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Influence of Cr, Ni, and Zn on the properties of pure clinker phases
Part I. C_3S

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Abstract

Results are reported on the influence of Cr, Ni, and Zn on the properties of the pure clinker phases C_3S, C_3A, and C_4AF. Part I deals with the most important clinker phase C_3S. Samples were prepared with dosages of 0.02, 0.1, 0.5, 2.5, and 5.0 wt.% of Cr, Ni, and Zn (in form of their oxides). The doped C_3S was investigated for the content of free lime, the rate of evaporation of the metals, and by X-ray powder diffraction. The rate of heat liberation of ground samples was followed by differential scanning calorimetry for 2 days. The hydration products were investigated by X-ray powder diffraction and scanning electron microscopy combined with an energy-disperse X-ray spectrometer. All in all the heavy metals only have an influence on the structure and reactivity of the C_3S when the dosage is much higher than in ordinary portland cement.

Keywords: C_3SiO_5; Chromium; Heavy metals; Zinc; Nickel

Within this article the influence of Cr, Ni, and Zn on the properties of C_3S will be presented. The influence of these oxides on the properties of C_3A and C_4AF will follow in Part II. Throughout this work, cement nomenclature is used: C_3S = tricalcium silicate, C_3A = tricalcium aluminate, C_4AF = tetracalcium aluminoferrite, and C = CaO.

The main components of the portland cement are CaO, SiO_2, Al_2O_3, and Fe_2O_3, and they are responsible for the composition of the main phases alite, belite, and the aluminate and ferrite phase. Minor components such as MgO, SO_3, and alkalis also have an influence on the clinker formation during the burning process, as well as on the hydration process of the cement. However, cement contains also heavy metals. These so-called trace elements come from the natural sources of the raw materials. More volatile components, like compounds of Hg, Pb, and Tl will evaporate and precipitate in 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].

Because of their low concentration, trace elements normally have no influence on the process of burning or the hydration process. With more frequent use of alternative fuels and raw materials, and due to geologically caused variation of the concentration of trace elements, their concentration can possibly rise within the typical range of the clinker and its following products.

In order to estimate the influence of higher concentrations of heavy metals on the formation of clinker and the hydration, tests were made with pure clinker phases and portland cements that were doped with heavy metals. To show effects, the amount of added heavy metals was in concentrations two or three dimensions higher than usual in practice.

1. Experimental

1.1. Heavy metals in clinker

As opposed to other publications, in this work all given concentrations refer to the metals and not to the oxides. Table 1 gives an overview of the concentration of heavy metals in the raw mixtures and clinkers. The table is completed with data about the amounts of trace elements in the soil and the crust of the earth.

To prepare samples with higher concentrations of heavy metals, 0.02, 0.1, 0.5, 2.5, and 5.0 wt.% of Cr, Ni, and Zn were added to pure C_3S and were burned together. The metals were introduced as Cr_2O_3, NiO, and ZnO.

1.2. Preparation of samples

Pure C_3S was produced by burning stoichiometric amounts of $CaCO_3$ and SiO_2 (reagent grade) once for 2 h and

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Table 1
Concentration of heavy metals in the raw mixtures and clinkers

			Raw mix		Clinker			
Element	Crust of the earth [16] (minimum, maximum)	Soil world-wide [17] (average)	HMB* [18] (minimum, maximum, average)	VDZ** [19] (minimum, maximum)	HMB* [18] (minimum, maximum, average)	VDZ** [20] (minimum, maximum)	UK [21] (minimum, maximum, average)	USA [22] (minimum, maximum, average)
As	1, 13	5	3, 28, 11	3, 15	2, 87, 15	2, 15	10, 160, 43	5, 71, 19
Cd	0.03, 0.3	0.5	0.04, 1.0, 0.2	0.04, 0.15	0.01, 1.5, 0.2	0.01, 1.5	<0.1, 1.0, 0.4	0.03, 1.12, 0.34
Cr	4, 2980	200	23, 39, 27	23, 34	11, 319, 30	10, 90	51, 96, 70	23, 422, 76
Cu	4, 87		–, –, 17		5, 136, 40		16, 192, 44	
Hg	0.004, 0.4	0.08	0.02, 0.6, 0.07		<0.02, 1.2, 0.2	<0.01, –		<0.001, 0.039, 0.014
Ni	2, 2000	40	18, 30, 22	18, 23	12, 397, 30	10, 50		10, 129, 31
Pb	1, 20	10	4, 23, 12	4, 15	1, 105, 25	5, 105	0.5, 88, 15	1, 75, 12
Tl	0.1, 0.5		0.1, 6.0, 0.5	0.21, 0.78	0.01, 1.2, 0.2	<0.01, –	0.04, 0.48, 0.28	0.01, 2.68, 1.08
V		100	32, 102, 50		10, 100, 30	20, 100	15, 111, 56	
Zn	16, 130	50	15, 90, 30	31, 47	29, 531, 60	40, 350	28, 198, 96	

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then three times for 12 h at 1520°C. In between, the material was ground into particles <125 μm in size. To enhance their effects, heavy metals were added in concentrations two or three dimensions higher than usual. The content of free lime of the resulting product was 0.45 wt.%. In the same way, C_3S with a higher content of free lime (1.18 wt.%) was produced.

