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Influence of Cr, Ni, and Zn on the properties of pure clinker phases Part II. C_3A and C_4AF

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Abstract

The results about the influence of Cr, Ni, and Zn on the properties of the pure clinker phases C_3S [1] C_3A and C_4AF are reported in two papers. Part II deals with the clinker phases C_3A and C_4AF. 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_3A and C_4AF were 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 was studied by differential scanning calorimetry. 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 reactivity of the C_3A and C_4AF when the dosage is much higher than in ordinary portland cement.

Keywords: $Ca_3Al_2O_6$; Calcium aluminoferrite; Chromium; Zinc; Nickel

An overall view on the question of heavy metals in cement and the concentrations of heavy metals in the raw mix and clinker was given in Part I [1]. In this work all given concentrations refer to the metals and not to the oxides, which is different than some other publications. Cement nomenclature is used: C_3S = tricalcium silicate, C_3A = tricalcium aluminate, C_4AF = tetracalcium aluminoferrite, and C = CaO.

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_3A and C_4AF. The metals were introduced as Cr_2O_3, NiO, and ZnO.

1. Experimental

Pure C_3A was produced by burning stoichiometric amounts of $CaCO_3$ and Al_2O_3 (reagent grade) once for 18 h and then twice for 24 h at 1450°C. In between the material was ground to <125 μm. The content of free lime of the resulting product was 0.02 wt.%. C_4AF was produced by burning stoichiometric amounts of $CaCO_3$, Al_2O_3, and Fe_2O_3 (reagent grade) three times for 6 h at 1320°C. In between the material was ground to <125 μm. The content of free lime at this point was 0.35 wt.%.

These starting materials were mixed with the heavy metal oxides and then burned twice for 3 h and ground to <125 μm between burning. In the case of C_4AF the temperature was remained unchanged (1320°C), but in the case of C_3A the burning temperature had to be lowered from 1450°C to 1400°C because the mixtures with higher concentrations of heavy metals molted at 1450°C and could not be removed from the platinum crucible.

For the following analysis, all samples were ground to the same fineness. Like the C_3S reported in Part I, the C_4AF-samples were ground to a fineness of 2700 ± 50 cm^2/g (measured with a lasergranulometer). In the case of C_3A it was impossible to achieve a fineness of 2700 cm^2/g with regular particle-size distribution curves; therefore the material was ground to the fineness of 4000 ± 50 cm^2/g.

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 phases 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 24 h.

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2. Results and discussion

2.1. Rate of evaporation and free lime

In order to detect the rate of evaporation of heavy metals during the preparation, all samples were analysed by graphite furnace atomic absorption spectrometry. The results show that none of the Cr, Ni, or Zn was evaporated.

The analysis of the free lime in the samples was done according to the method of Franke [2]. Compared to pure C_3A (0.0 wt.% CaO), there were only three samples with a higher content of free lime. These were samples with 5.0 wt.% of Cr (0.28 wt.% CaO), 2.5 wt.% of Zn (0.28 wt.% CaO), and 5.0 wt.% Zn (2.3 wt.% CaO). The results indicate that very high dosages of heavy metal lead to defects in the crystal lattice.

The addition of heavy metals to C_4AF does not effect the content of free lime in this phase. This is because the compound C_4AF (also called Brownmillerite) has a specially defined composition ($X = 0.5$) in the wide range of the solid solution of $Ca_2(Al_XFe_{1-X})_2O_5$, where $0 < X < 0.7$. Addition of several wt.% of CaO to pure C_4AF does not bring about detectable amounts of free lime either.

2.2. X-ray powder diffraction (XRD) of unhydrated phases

The crystal structure of pure C_3A is described as cubic C_I [3,4], but with additions of sodium a cubic structure C_{II} (1.0–2.4 wt.% Na_2O), an orthorhombic structure O (3.7–4.6 wt.% Na_2O), and even a monoclinic structure M (4.6–5.7 wt.% Na_2O) was synthesised. Si and Fe atoms can also stabilise the O or M modification [3].

