



	<b>Experiment title:</b> Identification of newly formed Co and Cr phases in cement using XRD	<b>Experiment number:</b> <b>01-02-672</b>
<b>Beamline:</b> <b>BM1B</b>	<b>Date of experiment:</b> from: 20-07-2004 to: 24-07-2004	<b>Date of report:</b> 28-02-2005
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Jon Are Beukes	<i>Received at ESRF:</i>
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Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of industrial and radioactive wastes in underground repositories. A mechanistic understanding of the processes governing the binding of heavy metals and anionic pollutants in cement systems is essential for long-term predictions of the environmental impact of cement-stabilized waste forms.

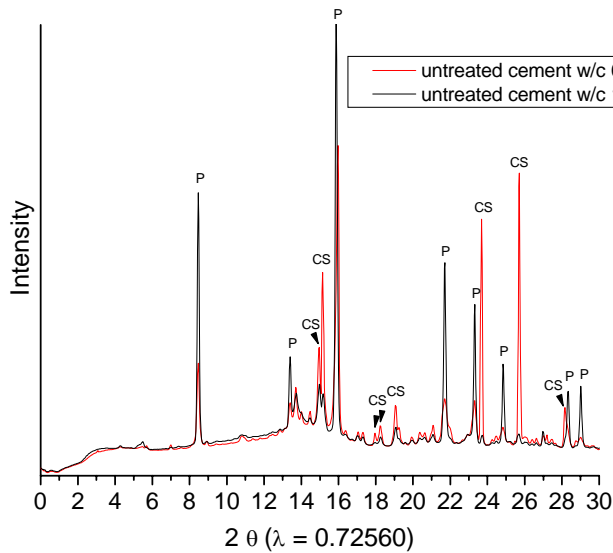
In this study, Co, Cr and Ni uptake by Hardened Cement Paste (HCP) have been investigated with the aim of improving our understanding of the influence of metals ions and of water/cement ratio on the cement hydration process. For this aim, HCP enriched with 5000 ppm of nitrate salts of the above mentioned metals (Co, Cr and Ni) were prepared at two different water/cement (w/c) ratios (w/c = 0.4 and 1.3) using a sulfate-resisting Portland cement and hydrated for 3, 30 and 150 days. High resolution powder diffraction (HR-XRD) measurements were carried out for both metal loaded HCP and untreated cement samples as well as reference material to detect the major phases and observe changes in the hydration process. From a chemical standpoint, hydrated HCP is a very heterogeneous material, composed mainly of calcium silicate hydrates, calcium hydroxide, calcium aluminates and highly reactive minor phases such as Fe- and Mn-oxides, which are formed upon the reaction of clinker material with water (hydration).

Preliminary data analysis shows that the clinker minerals (denoted as calcium silicates) are depleted and replaced mainly by crystalline calcium hydroxide (portlandite) and amorphous calcium silicate hydrates (not detectable). The hydration process is faster at w/c=1.3 than 0.4 if samples with the same hydration time are compared (Fig. 1). Fig 2 shows that there is an apparent difference in relative peak intensities attributed to clinker minerals and portlandite between untreated cement and metal loaded HCP samples. Data analysis revealed that a large portion of the clinker minerals had reacted during hydration of the metal loaded samples. However, the quantity of portlandite formed, which is one of the major crystalline hydration products, was less than in the untreated cement sample. This finding was most pronounced for the Co loaded HCP sample. Thus, the results of our study show that the addition of metals has an influence on the hydration process of cement and the quantity of hydration products formed. The results corroborate the findings from

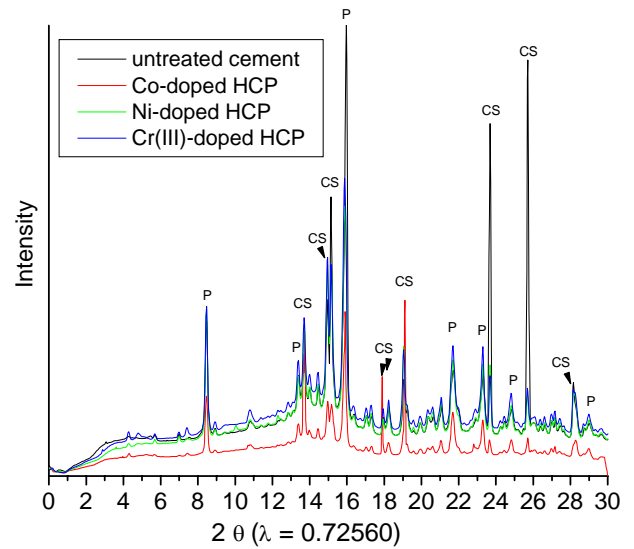
the study of Ouki & Hills (2002). These authors showed that adding nitrates salts of different metals to cement reduces the hydration kinetics of the cement itself.