With these starting materials, the heavy metal oxides were mixed and burned another two times for 6 h, with an intermediate grinding at 125 μm in between. This sample preparation has many advantages and was already done by Woermann et al. [2] in their chemical and structural investigations on the solid solutions of C_3S. For the following analysis all samples were ground to the same fineness of 2700 ± 50 cm^2/g (measured with a laser granulometer).

In order to analyse the hydration products, samples were mixed with water (water/cement ratio 0.50) and cured for 1, 7, or 28 days at 25°C in sealed containers. The hardened cement paste was ground with acetone to stop the hydration process and was then dried at 10–20 mbar over silica gel. The samples for microscopy were only dried and not ground.

The differential scanning calorimetry of the C_3S-pastes was done with 5.0 g of each sample and a water/cement ratio of 0.50. The heat of hydration at 25°C was observed for about 48 h.

2. Results and discussion

2.1. Rate of metal evaporation and free lime

In order to detect the rate of evaporation of heavy metals during the preparation, all samples were analysed by a graphite furnace atomic absorption spectrometry. The results show that neither Cr nor Ni was evaporated while the rate of evaporation of Zn during the burning for 12 h at 1520°C was about 25%. This has to be considered to judge the other results.

The analysis of the free lime in C_3S was done according to Franke's method [3]. The results are given in Table 2.

In order to judge the way in which the metal is incorporated into the C_3S, the concentration of metal in the clinker and the change of free lime during burning is given in Table 3. The results do not show any clear mechanism on first sight, because only five samples from every metal were analysed.

With the addition of Cr up to a concentration of 0.5 wt.%, the content of CaO decreases. With more added Cr, the free lime rises extremely. Fierens and Verhaegen [4] found a linear rise of CaO up to 1.2 wt.% of Cr; with more Cr they also found an extreme rise of the CaO content. Sakurai and colleagues [5] came to the same results, and showed that a higher content of Cr led to a decomposition of C_3S into C_2S and CaO. Woermann et al. [2] found that the maximum concentration of Cr to be incorporated into C_3S at 1550°C is 1.0 wt.%. All these authors found no decrease in free lime with the addition of Cr. In contrast to that, Sychev and Korneev [6] found a decrease of the free lime up to a concentration of 0.7 wt.% Cr; with a higher concentration of Cr, the content of free lime increased extremely.

These different effects at lower concentrations might have different causes. One might be the different way of sample preparation. Fierens and Verhaegen [4] used very small samples that had been moulded into tablets before burning. These tablets have a small surface, so it is unlikely that the Cr in the sample is oxidised by the atmosphere in the furnace. It is not known whether any of the authors did the preparation in an inert atmosphere to protect the sample from oxidation. Presumably, the valence of the Cr might vary according to the different ways of sample preparation, which then influences the incorporation into C_3S significantly. For instance, Sakurai [5] found the Cr in the formal valence + 4.6.

The concentration of free lime rises with the content of Ni. However, the ratio of the added Ni to the rise in free lime is not stoichiometric. Possibly some of the Ni was not incorporated and/or some of the Ni was oxidised during the preparation. Mtschedlow-Petrossian and coworkers [7] found a con-

Table 2
Analysis of free lime

	Free lime (wt. %) stoichiometric C_3S		Free lime (wt. %) C_3S with higher CaO-content	
Added concentration of metal (wt. %)	First burning	Second burning	First burning	Second burning
pure C_3S	0.33	0.32	1.11	1.11
Cr (0.02)	0.28	0.28	1.06	0.98
Cr (0.1)	0.11	0.09	1.00	0.42
Cr (0.5)	0.16	0.11	0.67	0.14
Cr (2.5)	4.32	4.05	4.57	4.79
Cr (5.0)	n.d.	13.20	n.d.	n.d.
Ni (0.02)	0.36	0.34	1.18	1.09
Ni (0.1)	0.42	0.39	1.18	1.12
Ni (0.5)	0.98	0.81	1.57	1.39
Ni (2.5)	1.32	1.23	2.10	2.07
Ni (5.0)	n.d.	2.47	n.d.	n.d.
Zn (0.02)	0.39	0.39	1.18	1.09
Zn (0.1)	0.48	0.45	1.30	1.23
Zn (0.5)	0.63	0.62	1.49	1.26
Zn (2.5)	2.24	1.82	2.80	2.40
Zn (5.0)	n.d.*	3.42	n.d.	n.d.

* Not detected.

tent of free lime of 1.32 wt.% with Ni being added (as NiO) at a rate of 0.63 wt.%, but since the content of CaO of the reference is unknown, a comparison with our results is difficult.