The XRD pattern of C_3A, even with high intakes of 5.0 wt.% of heavy metal, did not indicate a change of the crystal structure. It was remarkable that the XRD pattern of the samples with higher intakes of metal showed sharper diffraction patterns. Differing from the studies with C_3S [1], some newly formed compounds could be identified in the samples with 5.0 wt.% of heavy metal. In the sample with Cr the compounds $Ca_4Al_6O_{12}CrO_4$ and $Ca_6Al_4Cr_2O_{15}$ could be identified. The first compound is a chromate, with the valence of the Cr +6; in the second one the valence is still the same as in the raw material (+3). Since chromates are readily soluble, this first compound could be the reason for the easy leachability of Cr from concrete. $Ca_4Al_6O_{12}CrO_4$ was also identified in C_4AF with high intakes of Cr.

In samples with high intakes of Ni in C_3A or C_4AF, some of the NiO that had been put into the raw mix could still be found in the XRD pattern. It is unknown whether the reaction was incomplete or whether C_3A does not take in more Ni. Similar results were found with the addition of Zn; some of the ZnO was left unchanged. The XRD pattern as well indicated by new reflections that another new compound had been formed, but because of the low concentration, this compound could not be identified.

2.3. X-ray powder diffraction of hydration products

The hydration of all samples (C_3A and C_4AF) was done without adding any gypsum, because the addition of another component would have made the mixture more complex and the interpretation more difficult.

Depending on the conditions of the hydration of C_3A, there are several products conceivable. The hexagonal hydrates (C_4AH_{19}, C_2AH_8 and C_4AH_{13}) are metastable and convert to the cubic hydrate C_3AH_6, which is a hydrogarnet [3,4]. In our study, the hydration product of pure C_3A was mainly C_3AH_6; after 24 h some C_4AH_{13} was found and after 28 days some C_2AH_8. Within 24 h approximately 5% of the C_3A was left unhydrated and after 28 days the hydration was completed. The relatively low content of hexagonal hydrates in comparison to other investigations [5] is due to the higher temperature during curing and the low relative humidity during drying of the samples. At higher temperatures the hexagonal hydrates are less stable and Roberts [6] as well as Scheller and Kuzel [7] found that especially the hexagonal hydrates with a high content of water are very sensitive to drastic drying conditions.

In the samples with Cr the hydration products and the rate of hydration do not change until concentration reaches 0.5 wt.%. In these samples the hydration products are identical to those with pure C_3A, but the hydration is already complete after 7 days. With 2.5 wt.% of Cr, the hydration process is much slower and the concentration of the hexagonal hydrates is higher than in all other samples. After 24 h no $Ca_4Al_6O_{12}CrO_4$ (valence +6) was left, but the compound $Ca_6Al_4Cr_2O_{15}$ (valence +3) could still be detected. With a concentration of 5.0 wt.% of Cr, the hydration products are absolutely different from all other products. In the XRD pattern no C_3AH_6 could be found, but also only a small amount of hexagonal hydrates could be found. Generally, the patterns were hard to interpret. Tashiro and Oba [5] found that the hydration of C_3A with 12.3 wt.% of Cr_2O_3 (mixed with C_3A and not burned) was retarded, but the hydration products were identical to those of pure C_3A.

The hydration process of the C_3A that had been doped with Ni was not affected at all. Even concentrations of 5.0 wt.% of Ni did not lead to other hydration products of the C_3A, but some NiO from the starting material was found in the XRD pattern.

Up to 0.5 wt.% Zn also had no effect on the hydration of C_3A. But with higher concentrations of 2.5 and 5.0 wt.% Zn, the hydration was slightly retarded and the content of hexagonal hydrates increased. In these samples the compound $Ca(Zn(OH)_3)_2 \cdot 2H_2O$ could be found. Lieber [8] identified this compound during the early hydration of cement, when the cement paste was retarded by Zn. Tashiro and Oba [5] found in their work that the hydration of C_3A with 7.0 wt.% of ZnO (just mixed with C_3A and not burned) was retarded, and less C_3AH_6 and more hexagonal hydrates formed. They did not report any other hydration product containing Zn.