A further experiment was conducted by adding Co to fully hydrated cement. The HR-XRD data again revealed that the major mineral phase is portlandite. Furthermore, it appears, that one of the small reflections could be attributed to CoOOH (Fig. 3). This finding is consistent with previously conducted Co K-edge x-ray absorption spectroscopic measurements.

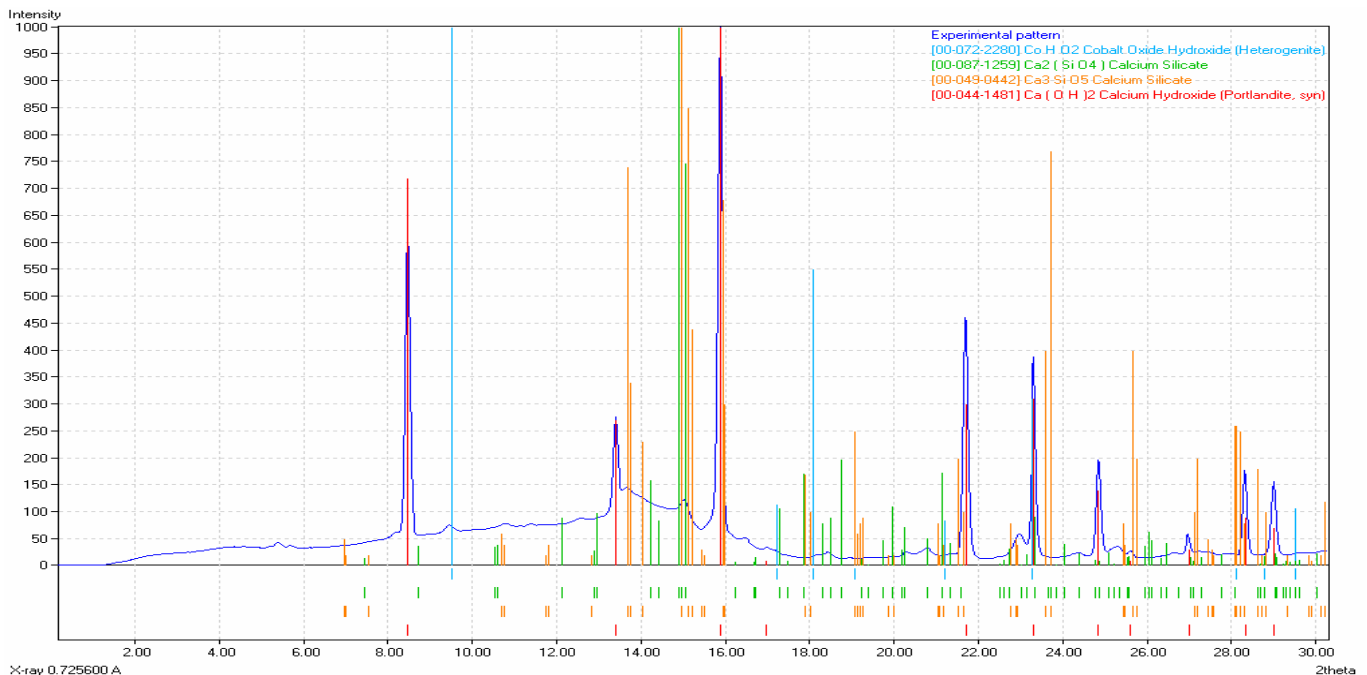
Data analysis is currently ongoing to further characterize the different metal-containing mineral phases and the effect of added metal ions on the hydration process of cement.



**Fig. 1.** XRD pattern of untreated cement at different water/cement (w/c) ratios after 30 days of hydration. P = Portlandite (calcium hydroxide); CS = calcium silicates



**Fig. 2.** XRD pattern of untreated cement and metal enriched HCP at water/cement (w/c) ratio of 0.4 after 30 days of hydration. P = Portlandite (calcium hydroxide); CS = calcium silicates



**Fig. 3.** XRD pattern of fully hydrated cement sample rich in Co ( $\lambda = 0.72560$ ).

## References

Ouki S.K. & Hills C.D. (2002). *Waste Management*, **22**, 147-1151.