At low concentrations of Zn in C_3S, there is no relation between the rise of free lime and the content of Zn. From 0.5 to 5.0 wt.% of Zn, the concentration of free lime rises linearly with the concentration of Zn. Hahn and colleagues [8] found that the limit of Zn incorporated into C_3S at 1400°C was 4.0 wt.%, while Odler and Abdul-Maula [9] found that C_3S could take up to 3.6 wt.% of Zn. There is a stoichiometric relationship between the addition of Zn and the rise of free lime, so it is most likely that Ca is substituted by Zn.

Different mechanisms of incorporation of the metal X into the C_3S have to be considered [10]:

- CaO is substituted for X.
- SiO_2 is substituted for X.
- CaO and SiO_2 are substituted for X.
- Occupation of octahedral and tetrahedral sides by X.

If the metal is not incorporated into the lattice, it is either left unchanged or has formed a new compound after reaction with C_3S.

2.2. X-ray powder diffraction of unhydrated phases

After Taylor [11] there are seven modifications of C_3S. The investigation of polymorphism of C_3S is complicated by the extremely similar modifications and by the very small transformation enthalpies. The polymorphism as a function of temperature is given in Fig. 1.

In pure C_3S at room temperature, the T_1 polymorph is the only stable one, but a foreign ion introduced into the C_3S crys-

Table 3
Concentration of metal in the clinker and the change of free lime during burning

Added metal (wt. %)	Concentration of metal (mol %)	Difference of CaO stoichiometric C_3S ΔCaO (mol %)	Difference of CaO C_3S with higher CaO content ΔCaO (mol %)
Cr (0.02)	0.09	−0.16	−0.53
Cr (0.1)	0.44	−0.93	−2.75
Cr (0.5)	2.15	−0.85	−3.83
Cr (2.5)	10.17	13.63	13.46
Cr (5.0)	19.05	37.58	n.d.
Ni (0.02)	0.08	0.08	−0.08
Ni (0.1)	0.39	0.28	0.04
Ni (0.5)	1.92	1.17	1.13
Ni (2.5)	9.13	3.80	3.80
Ni (5.0)	17.20	8.21	n.d.
Zn (0.02)*	0.02	0.28	−0.08
Zn (0.1)*	0.26	0.53	0.49
Zn (0.5)*	1.30	1.21	0.61
Zn (2.5)*	6.20	5.84	5.05
Zn (5.0)*	12.08	11.52	n.d.

* Rate of evaporation is taken into consideration; n.d. = not detected.

$$T_1 \overset{620\text{ °C}}{\rightleftarrows} T_2 \overset{920\text{ °C}}{\rightleftarrows} T_3 \overset{980\text{ °C}}{\rightleftarrows} M_1 \overset{990\text{ °C}}{\rightleftarrows} M_2 \overset{1060\text{ °C}}{\rightleftarrows} M_3 \overset{1070\text{ °C}}{\rightleftarrows} R$$

Fig. 1. Polymorphism of C_3S as a function of temperature [11].

tal lattice modifies the lattice energy and one of the other polymorphic forms is stabilised at room temperature [10]. In portland cement clinker mainly M_1, M_2, or a mixture of both structures is found [11]. Both structures are stabilized by the incorporation of MgO, but other ions are also to be found.

To study the polymorphism of C_3S and its solid solutions, especially the angles $2\,\Theta = 51–52$ ° and 31–33 ° ($Cu_K\alpha$-radiation) were examined. With very high dosages of heavy metals (2.5 wt.%), the modification of C_3S changes (Fig. 2).

While the addition of Cr up to 0.5 wt.% does not have any effect on the modification of C_3S, at a concentration of 2.5 wt.% Cr at least part of the C_3S is in the T_2 modification, and some of the C_3S is decomposed into C_2S and C. Woermann et al. [2] as well as Sakurai et al. [5] found no change in the modification of C_3S up to 1.0 wt.% Cr either, but Sakurai found the T_2 modification between 1.0 and 1.2 wt.% of Cr. The decomposition of C_3S at higher concentrations of Cr_2O_3 has already been described several times [4,5,12].

The X-ray diffraction pattern in Fig. 3 illustrates that the addition of Ni causes a gradual transformation from the T_1 to the T_2 polymorph. With more than 2.5 wt.% Ni, no further change in the X-ray diffraction pattern is detectable. The X-ray diffraction pattern of C_3S with 0.6 wt.% Ni recorded by Mtschedlow-Petrossian [7] is very similar to the one in Fig. 3 (2.5 wt.% Ni), but was attributed to a monoclinic modification.

