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High intakes of Cr, Ni, and Zn in clinker
Part II. Influence on the hydration properties

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Abstract

This work presents the results of the hydration of cements with high intakes of Cr, Ni, and Zn. The cements were produced from clinkers that were doped with 200 to 25,000 ppm of heavy metal. Investigations on the clinkers were presented in Part I. In this paper the rate of heat generation of the cements in the first 2 days was analysed by differential scanning calorimetry. The hydration products were investigated by scanning electron microscopy combined with energy-dispersive X-ray spectrometer and also by X-ray powder diffraction. The initial setting of some samples was tested, as well as the strength. The results show that heavy metals only have an influence on the hydration properties of the cements if the dosage is much higher than in ordinary Portland cement.

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

1. Introduction

The subject of this paper is the study of changes in the hydration properties of cements made from clinker with Cr, Ni, and Zn compared to undoped cements. It is also interesting to see if these changes correlate with the composition of the clinker; therefore, three different types of cements were used. The phase composition of the corresponding clinker without heavy metals is shown in Table 1; PC refers to ordinary Portland cement; SRPC is sulphate-resisting Portland cement; and WPC is white Portland cement. The composition of all other clinkers, together with a more detailed introduction to this work, is given in Part I of this paper [1], which deals with the doped clinker used for the production of the cements in this work.

2. Methods

For the preparation of the doped cements, the clinker was crushed (<0.5 mm) with a jaw crusher and then ground in a ball mill together with a mixture of gypsum and anhydrite (50 wt.% + 50 wt.%). This mixture was calculated to give an SO_3 content of 3.2 wt.% in the cement. It was ground for 30 min, homogenised, and then the fineness was measured with a laser granulometer. Finally, the cement was ground until the specific surface was $3{,}500 \pm 50$ cm^2/g (measured with a laser granulometer).

3. Results and discussion

3.1. Fineness

The check for the fineness after 30 min and the total grinding time were done to detect any possible effect the metals might have on the grindability of the clinker. A similar work was done by Tsivilis and Kakali [2], who found a dependence of the grindability on the doped metal. However, in this work different concentrations of the metals produced no clear influence on the grindability.

3.2. Differential scanning calorimetry

With the differential scanning calorimetry (DSC) the heat of hydration of a cement during the early stage of hydration can be analysed. A sample of 5 g of cement in a test tube and 2.5 g of water in a syringe were placed in the apparatus and heated to 25°C. When the cement and the water had the same temperature, the water was injected into the test tube and the heat of hydration was recorded.

None of the samples with 200 or 1,000 ppm of heavy metals showed any difference in the development of the heat of hydration compared to the control sample. This

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Table 1
Phase composition of the clinker without heavy metal (wt.%)

Clinker	Alite	Belite	Aluminate	Ferrite	Free lime
PC	65	16	4	14	1
SRPC	72	5	1	21	1
WPC	89	1	9	–	1

means that a concentration of up to 1,000 ppm of Cr, Ni, or Zn in the clinker does not have any influence on the early stage of hydration of the cement.

Even at concentrations of 5,000 ppm, the influence on the hydration of the cement was insignificant. In the samples with 5,000 ppm of Ni, the rate of hydration was not changed compared to the control sample, but in cements with Cr or Zn a slight acceleration of the hydration could be detected. This might be the result of defects in the crystal lattice of the alite created by the heavy metals.

In Fig. 1 the heat of hydration of the three different cements with 2.5 wt.% of Cr, Ni, and Zn and the control sample is shown. The diagram is limited to 30 J/gh, because the initial reaction gave no further information.

In all of the three different cements, 2.5 wt.% of Cr shortened the induction period and therefore the hydration of the cement was accelerated. This acceleration had been found in an earlier study, where doped C_3S (2.5 wt.% Cr) was hydrated in the same way [3]. The doped samples of clinker contained much more belite + CaO than the control sample and therefore the concentration of alite was very low. It seems that either the belite in the clinker was activated by Cr and CaO or that it was a more reactive modification of the belite (α'-C_2S). It is remarkable that the samples with a high intake of Cr in the cement had an expansion reaction. The test tubes with the WPC and the SRPC burst within 1 day. The test tube of the PC with Cr was still intact after 2 days. The expansion reaction most likely was caused by the free lime in the cement. In the PC with 2.5 wt.% Cr, the content of CaO was 3.3 wt.% and in the SRPC and the WPC the content was more than 5 wt.%. Imlach [4], who also found an accelerated heat generation during the early hydration of cements with Cr, did not find any explanation for this effect.

