed. In every clinker, the composition of every phase was analysed at five to eight points. In Tables 4, 5, and 6, the analysed composition of the phases in the clinker is shown. It has to be considered that the aluminate and ferrite were not crystallised very well, and consequently these phases were more difficult to analyse. The analyses were done without a standard; therefore results can not give the absolute value.

Cr is preferentially found in the silicate phase, especially in belite. In the clinker, belite with a high concentration of Cr can be found next to CaO (see Fig. 5). In addition, in the PC clinker a new phase was found that was rich in K and Cr.

Table 5
Composition of the phases in the SRPC clinker

Phase	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	MeO
Control							
Alite	69.2	26.3	1.2	1.5	1.5	0.4	
Belite	61.1	34.1	1.1	1.9	0.3	–	
Ferrite	45.5	5.7	12.9	30.7	4.7	0.5	
Dark matrix	48.2	11.8	13.2	17.9	3.6	5.4	
Zn 25,000							ZnO
Alite	69.5	25.5	1.1	1.5	1.1	0.4	0.9
Belite	61.3	33.9	1.1	1.5	0.4	1.0	0.9
Ferrite	45.0	4.2	8.2	32.1	3.0	0.4	3.5
Ni 25,000							NiO
Alite	68.9	26.4	1.2	1.3	0.6	0.5	1.2
Belite	62.1	33.0	1.3	1.8	0.5	0.9	0.6
Ferrite	45.2	4.3	13.1	32.1	1.2	0.5	3.5
Dark matrix	44.6	9.9	14.0	14.7	2.7	4.7	9.3
$MgNiO_2$	2.8	0.9	0.4	1.9	37.0	0.1	56.8
Cr 25,000							Cr_2O_3
Alite	69.2	25.3	1.0	1.2	1.4	0.4	1.5
Belite	60.5	28.2	2.0	2.5	0.5	0.8	4.5
Ferrite	46.9	4.8	13.7	24.6	5.6	0.3	4.1

The average mass-ratio of K_2O/Cr_2O_3 was 0.715. A compound with a similar mass-ratio of 0.618 is $K_2Cr_2O_7$. Because of the oxidising condition during the clinker-burning process, it is possible that at least some of the Cr was oxidised. This compound is missing in the other two clinkers because of the much lower concentration of K (see Table 1).

Also of interest is the distribution of Ni. Only a little of the Ni was found in the clinker phases, mainly in the matrix. In the white crystals that often had a hexagonal shape (see Fig. 6), already specified in the examination by light microscopy, the concentration of Ni and Mg was very high. The mass-ratio for NiO/MgO of this newly formed phase in the PC was 1.39 and in the SRPC was 1.53. For $MgNiO_2$ the mass-ratio is 1.85. Neither the new compound in the PC clinker nor in the SRPC clinker had the exact stoichiometry of $MgNiO_2$, but the results are supported by recent studies by Lopez et al. [13]. They found a new phase in clinker doped with Ni that had a composition nearly that of $MgNiO_2$. Possibly the $MgNiO_2$ is dissolved in MgO and forms a nonstoichiometric compound. The concentration of Mg in the PC clinker is 1.67 wt.%, and in this clinker the content of $MgNiO_2$ was quite high. Less $MgNiO_2$ was found in the SRPC clinker where the concentration of Mg is 1.22 wt.% and no $MgNiO_2$ was found in the WPC clinker with only 0.31 wt.% Mg. In the WPC clinker a nonstoichiometric aluminate with a high concentration of Ni was found (see Fig. 7).

Zn is preferentially found in the matrix. If the clinker contains aluminate and ferrite like PC, more of the Zn is found in the aluminate. In the absence of aluminate like in SRPC, the Zn is found in the ferrite. In the WPC clinker three different phases can be found in the matrix, which can