In the absence of gypsum, the hydration products of C_4AF are very similar to those that are formed during the hydration of C_3A [3,4,9], although the rate of hydration is found to be much lower. At low temperatures, hexagonal hydrates such as $C_4(A,F)H_{19}$ or $C_4(A,F)H_{13}$ are stable hydration products, but at about 20°C they soon convert to $C_3(A,F)H_6$. In a few cases $Fe(OH)_3$ was found by scanning electron microscopy (SEM), but this hydration product was never detected by XRD, so it seems to be amorphous.

In our experiments, C_3AH_6 was the main hydration product found by XRD. No product was found to contain Fe. After one day, the sample from pure C_4AF contained small amounts of C_4AH_{13} that could no longer be detected after 28 days of hydration.

After one day, the rate of hydration of the sample from pure C_4AF and the sample with Ni were identical and the rate of hydration of the sample with Zn was about 70% that of pure C_4AF. In the sample with Cr, absolutely no C_3AH_6 could be detected by XRD, but a small amount of C_2AH_8 was found. In the same sample, the compound $Ca_4Al_6O_{12}CrO_4$ was still unchanged.

Within 7 days, the hydration was nearly completed and the hydration products of all samples were similar, except for the sample with Cr. In the latter, much of the starting material was left. The same results were found after 28 days. Only the hydration of the sample with Cr remained incomplete and much C_4AH_{13} and C_2AH_8 was found.

2.4. Differential scanning calorimetry of pastes

As in the other investigations no gypsum was added. The fineness of grinding and the content of free lime did not effect the heat liberation as much as in the case of C_3S.

Fig. 1 shows the hydration of pure C_3A and of the samples with 2.5 wt.% of Cr, Ni, and Zn. Ni does have a small effect on the heat liberation during hydration of C_3A. The results are within the reproducibility of the measurement. But Cr and Zn have a great influence on the heat liberation. Both metals reduce the maximum rate of heat liberation, but the length of the hydration process until the occurrence of the maximum of heat liberation is unchanged. Only in the case of Zn there is a second maximum of heat liberation at about 30 min.

During the hydration of C_3A with 0.5 wt.% of Cr, the reaction is retarded and the maximum rate of heat liberation appears about 10 min later than in the case of pure C_3A, but the rate of maximum heat liberation is comparable to the one with pure C_3A. At lower concentrations there is no difference to pure C_3A.

In the sample with 0.5 wt.% of Zn, there is a maximum of heat liberation that lies between that of pure C_3A and the sample with 2.5 wt.% of Zn. The results of Tashiro and Oba [5] support these results.

The heat liberation of pure C_4AF and the samples with 2.5 wt.% of Cr, Ni and Zn is shown in Fig. 2. Compared to