With 2.5 wt.% of Ni, there was almost no change in the duration from the beginning of the hydration until the maximum rate of heat generation. Doped samples of C_3S were accelerated, but this effect was due to the higher content of free lime [3]. The doped cements in this study had a content of free lime that was comparable to that of the control sample. As mentioned in Part I of this study, a new phase $MgNiO_2$ was found in the clinker with high intakes of Ni. This compound is inert during the hydration. Kakali et al. [5] also found in their work that an intake of Ni had no effect on the hydration of Portland cement.

In all cements with 2.5 wt.% of Zn, the induction period was lengthened and therefore the hydration was delayed. However, the curves of the heat generation were different. In the case of the SRPC and the WPC, there was a long induction period of several hours after the initial reaction with nearly no heat of hydration. There was no such period in the PC. After the slowdown of the initial reaction, a slow acceleration of the heat generation occurred. There is no clear reason for this different behaviour, but the PC was rich in minor components and therefore these could have caused a change in the behaviour of the Zn.

The retardation effect of Zn was described several times. Lieber [6,7] found a strong retardation of the hydration even with little intakes of Zn, but in their paper it was not mentioned whether the raw meal had been doped with Zn or if the cement had been doped. This is very important, because the compound of the Zn is significant for the reaction. Lieber supposes that the formation and precipitation of $Ca[Zn(OH)_3 H_2O]_2$ was responsible for the retardation. Arliguie et al. [8] proposed that an amorphous layer of $Zn(OH)_2$ on the unhydrated cement particles retarded the hydration.

3.3. X-ray diffraction

The hydration of the cements was observed with X-ray diffraction (XRD) for 28 days. The cements were mixed with water (water/cement ratio = 0.4) and stored in sealed containers for 1, 7, or 28 days at 23°C. Afterward, the samples were crushed to <63 μm and vacuum-dried over silica gel. The samples then were measured with a X-ray diffractometer (model D 500 by Siemens, Cu K_α radiation) in the range from $2\Theta = 10$ to 65°. To detect the progress of hydration, the height of the alite peak at 32.3° was determined. The peaks of the Portlandite were not suitable for detecting the progress of the hydration because of the preferred orientation of the minute plates.

Within the measuring accuracy of this procedure, there was no difference in the content of alite in the control sample and in the samples with up to 5,000 ppm of heavy metals.

In all samples with 2.5 wt.% of Cr, the content of alite was much lower than in the control sample and the hydration of the alite was quite slow. The hydration of the samples with 2.5 wt.% Ni was nearly identical to that of the control sample. The content of $MgNiO_2$ did not change during the hydration process. After 1 day of hydration the content of alite in the samples with 2.5 wt.% of Zn, especially in the SRPC, was much lower than in the other samples. This corresponds to the results of the DSC. After 7 and 28 days the content of alite in all cements with Zn was comparable to that of the control sample.

3.4. Scanning electron microscopy and energy-dispersive X-ray spectrometry

Hydrated samples of the control cements and cements with 5,000 and 25,000 ppm of heavy metals were analysed with the scanning electron microscope (SEM) and the energy-dispersive X-ray spectrometer (EDS). The 28-day-old hardened cement paste was vacuum-dried over silica gel and then small pieces were coated with carbon.

The main phases in the hydrated cements were Portlandite, C-S-H phases, and ettringite. The range in the composition of these phases was quite wide. In some regions with no special morphology the content of iron and aluminium was very high.

In the samples with 25,000 ppm Cr, the heavy metal was mainly found in the C-S-H phases. The distribution of Cr in the clinker showed that this metal was mainly fixed in the silicate phase (see Part I of this report [1]). Consequently, the Cr remained in the phase where it had been before the hydration. In some regions of the C-S-H phases, the concentration of Cr was very high (up to 6 wt.%). The cause of this Cr enrichment cannot be explained reliably by the methods of testing used.

In the clinker Mg and Ni formed a new phase that was identified as $MgNiO_2$ (see Part I of this report [1]). Since the $MgNiO_2$ was still found in the hydrated samples, it is obvious that it could not have reacted with the water. In the clinker that contained less Mg, there was also found a higher concentration of Ni in the matrix. In these samples the Ni was mainly found in the hydration products of the aluminate and ferrite phase.