Since the effect of Zn as a mineralizer is well known, there are many publications about the influence of Zn on the burning of raw mixtures to clinker as well as on the effect of Zn on C_3S. Odler and Abdul-Maula [9] did a very extensive study on Zn in C_3S. In contrast to other publications, they have described the manufacture of the samples precisely and have also analysed the rate of evaporation. An other extensive work was published by Bigaré and coworkers [13], but unfortunately there is no indication whether the published concentrations of Zn represented those contained in C_3S after the preparation or the concentrations that had been added before the burning. The results of both studies together with our own results (X-ray diffraction patterns are shown in Fig. 4) are summarised in Table 4. The results of our study are in accordance with those of the other works.

2.3. X-ray powder diffraction of hydration products

The X-ray diffraction patterns of the hydrated samples (1, 7, and 28 days) showed an increase of the portlandite reflection, but all C-S-H phases were amorphous to X-ray powder diffraction. The hydration product of C_3S with 2.5 and 5.0 wt.% heavy metal sometimes contained other products in very low concentration that could not be identified. In order to measure quantitatively the content of portlandite, the hydration products were also identified by thermogravimetry.

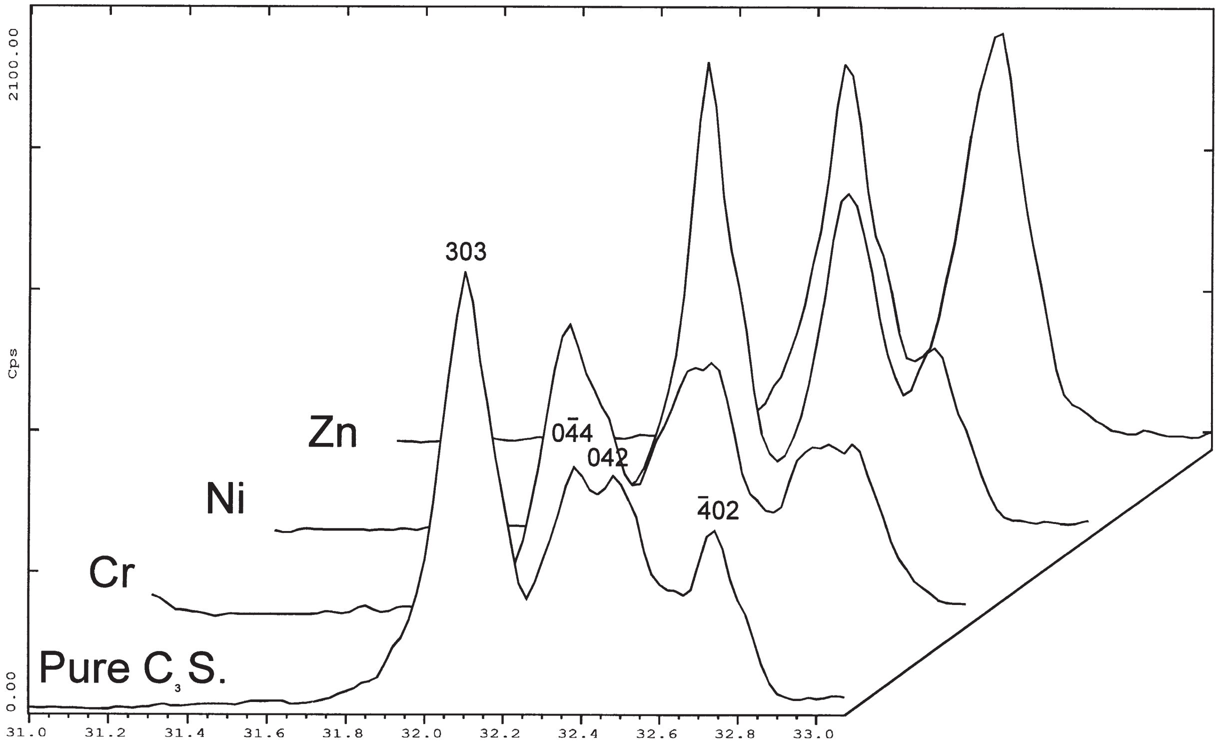

Fig. 2. X-ray diffraction pattern of pure C_3S and samples with 2.5 wt.% of heavy metal. Pure $C_3S \rightarrow T_1$, Cr $\rightarrow T_2 + C_2S$; Ni $\rightarrow T_2$; Zn $\rightarrow M_2$.