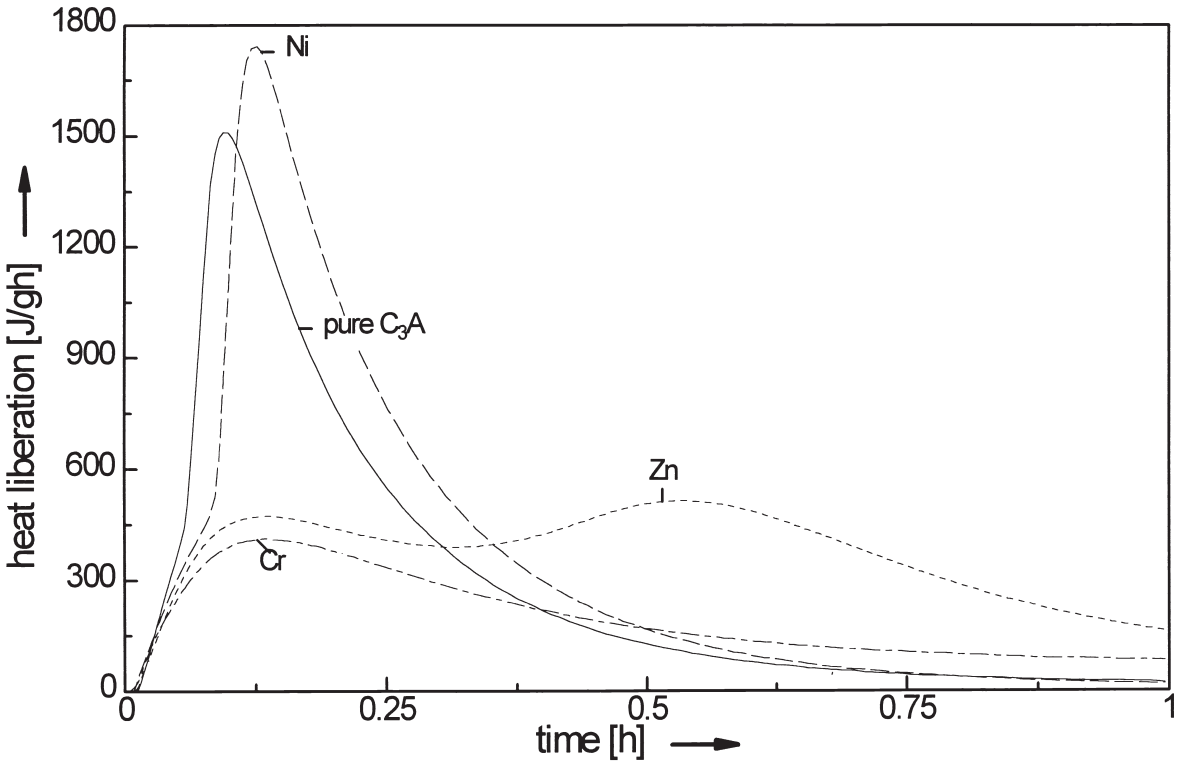

Fig. 1. Hydration of pure C_3A and C_3A with 2.5 wt.% of Cr, Ni, and Zn.

pure C_4AF, Ni gives a higher rate of maximum heat liberation.

The effect of Zn on the heat liberation is very small. This contrasts with the effect of Cr. In the first 10 h there is nearly no heat evolution. After 15 h a small maximum of heat evolution occurs that is, however, only about 1% of the height of the maximum found during the hydration of pure C_3A. This retardation appears also when C_4AF is mixed with water. There is no initial setting of the paste within 20 h.

When only 0.5 wt.% of heavy metals were added to the C_4AF, in none of the experiments does a change in heat liberation occur. Even the sample with Cr did not show any difference to pure C_4AF.

2.5. SEM

Some of the unhydrated and hydrated samples were investigated with an SEM that had been connected to an energy-disperse X-ray spectrometer (EDS). All unhydrated samples showed a homogeneous distribution of the added heavy metals. Only Ni was sometimes distributed inhomogeneously.

Fig. 3 shows a typical picture of the hydrated C_3A with hexagonal and cubic hydration products. Several authors investigated the hydration products of C_3A by SEM [10,11]. The icositetrahedron is typical of C_3AH_6 and the hexagonal phase normally appears in small plates.

The effects of Cr on the hydration of C_3A become visible in Figs. 4 and 5. In the hydration product no icositetrahedron could be found, only small plates and an octahedral product. In some regions these products occurred separately, in other regions they were mixed. Analyses by EDS showed that Cr was accumulated in the small plates and the concentration of Cr in the octahedral phase was below the detection sensitivity. It is most likely that both hydration products are hexagonal and that they are stabilised by Cr. An other sample with 5.0 wt.% of Cr contained only small plates. In the same sample were also regions with a very high concentration of Cr (see Fig. 6). Samples with a Cr concentration of 0.5 wt.% did not show significant differences compared to the sample from pure C_3A. The samples doped with Ni did not show any change in the morphology of the hydration products, even with high intakes of metal.