In the samples of the PC and the SRPC, Zn was concentrated in the hydration products of the aluminate and ferrite phase. In the WPC there was also a high concentration of Zn in the Portlandite.

In the samples with 5,000 ppm of heavy metals, no enrichments of heavy metals were found, but this was attributed mainly to a quite high detection limit of the EDS.

3.5. Initial setting

The initial setting of the cements was determined with a water/cement ratio of 0.28 for the PC and 0.30 for the SRPC and the WPC. The tests were made in conical rings (upper diameter = 65 mm, height = 41 mm) with a needle of 52 g and a diameter of 3 mm. The initial setting curves of the cements with 5,000 and 25,000 ppm of heavy metals are shown in Figs. 2 and 3.

In the samples with 25,000 ppm of Cr, the initial setting was accelerated in all cases (see Fig. 2). This concurs with the results of the DSC and may be caused by an activated modification of belite (α'-C_2S).

The curve of initial setting of the PC with 25,000 ppm Ni is nearly identical to that of the control sample. In the corresponding samples of the SRPC and the WPC, the initial reaction was slightly slowed down. The small influence of Ni, especially on the initial setting of the PC, is mainly caused by the inert $MgNiO_2$ that was formed during the clinkering process. In the SRPC and the WPC with a lower content of Mg (and less Ni to form $MgNiO_2$), the influence of Ni on the initial setting was higher.

The influence of Zn on the initial setting is more complicated. The curve of initial setting in . 2 shows a delayed reaction of the PC with 25,000 ppm of Zn, as had been expected after the results of the DSC. There are many references to such a retardation in the literature. But the samples of the SRPC showed a highly accelerated initial setting and the WPC was also accelerated. These results were in contrast to the DSC, which showed that the hydration of all three cements with 25,000 ppm of Zn was decelerated. When the sample of the SRPC was taken out of the conical ring, it showed unusual behaviour. The cement paste was not hard but thixotropic: When it was not touched, it seemed to have hardened, but when it was shaken or vibrated it became plastic. As can be seen in Fig. 2, the initial setting of the WPC was only accelerated up to 120 min, but then the initial setting continued very slowly.

The differences in the curves of initial setting of the cements with 5,000 ppm of heavy metals were much smaller. The initial setting of the PC was accelerated only slightly by Cr; that of the SRPC and the WPC was accelerated more strongly. Ni did not have a strong influence on the setting of any of the cements. Zn slightly accelerated the initial setting of the PC; the influence on SRPC was quite small, but the influence on the initial setting of the WPC was higher than that with 25,000 ppm of Zn.

The curves of the initial setting of the cements with 1,000 ppm of heavy metals were so similar that the differences were within the ranges of exactness of the production of the samples and the test method. It can be summarised that the doping of up to 1,000 ppm of Cr, Ni, and Zn does not have any influence on the initial setting of the cements.

3.6. Strength of cement mortars

The strength development of a cement is one of the most important properties for practical use; therefore, the strength development of the cements was tested. Test specimens ($1.5 \cdot 1.5 \cdot 6.0$ cm) of mortars with a water/cement ratio of 0.32 and an aggregate/cement ratio of 1 were produced from all cements with 5,000 and 25,000 ppm of heavy metal. The development of the compressive and flexural strength and the modulus of elasticity were nearly identical, and therefore only the compressive strength is discussed in this paper. The results of the compressive strength tests can be seen in Figs. 4 and 5.

At 7 and 28 days the samples with 25,000 ppm of Cr had the lowest strength (see Fig. 4). This was due to the low content of alite and the very high content of free lime and belite. Normally the strength of a cement rich in belite rises slower and the free lime leads to expansions that lower the strength by small cracks.

The influence of 25,000 ppm of Ni on the strength of the cement was very small. In the PC and the SRPC the strength after 28 days was somewhat higher than in the control sample; in the WPC there was no difference compared to the control sample. A possible interpretation of this result is that the formation of the new phase $MgNiO_2$ leads to a lower concentration of Mg in the alite, which then reacts differently than the control sample. In the WPC the content of Mg was low and the Ni was mainly found in the interstitial material. Therefore, the composition of the alite did not change compared to the control sample.