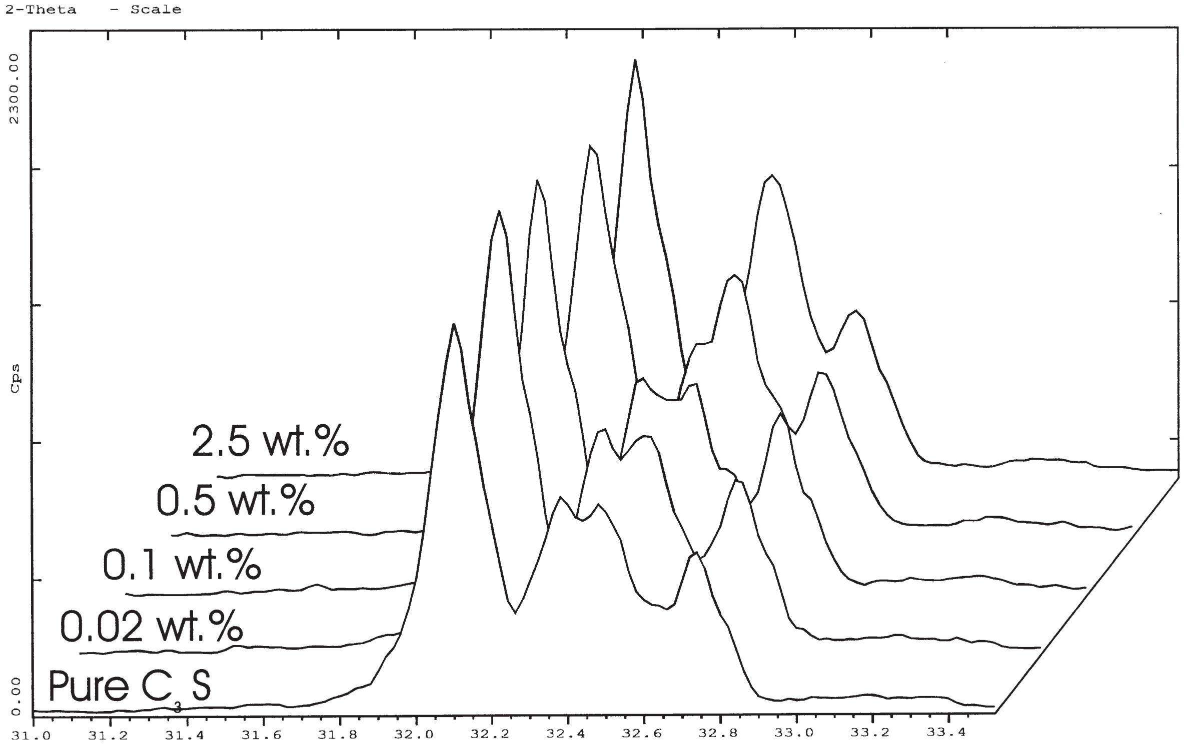

Fig. 3. X-ray diffraction pattern of C_3S with Ni. Pure $C_3S \rightarrow T_1$, 0.02–0.5 wt.% $\rightarrow T_1 + T_2$; 2.5 wt.% $\rightarrow T_2$.

2.4. Differential scanning calorimetry of C_3S pastes

The fineness of grinding and the content of free lime have an important influence on the hydration of C_3S. To eliminate these effects, all samples were ground to the same fineness of 2700 ± 50 cm^2/g (measured by a laser granulometer).

Additional samples of C_3S were prepared with contents of 1 and 5 wt.% of free lime. The heat of C_3S hydration with