The C_3A doped with 2.5 wt.% of Zn did not show significant differences in the morphology either, but it was noticeable that the icositetrahedron contained more defects. The EDS proved that C_3AH_6 contained only a little of the added Zn. Instead there were regions with a very high concentration of Zn, some of which were amorphous and seemed to be a residue of the added ZnO. Another region with a high concentration of Zn is shown in Fig. 7. The hydration product consists of long branched needles. The EDS showed that beside Zn, these needles contain only calcium. Therefore, this compound is probably $Ca(Zn(OH)_3)_2 \cdot 2H_2O$, which had already been found in the XRD pattern.

Tashiro and Oba [5] hydrated pure C_3A and samples that had been doped with 7.0 wt.% of ZnO or 12.3 wt.% Cr_2O_3.

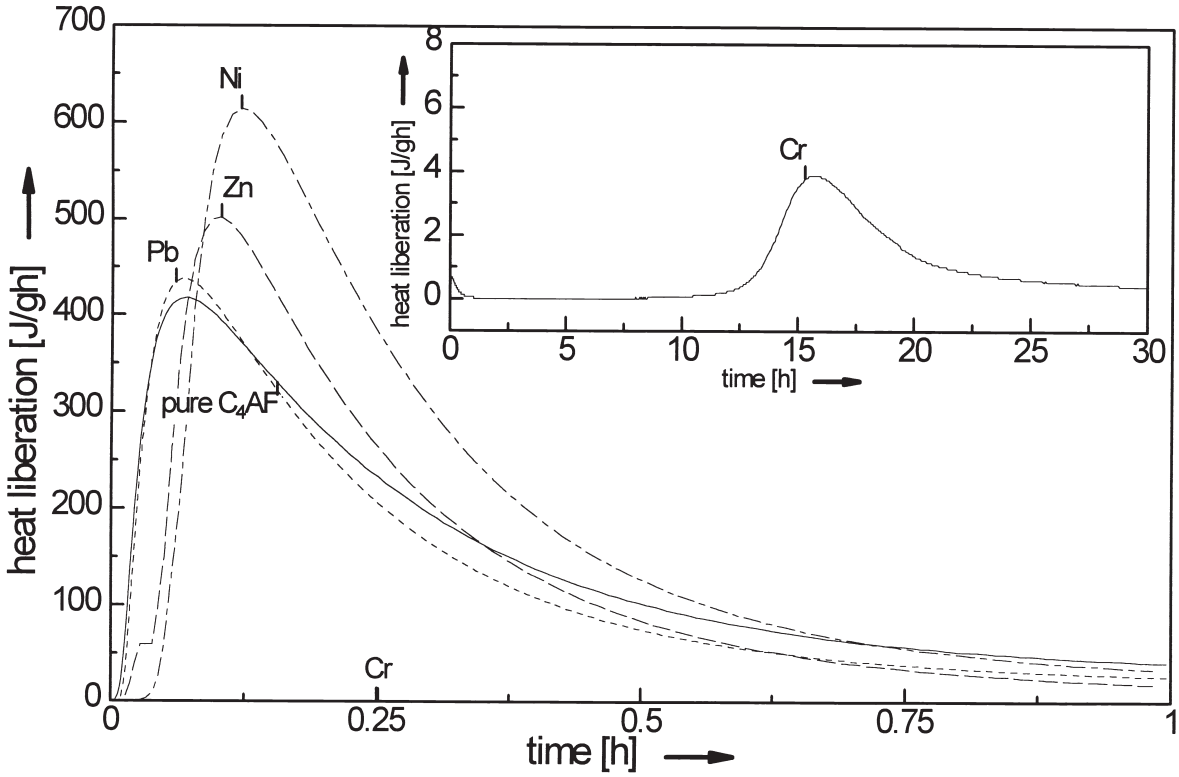

Fig. 2. Hydration of pure C_4AF and C_4AF with 2.5 wt.% of Cr, Ni, and Zn.