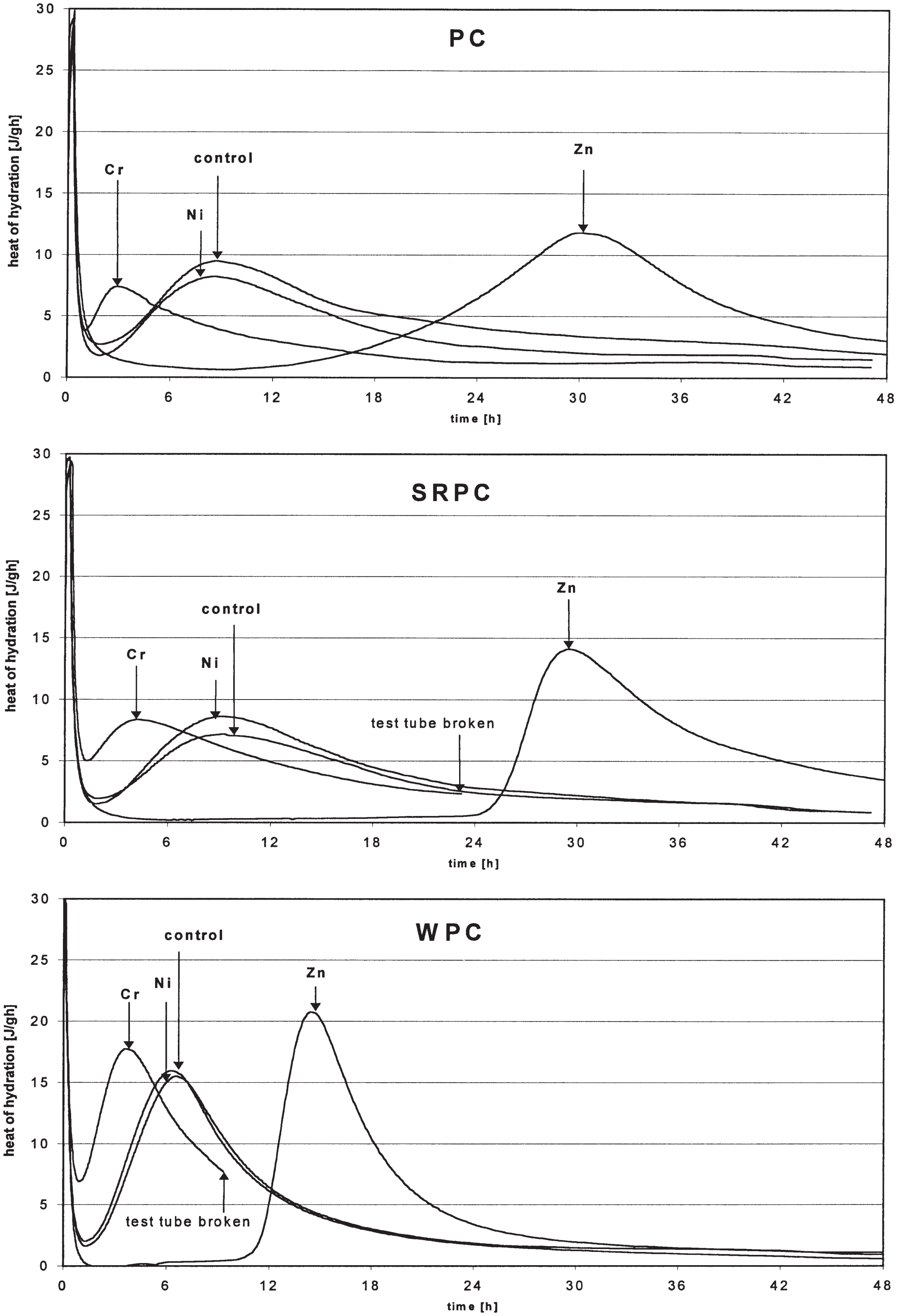

Fig. 1. Heat of hydration of the PC, the SRPC, and the WPC and samples with 25,000 ppm of Cr, Ni, and Zn.