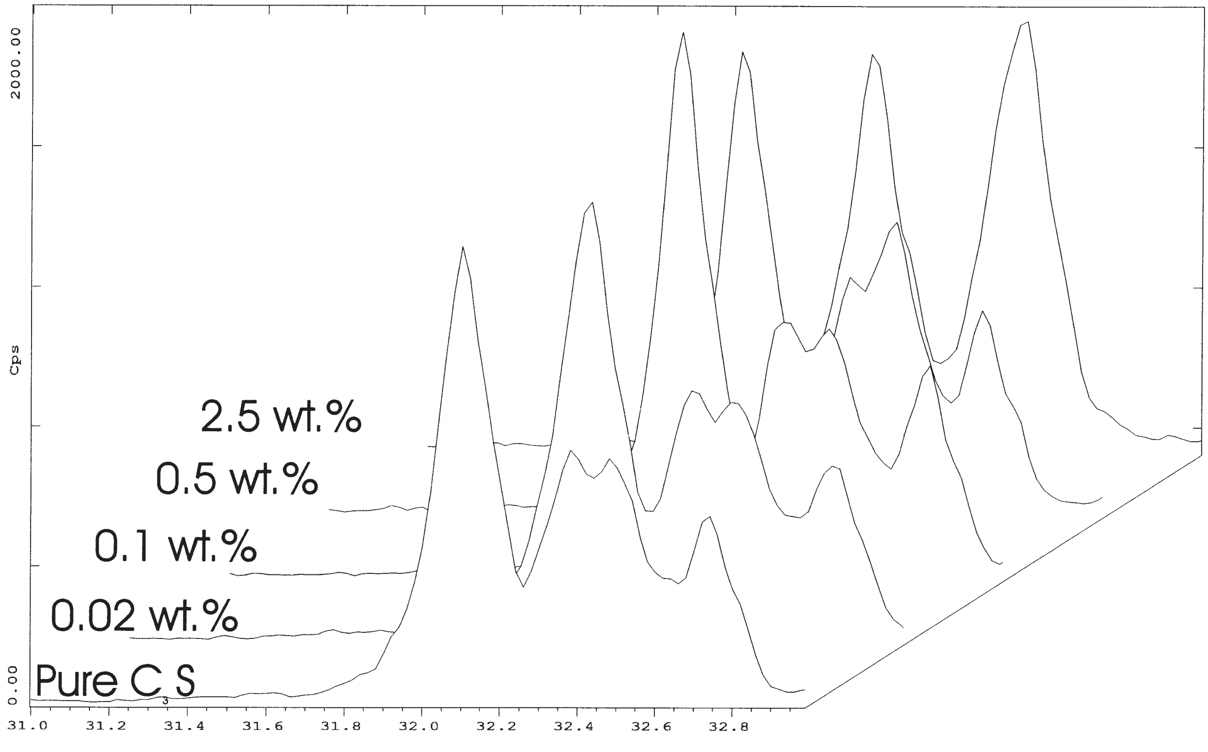

Fig. 4. X-ray diffraction pattern of C_3S with Zn. Pure C_3S + 0.02–0.1 wt.% $\rightarrow T_1$; 0.5 wt.% $\rightarrow T_2$; 2.5 wt.% $\rightarrow M_2$.

Table 4
Results of studies

Work	Modification	T_1	T_2	M_1	M_2	R	Limit
Odler [9]	Zn added (wt %)	0.0–0.8	1.2–2.4	2.8	3.2	3.6–4.4	3.8
	Zn analysed (wt %)	0.0–0.3	0.4–1.0	1.2	1.2	1.5–1.6	
Bigaré [13]	Zn* (wt %)	0–0.6	0.6–1.4	1.4–1.8	1.8–3.6	3.6–4.0	4.0
Own samples	Zn added (wt %)	0.0–0.10	0.50		2.50	5.00	
	Zn analysed (wt %)	0.0–0.08	0.38		1.88	3.75	

*Not mentioned if added or analysed concentration.

different concentrations of CaO is shown in Fig. 5. A content of 1 wt.% of free lime accelerates the hydration by approximately 4 h, but the maximum rate of heat liberation is reduced. With 5 wt.% of free lime there is no further acceleration of the hydration and the maximum rate of heat liberation remains similar to that of pure C_3S.

The hydration of pure C_3S and the samples with 2.5 wt.% of heavy metal are exemplary, compared in Fig. 6. When interpreting the effects of the metals, it has to be taken in account that the doped samples had a higher concentration of free lime than the pure C_3S (see Table 2).

Below a concentration of 0.5 wt.% Cr, the heat liberation is similar to that of the mixture with pure C_3S. Cr does accelerate the hydration at concentrations of 0.5 and 2.5 wt.% of Cr. Even if you take into account that the content of free lime in the samples with Cr is higher than that of pure C_3S, the heat of hydration is more accelerated than in the samples of C_3S with 1 or 5 wt.% of CaO. The measured effects of C_3S doped with Cr comparable to the ones measured by Sakurai et al. [5], who worked with Cr-doped cements. Mtschedlow-Petrossian [7] found an acceleration of the hydration of Cr-doped C_3S, as well.

The hydration of the sample with 2.5 wt.% of Ni is also accelerated compared to that of pure C_3S. But keeping in mind the content of free lime, there is almost no acceleration compared to the hydration of C_3S with 1 wt.% of CaO. A contrary effect of Ni on the hydration of C_3S was determined by Mtschedlow-Petrossian and coworkers [7]. By hydrating a sample of C_3S with 0.6 wt.% of Ni (in the form of NiO), they found an extreme deceleration of the heat liberation. In contrast to that they found a slight acceleration of the reaction by adding Ni_2O_3 instead of NiO. Therefore, in our own experiment at least some of the NiO might have been oxidised to Ni_2O_3 while burning the sample in the furnace.

Zn was the only metal in this investigation that decelerated the heat liberation, even though the sample with 2.5 wt.% of Zn contained 1.8 wt.% of CaO. This sample was also the one with the highest maximum of heat liberation of