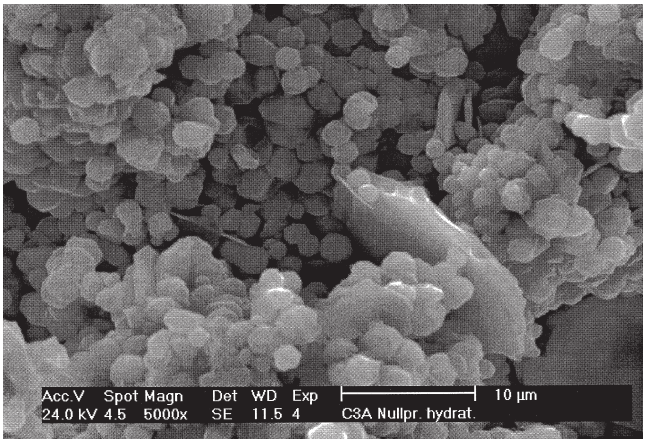

Fig. 3. SEM of hydrated C_3A.

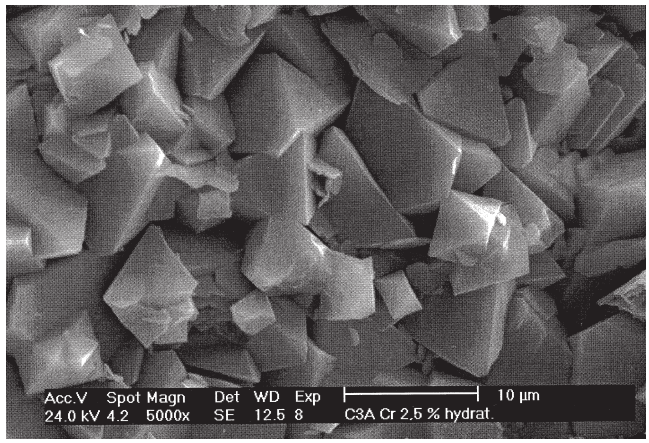

Fig. 5. SEM of hydrated C_3A with 2.5 wt.% of Cr.

The hydration products of the pure C_3A looked similar to those of our investigations. The hydration products of the Cr and Zn containing samples both consisted mainly of small plates. Tashiro and Oba [5] did not interpret these products, but the XRD pattern indicates that the samples with only a small amount of C_3AH_6 contain more small plates.

As mentioned in the chapter about XRD, the hydration products of C_4AF are similar to those of C_3A. The pictures taken by the SEM confirm this. The hydration products of C_4AF contain on one hand the icositetrahedron of C_3AH_6 with some Fe and many defects. Apart from these, there was an amorphous product with a high concentration of Fe. An example of the hydration product of pure C_4AF is shown in Fig. 8.

Samples with Cr are different. The hydration product (see Fig. 9) contains a poorly crystallised octahedral phase with many defects, small plates, and a third phase that is of pure crystallinity and may consist of fragments of the two other phases. In the small plates, the concentration of Fe and Cr is higher and that of Ca is lower than in the octahedral phase, where the concentration of Cr is below the detection sensitivity. The poorly crystallised third phase contains areas with a high concentration of Fe and areas with a very low concentration of Fe. At the same time the concentration of Cr is much higher in the area of higher concentration of Fe.

In the sample doped with Ni, a matrix was found that looked amorphous and had a low concentration of Fe and nearly no Ni. Another faulty crystalline phase was surrounded by the amorphous phase and consisted of about 75 wt.% Fe_2O_3, 20 wt.% CaO, and Al_2O_3 and Ni.

The sample with 2.5 wt.% of Zn is shown in Fig. 10. The sample contains poorly crystallised icositetrahedra that are surrounded by small plates. As in the case of Cr, the heavy metal is accumulated in the small plates that also contain a high concentration of Fe.