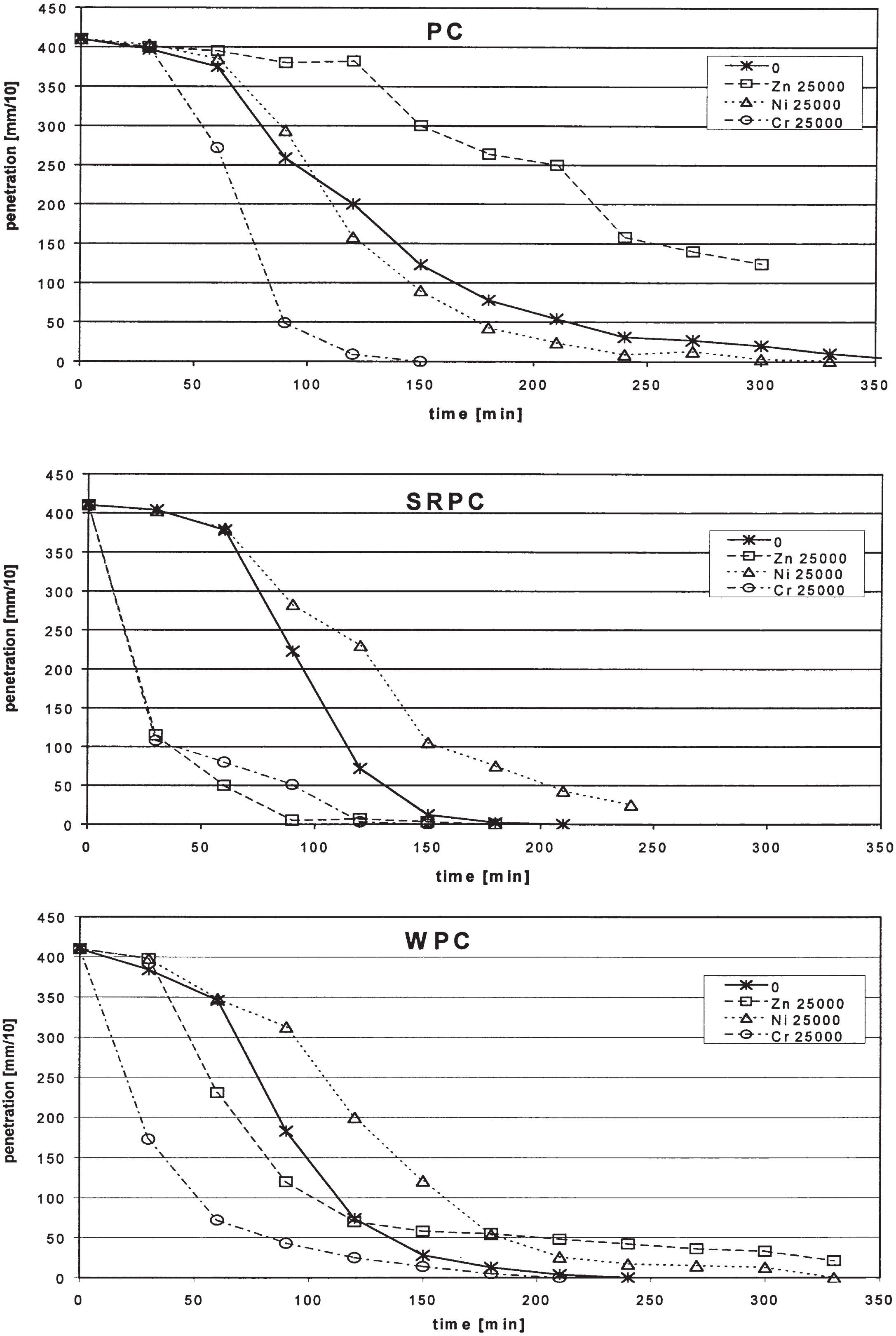

Fig. 2. Curves of initial setting of cements with 25,000 ppm of heavy metals.