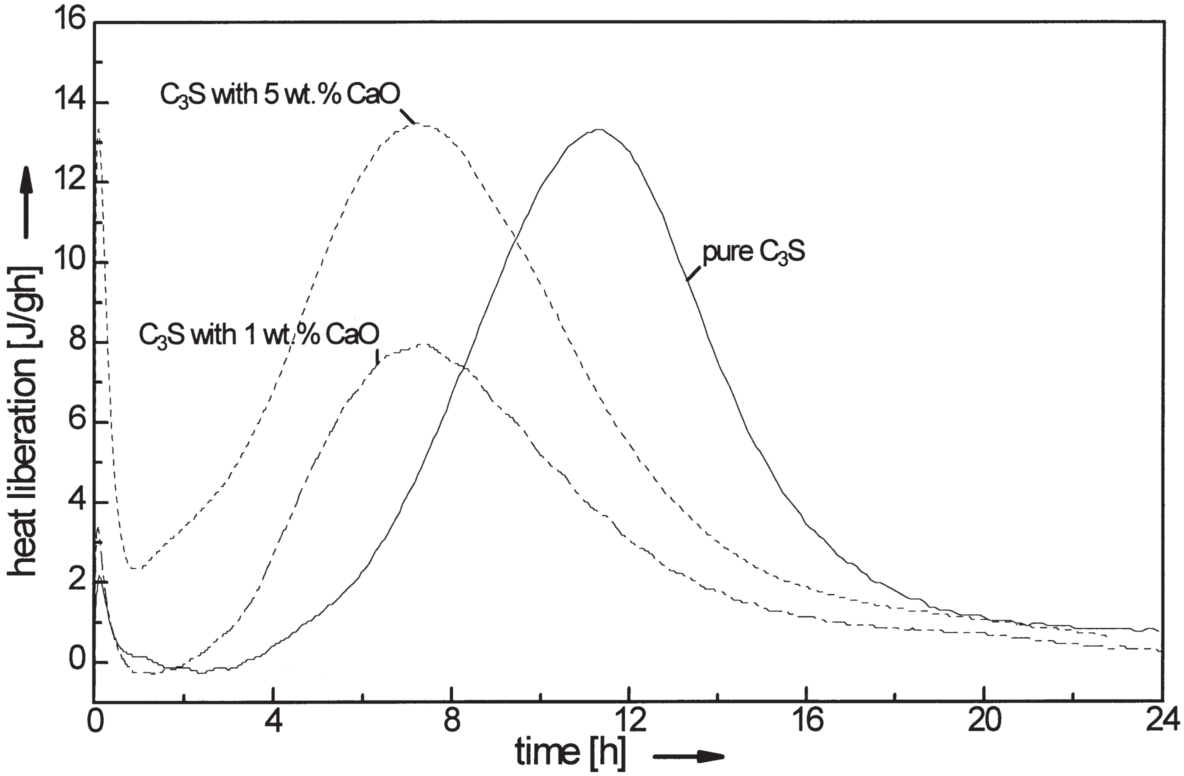

Fig. 5. Hydration of C_3S with different concentrations of CaO.

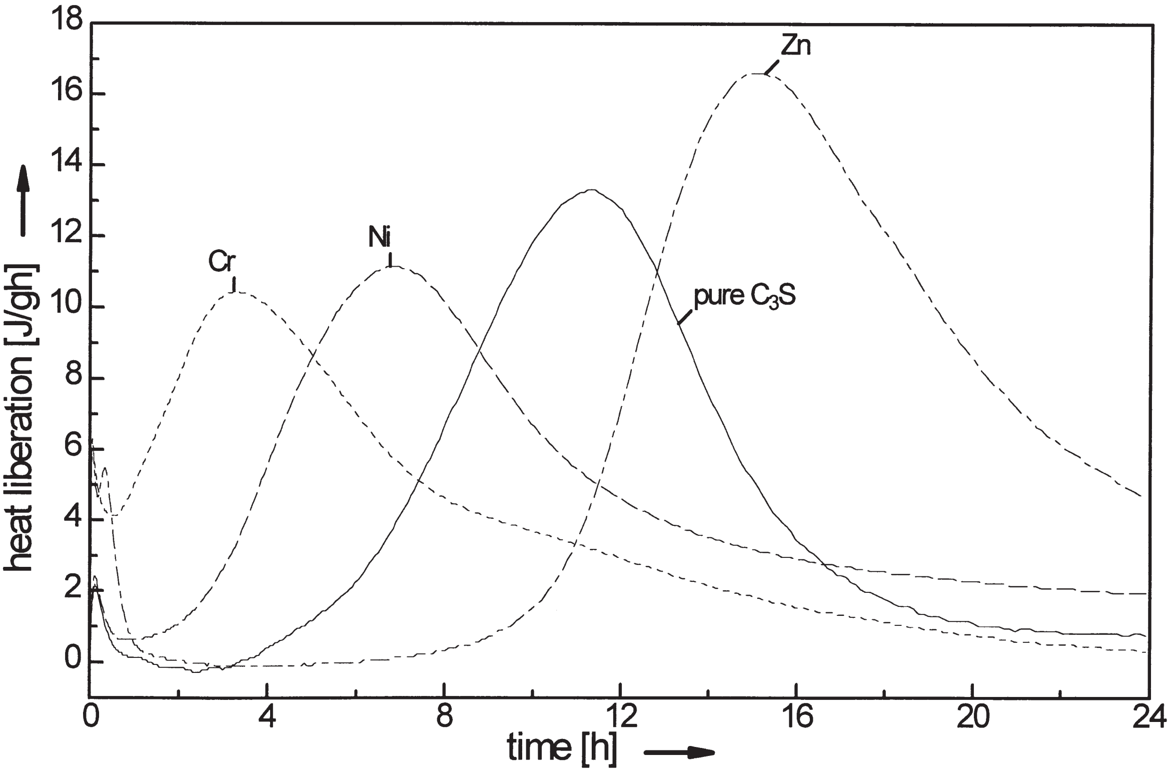

Fig. 6. Hydration of pure C_3S and C_3S with 2.5 wt.% of Cr, Ni, and Zn.