3. Conclusion

None of the tested concentrations of the heavy metals Cr, Ni, and Zn shows a change in the modification of C_3A or C_4AF. In some cases of very high dosage new compounds were detected. In C_3A with 5.0 wt.% of Cr the amount of free lime rose slightly and in the sample with 5.0 wt.% of Zn there was a significant content of free lime. The other

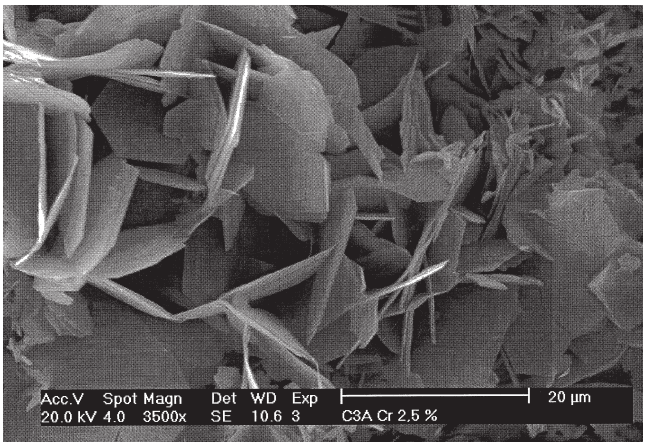

Fig. 4. SEM of hydrated C_3A with 2.5 wt.% of Cr.

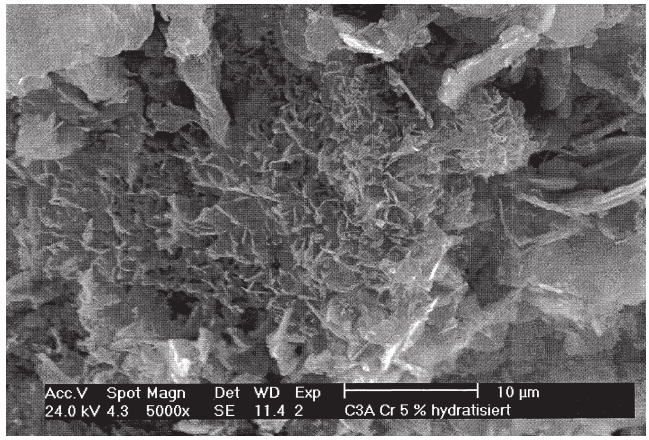

Fig. 6. SEM of hydrated C_3A with 5.0 wt.% of Cr.

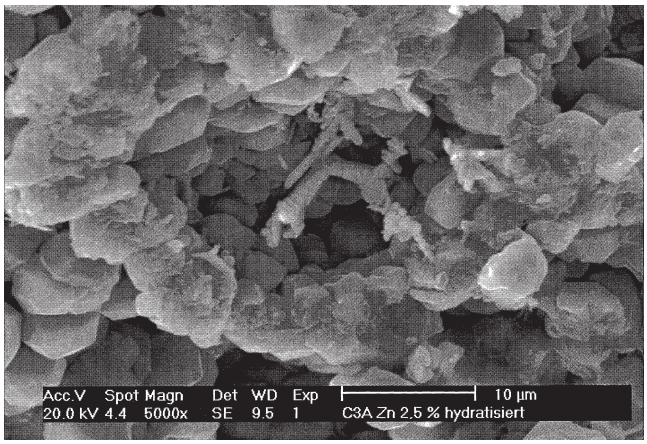

Fig. 7. SEM of hydrated C_3A with 2.5 wt.% of Zn.

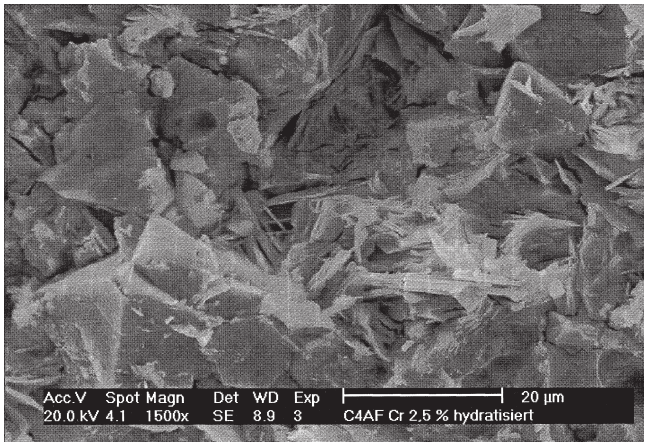

Fig. 9. SEM of hydrated C_4AF with 2.5 wt.% of Cr.

concentrations did not significantly effect the content of free lime in C_3A. In C_4AF no free lime could be detected at all.