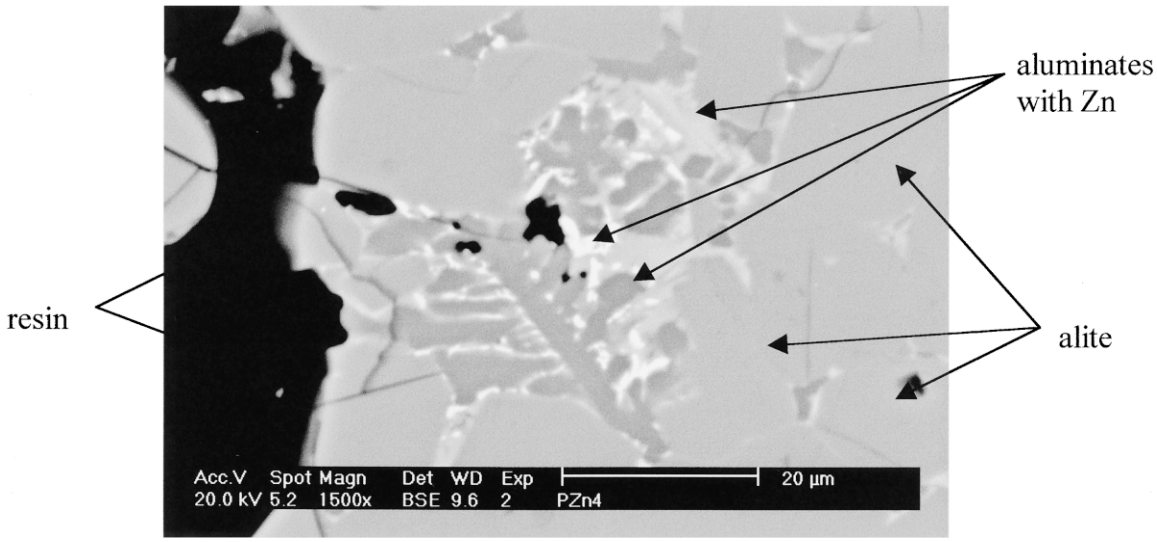

Fig. 5. Belite and free lime in PC with 25,000 ppm Cr: because of the high concentration of Cr the reaction of belite and CaO to form alite is hindered.

be differentiated by the brightness of the BSE image (see Fig. 8). With light microscopy these phases could not be differentiated. The very high concentrations of Zn in the bright phases are due to the low concentration of aluminate and ferrite in the clinker, so the new phases with a low concentration of Zn, as they were found in the PC clinker and the SRPC clinker, could not be formed.

Other authors [4,14,15] found comparable results. Because of the low content of Mg and K in the raw meal they used, they could not find the newly formed phases $MgNiO_2$ and $K_2CrO_4/K_2Cr_2O_7$.

3.5. X-ray diffraction

All samples were analysed by X-ray diffraction (XRD). With XRD the phase composition can be estimated and newly formed compounds can also be found. The detection limit for compounds with a complex crystallographic structure is especially quite high and compounds that are X-ray-amorphous cannot be detected at all.

The samples with high intakes of Cr contained less alite and more belite. In these samples, the modification of the belite was α'-C_2S. No K_2CrO_4 and/or $K_2Cr_2O_7$ was found in the XRD pattern as with the EDX. This is due to the low concentration and bad detectability of these compounds. Compared to that, the $MgNiO_2$ has a cubic structure, and the detectability of $MgNiO_2$ by XRD is very good. It was detected in all clinkers with 2.5 wt.% of Ni and was detected also in a very low concentration in clinkers with 0.5 wt.% of Ni. The concentration of the $MgNiO_2$ rose with the concentration of Mg in the clinker.

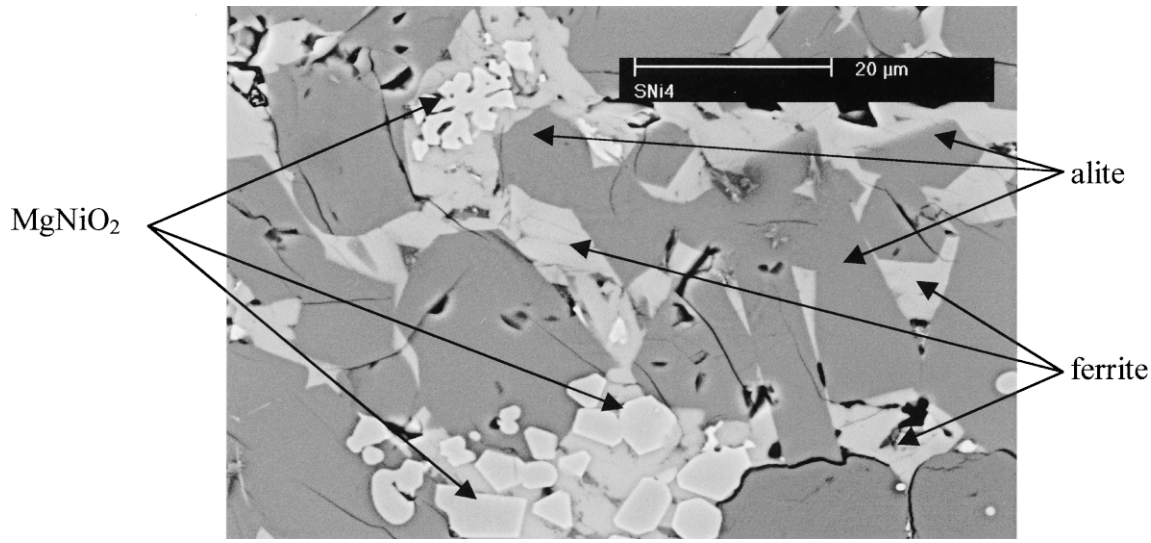

Fig. 6. Newly formed compound of $MgNiO_2$ in different shapes in SRPC with 25,000 ppm of Ni.