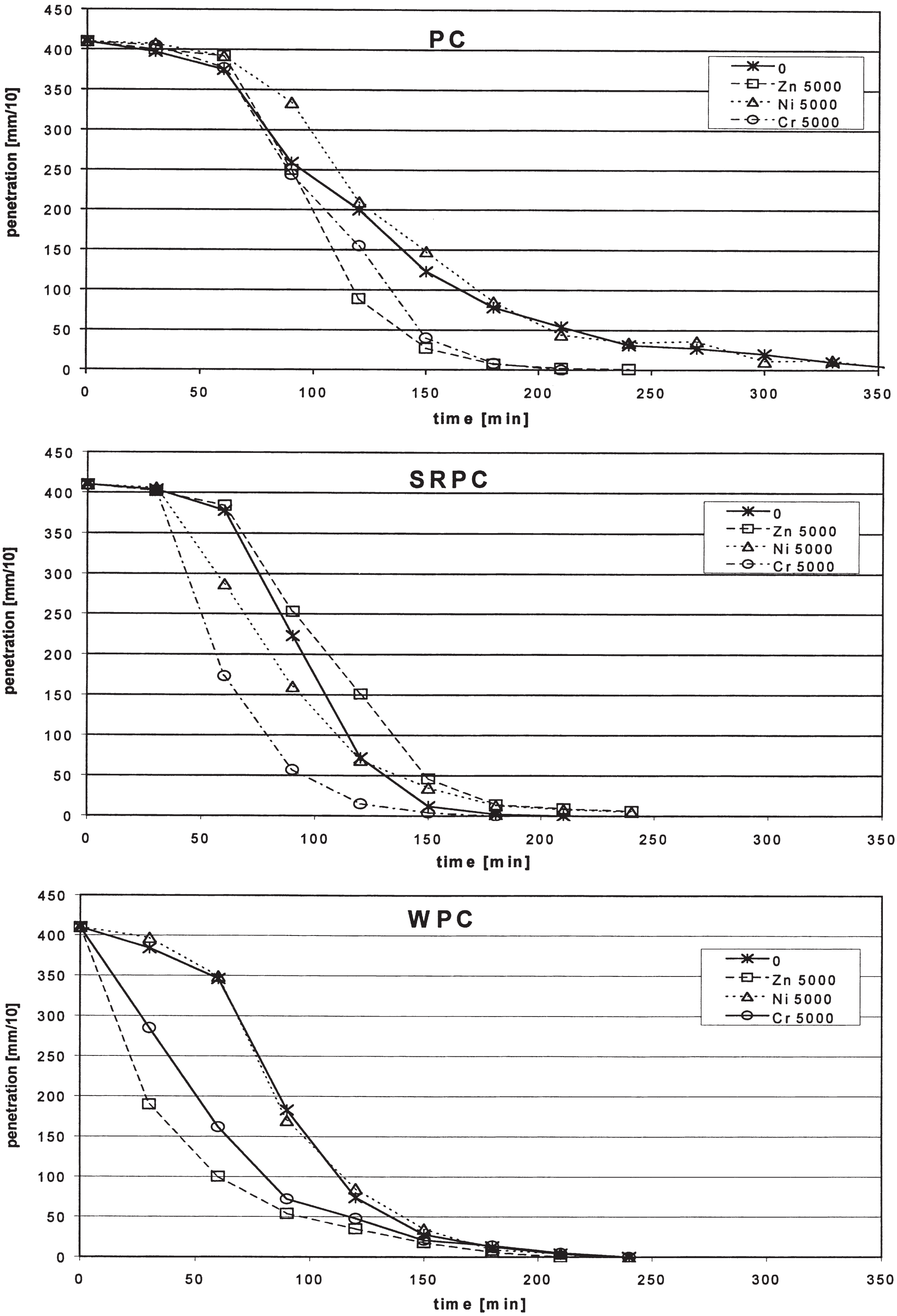

Fig. 3. Curves of initial setting of cements with 5,000 ppm of heavy metals.