With up to a concentration of 0.5 wt.% of added metals, the heat liberation during the hydration of C_3A and C_4AF is not affected. During the hydration of C_3A with 2.5 wt.% of heavy metal, Ni has no influence on the heat liberation, but Cr and Zn lowered the heat of hydration significantly without changing the time where the maximum heat evolution occurred. In C_4AF the addition of 2.5 wt.% of Ni leads to a higher heat evolution, while Zn has no effect. At the same concentration, the addition of Cr prevents the hydration of C_4AF almost completely and there is no final setting of the paste within 20 h.

The SEM verifies that the morphology of the hydration products of the samples with 2.5 wt.% of heavy metal in C_3A and C_4AF changes. In the hydration product of pure C_3A there were mainly icositetrahedra and some small plates. In the product with Cr octahedrons and small plates were found in the same amounts. The Cr was accumulated in the small plates. The phases in the sample doped with Zn looked similar to the sample from pure C_3A, but there were also crystalline hydration products most likely to be $Ca(Zn(OH)_3)_2 \cdot 2H_2O$.

The hydration products of C_4AF consist mainly of icositetrahedra with defects and an amorphous phase with a high concentration of Fe. In the sample with Cr there are the small plates with a high concentration of Cr and also octahedra found in C_3A with Cr. All the heavy metals are accumulated in regions that are also rich in Fe.

An overall result of this study is that heavy metals can have a decisive effect on the properties of all pure clinker phases, but the concentration when the first effects can be determined is high above the natural concentration of heavy metals in clinker and cements. Even concentrations up to 0.1 wt.% (for Cr and Ni about 20 and for Zn about 5 times higher than the natural concentration) would not have any effect on the properties of the pure phases.

Acknowledgments

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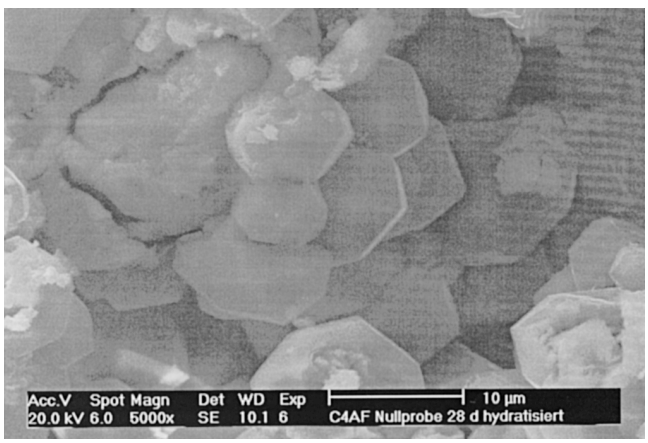

Fig. 8. SEM of hydrated pure C_4AF.

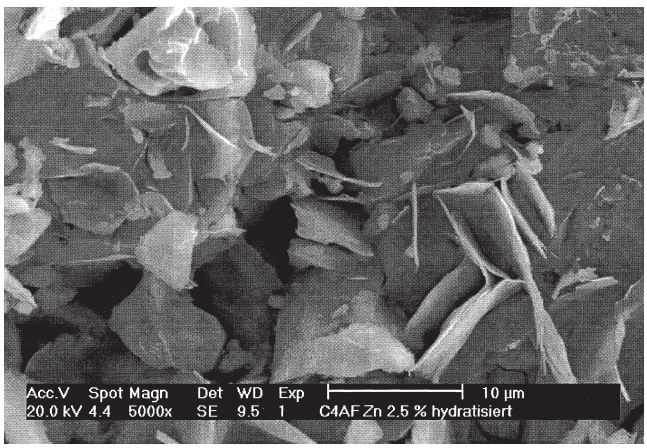

Fig. 10. SEM of hydrated C_4AF with 2.5 wt.% of Zn.

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