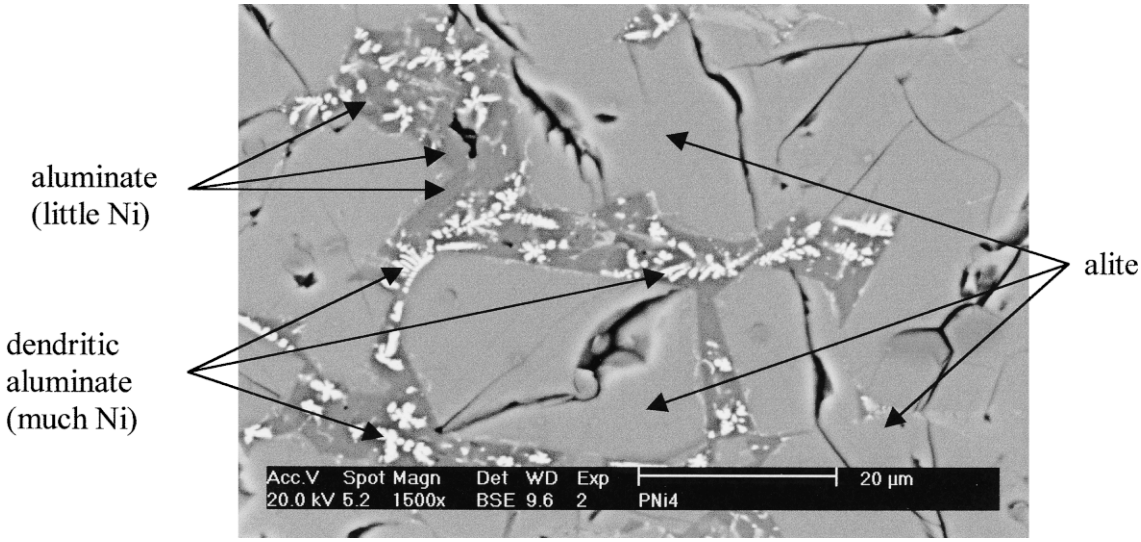

Fig. 7. WPC with 25,000 ppm of Ni: the aluminate contains compounds that are rich in Ni.

3.6. Mercury intrusion porosimetry

In the literature it is reported that some heavy metals (especially Zn) improve the sintering of the clinker. This improvement should also show a change in the porosity of the clinker. The mercury intrusion porosimetry was measured at some samples of PC to verify this. The mercury intrusion porosimetry of some samples is shown in Fig. 9.

With the exception of the sample with 2.5 wt.% of Cr, there was no significant change in the total porosity, but there was a shift in the porosity for the samples with 0.5 to 2.5 wt.% of Cr or Zn. In Fig. 9 the distribution of the pores in the clinker with 2.5 wt.% is shown. The sample with 2.5 wt.% Ni only shows a very small change in the area of 200 μm; the rest of the porosity is nearly equal to that of the control sample. In the range of 8 to 50 μm, the porosity of the clinker with 2.5 wt.% Cr is much higher than that of the other clinker, whereas the porosity of the sample with 2.5 wt.% of Zn is much lower. With 0.5 wt.% of heavy metal, these effects are much lower and with 0.1 wt.% there is no detectable effect of the metals on the porosity at all. It is most likely that the doped heavy metals change the viscosity of the liquid phase of the clinker during the burning process and this has an influence on the total porosity and the distribution of the pores.

4. Conclusions

The heavy metals Cr, Ni, and Zn have no influence on the formation of the clinker phases during the burning process at concentrations that are normally present in clinker.