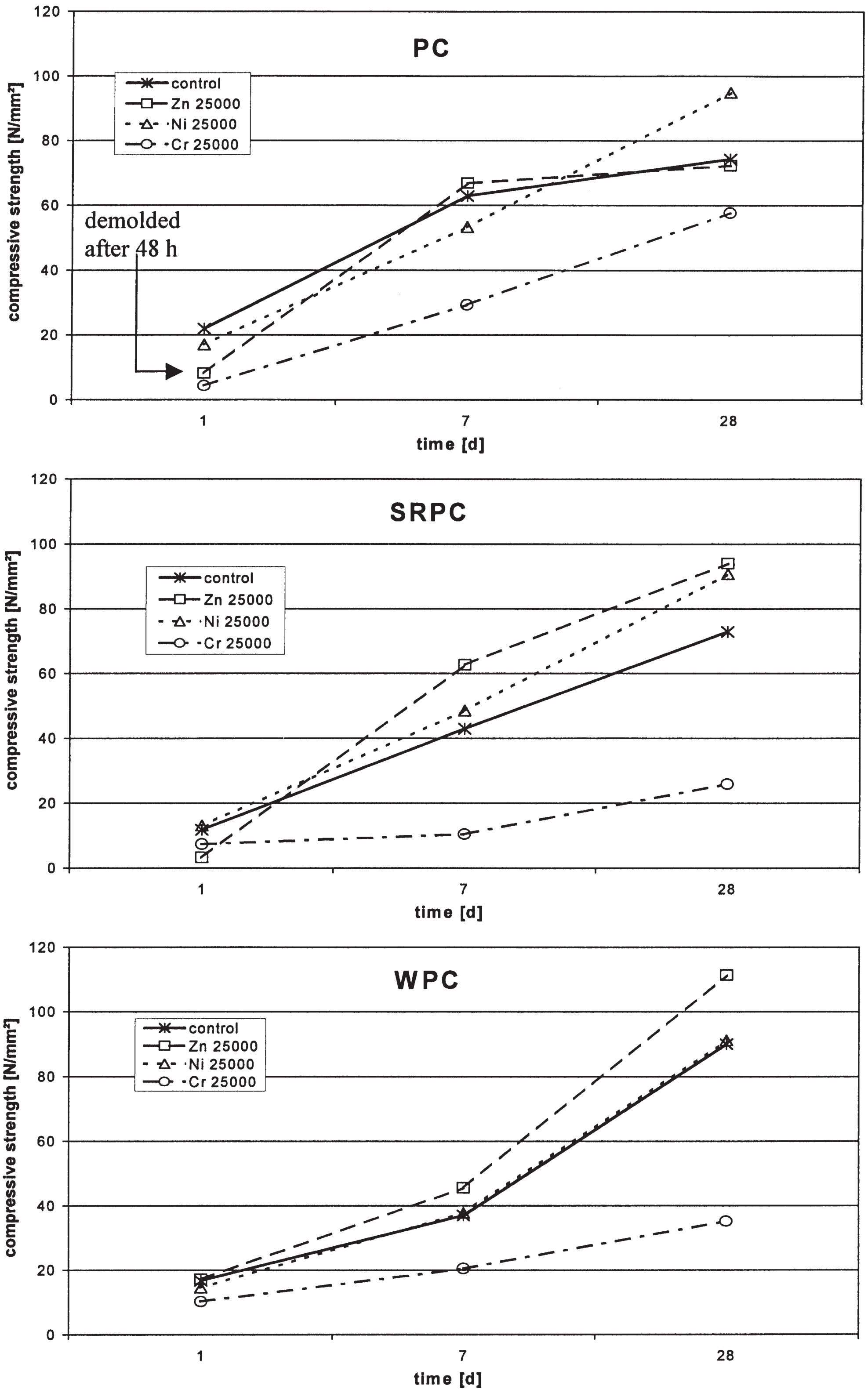

Fig. 4. Compressive strength of mortar: control sample and samples with 25,000 ppm heavy metal.