all. The sample with 0.5 wt.% of Zn (0.6 wt.% CaO) showed practically no change compared with the pure C_3S. Mtschedlow-Petrossian et al. [7] showed in their work that the addition of Zn to C_3S (0.6 wt.%) results in a different duration of hydration up to the maximum of heat liberation, but the heat liberation was higher than that of pure C_3S. Odler and Abdul-Maula [9] found similar results, but the content of free lime in their samples was <0.25 wt.%.

The retardation may be caused by a reaction similar to the one suggested by Jawed and colleagues [14] for the retardation of C_3S by $ZnCl_2$. The Zn in the clinker can react to $Zn(OH)_2$; if the hydroxide reacts with additional hydroxyl ions to form a complex oxyanion, which may precipitate as an insoluble calcium salt, then the hydration will be retarded until these reactions are completed because both $[OH^-]$ and $[Ca^{2+}]$ are kept low. Lieber [15] found $Ca(Zn(OH)_3)_2) \cdot 2H_2O$ during the early hydration of cement, when the cement paste was retarded by Zn. So it is conceivable that during the induction period $Ca(Zn(OH)_3)_2) \cdot 2H_2O$ is formed. The consequence of this formation is that the concentration of Ca^{2+} and OH^- is kept low and the required supersaturation does not occur until the formation of $Ca(Zn(OH)_3)_2) \cdot 2H_2O$ is completed.

2.5. Scanning electron microscopy

Some of the unhydrated and hydrated samples were investigated with a scanning electron microscope (SEM) that had been connected to an energy-disperse X-ray spectrometer (EDS). The composition of pure C_3S and that of the samples with Cr and Zn were homogeneous. In the sample with Ni there were some inhomogeneities.

Fig. 7 shows a typical picture of the hydrated C_3S with hexagonal portlandite and the C-S-H phases. The analysis of the composition of the two phases by EDS showed that the heavy metals were mainly fixed in the C-S-H phases. The concentration of the heavy metals in the portlandite was in most cases below the detection sensitivity. In the samples with Ni and especially with Cr the areas of the portlandite and C-S-H phases were less extensive than the ones in the sample made from pure C_3S, the opposite of what was found in the samples with Zn.

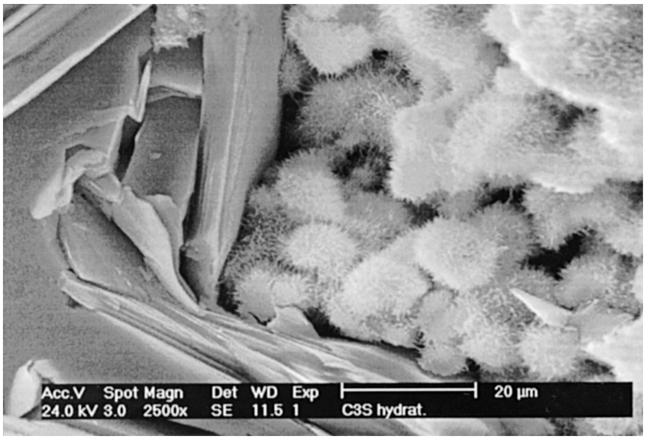

Fig. 7. SEM of hydrated C_3S.

3. Conclusion

Low concentrations of heavy metals do not have any influence on the modification of C_3S. At concentrations of at least 0.5 wt.% the heavy metals Cr, Ni, and Zn can change the modification of C_3S and especially high intakes of Cr lead to a decomposition. Intakes of up to 0.5 wt.% Cr lower the content of free lime, while higher concentrations of Cr and the addition of other metals at any concentration cause an increase in free CaO. The metals are distributed homogeneously in the clinker.

A high content of free lime (1–5 wt.%) in C_3S does accelerate the hydration process. None of the heavy metals had an effect on the hydration process at concentrations of up to 0.1 wt.%. Concentrations of 2.5 wt.% Cr distinctively accelerate the heat liberation. The effect of Ni is not considerably higher than that with comparable concentrations of free lime in pure C_3S. Zn retards the heat liberation.

Investigations by SEM combined with EDS gave evidence of the accumulation of the heavy metals in the C-S-H phases. Ni and Cr lead to more extensive areas of portlandite and C-S-H phases, while these areas were less extensive in the samples with Zn.

All the heavy metals only have an influence on the structure and reactivity of the C_3S when their dosage is much higher than in ordinary portland cement. Dosages that are about 20 times higher for Cr and Ni or 10 times higher for Zn than in ordinary portland cement have no influence on C_3S.

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