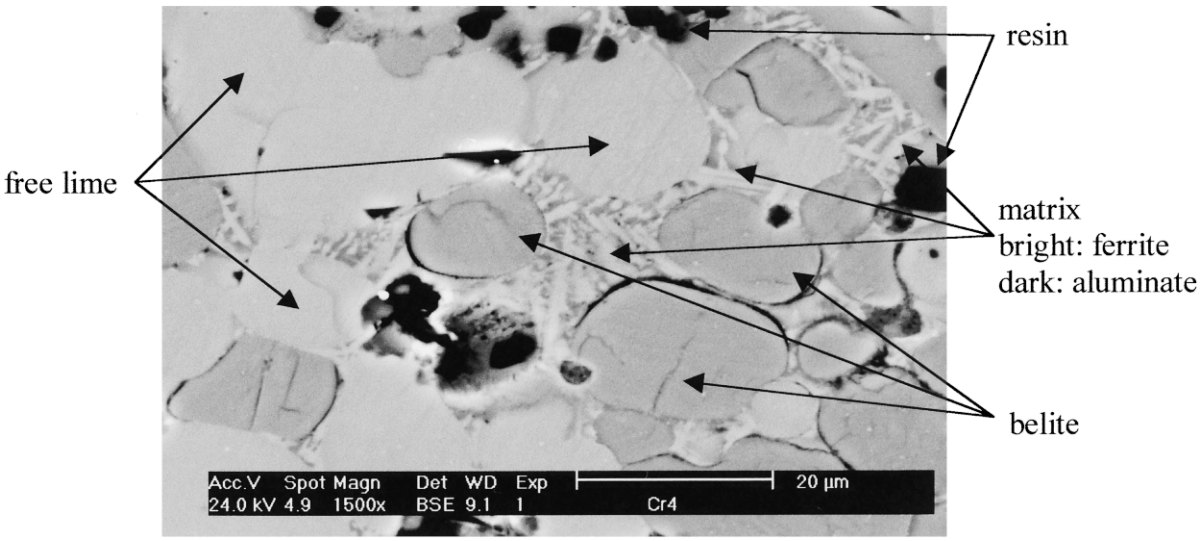

Fig. 8. Aluminate with different concentrations of Zn in WPC with 25,000 ppm of Zn.

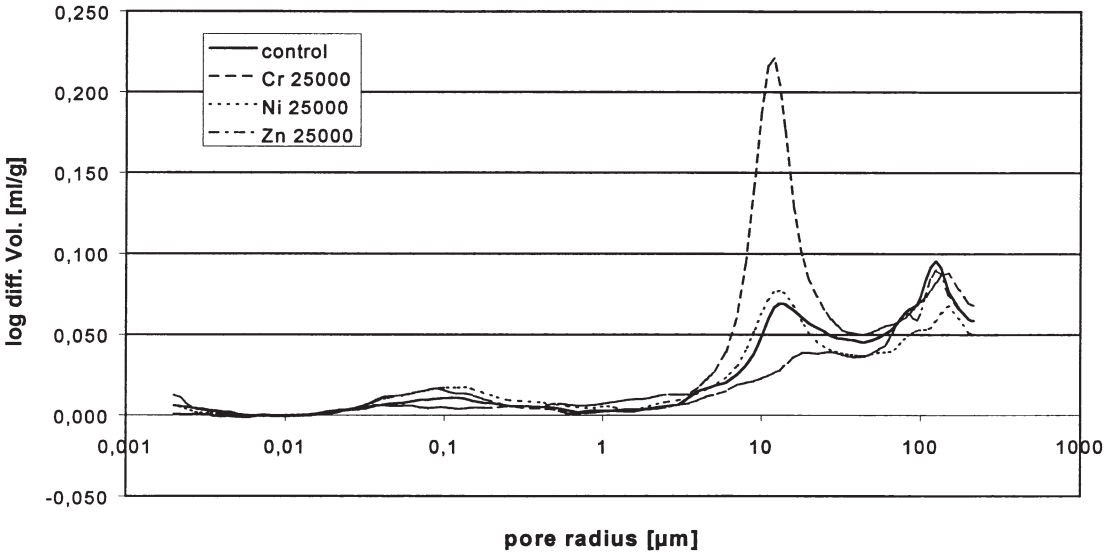

Fig. 9. Mercury intrusion porosity: control sample and clinker with 2.5 wt.% heavy metals in PC.

Even at concentrations that are 10 to 20 times higher, no changes could be detected. However, very high intakes of Cr, Ni, and Zn cause changes. Up to 0.5 wt.% Cr lowers the content of free lime in the clinker, but 2.5 wt.% leads to the decomposition of the alite and consequently to more belite and free lime. Cr is mainly found in the belite, but if the concentration of K is high enough in the clinker, K_2CrO_4 and/or $K_2Cr_2O_7$ is formed also. Even high intakes of Ni have only marginal effects on the content of free lime as well as on the content of the phases. In clinkers with higher concentrations of Mg, a new compound $MgNiO_2$ could be detected; the remaining Ni was in the matrix. Zn also had only little influence on the content of free lime. It was mainly found in the matrix and formed new phases with different concentrations of Zn.

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