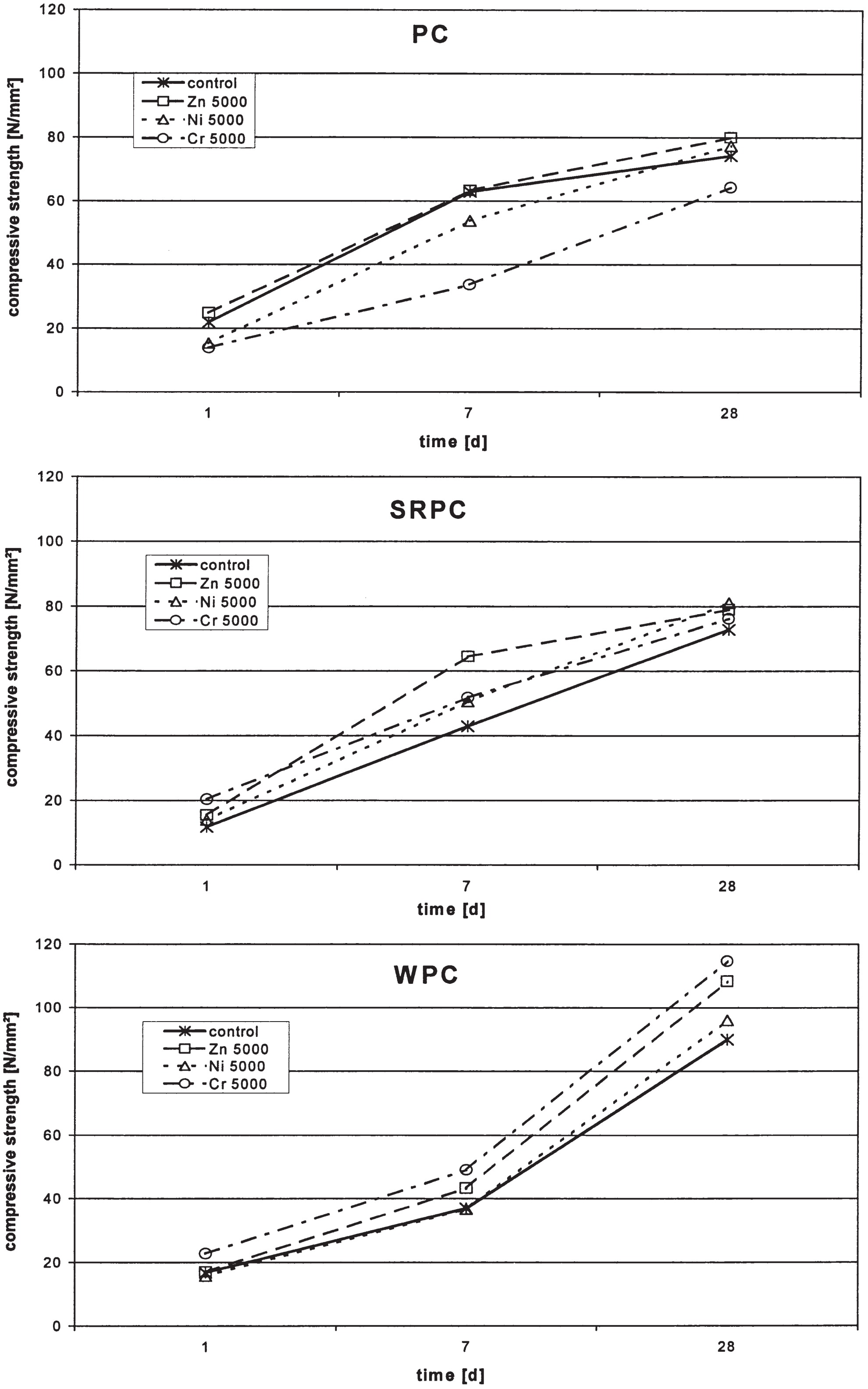

Fig. 5. Compressive strength of mortar: control sample and samples with 5,000 ppm heavy metal.

The effect of Zn changes during the periods of hardening. The strength after 1 day was very low in the case of the SRPC, and it was too low for demoulding the sample of the PC (see Fig. 4). There was no effect on the 1-day strength of the WPC because the retardation in the hydration of the WPC in the early period was smaller than that for other cements (considering also the influence of Zn on the heat of hydration). In the later periods of hydration, the cements with 25,000 ppm of Zn were normally the ones with the highest strength.

In the SRPC and the WPC with 5,000 ppm of heavy metals, the strength was always higher than in the control sample or comparable to the control sample. The partially positive effects might be caused by small amounts of heavy metals in the silicate phase that give more crystal lattice defects and therefore activate the hydration. It was not found for the PC with 5,000 ppm of Cr, where in all periods the strength was lower than in the control sample. This different behaviour might be caused by the different composition of the PC in which the content of minor element is higher than in the other cements. Tests with the PC with 1,000 ppm of Cr, Ni, or Zn showed that the heavy metals in this concentration have no influence on the strength.

4. Conclusions

The heavy metals Cr, Ni, and Zn have no influence on the strength of cement mortar and the initial setting or hydration of the cements at concentrations that are normally present in the clinker. Even at concentrations that are 10 to 20 times higher than normal, no changes could be detected. These concentrations are still too low to cause detectable changes in the concentration and composition of the clinker phases and therefore the technical properties were not affected. Very high intakes of Cr, Ni, and Zn can cause changes in the hydration properties. At high concentrations Cr accelerates the hydration of the cement and also the initial setting. The strength is lower than in the control. Even in higher concentrations, Ni has only very little influence on the hydration of the cement and the initial setting is only slightly retarded. The strength of mortars with Ni was equal to or higher than the control. Zn has a strong retardation effect on the hydration of cement and also leads to a retardation of the initial setting. In most cases the strength of mortars with Zn is higher than the control.

Acknowledgments

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