Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

Retention mechanisms in mortars of the trace metals contained in Portland cement clinkers

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Portland cement clinker is made of limestone and clays heated up to 1450°C. These raw materials, as well as the fossils fuels fired in the kiln, contain trace amounts of heavy metals, just like any natural resource. Furthermore, flammable residues such as low-grade coals, tyres, solvents, are commonly used in substitution of coals or fuels. The co-firing of *waste derived fuels WDF* in cement kiln must comply with the European regulation 94-67 (December 16th 1994).
Some of these WDF may present significant metal contents. However it must be highlighted that the wastes fed in the kiln never exceed a few percent of the mass inlet, so in most cases, the total metal content is not significantly affected by the co-firing of WDF[1], excepted if a waste exhibits a level of one metal specially higher than the average content of the raw material. It is mainly the case for lead fairly abundant in some used oils, and zinc brought by old tyres ; that's why these metals have been chosen for our study, along with chromium which is known for producing soluble and hazardous chromates in cement.

The first part of the experiments carried out in this study concerned the leaching behaviour of industrial mortar bars contacted with deionised water. We showed that the metal concentrations in the leachates are very low and often non detectable. These results confirmed previous works related in the literature[2-5]. Furthermore, various measurement campaigns also proved that the mortars coming from kiln burning WDF do not exhibit metal release higher than the samples produced with classic fuels[4-5].

Yet the leaching behaviour of the **trace** metals is not fully explain in the literature. In order to explain the effectiveness of their retention in the mortar bars, the second part of our study was dedicated to the understanding of the containment mechanisms of the trace metals, and of the experimental parameters controlling their release. We have therefore designed more specific experiments :

- Laboratory samples have been enriched in metals during clinkerisation, up to ten times the usual metal content in industrial samples. They should ease the observation of the metal release, and therefore provide a better understanding.

Also, complementary leaching tests in chemical or physical contexts more or less aggressive for the cement matrix appeared very fruitful :

- The influence of the pH on the metal release have been studied, using leaching tests of monoliths in various leachants, more or less aggressive for the cement material ;

- Extraction experiments on crushed material have been undertaken to assess the fixation of the metals in the matrix itself by **purely chemical mechanisms**, after elimination of all the transport phenomenon.

These leaching parameters have obviously nothing to do with the conditions of use of cement based material, and are merely experimental tools to assert the release mechanisms.

This paper is essentially focused on the second part of our experiments, concerning the **retention mechanisms** of the trace metals.

Experimentals

Four industrial clinkers have been chosen amongst French production for their levels of chromium, zinc or lead higher than the average. The corresponding raw materials had also been provided, from which « replicates » of the industrial clinkers were synthetised in an electrical laboratory furnace. Corrective additions of metals were made, so as to obtain identical metal contents in the industrial samples and in the laboratory replicates (table 1). The release behaviour of the mortars made from these first two sets of samples were compared, using the tests described below.

mg/kg	Cr	Pb	Zn
I Industrial	101	32	200
I Replicate	98	6	192
II Industrial	58	2	224
II Replicate	62	13	228
III Industrial	118	24	246
III Replicate	155	14	248

table 1 : Heavy metal contents of the industrial samples and their laboratory replicates

A third set of clinkers was made in laboratory furnace, from an industrial raw meal that have been enriched in chromium, zinc and lead before the clinkerisation. Three metal levels were chosen, up to ten times the maximum concentrations usually encountered in industrial samples (table 2). The levels of hexavalent chromium have also been checked afterwards.

mg/kg	Cr_{total}	Pb	Zn	Cr(VI)
B	180	150	230	100
M	1005	680	1090	610
H	1810	1805	1920	1120

table 2 : Heavy metal contents of the enriched laboratory cements

These three sets of samples have been crushed after addition of gypsum, so as their final composition and their hydraulic properties are similar to industrial Portland cement.

Mortars have been prepared with the usual Cement/Sand/Water ratio = 1/3/0.5, and were mould in cylindrical bars ; after 28 days of maturation at 20°C and 98% of relative humidity, they were cut into disks of 1,4 cm high and 8 cm in diameter (volume 70,4 cm^3, surface 132 cm^2, weight 152±2g).

These test samples were submitted to sequential leaching tests in deionised water during 100 days overall, according to the following :

- Static, batch leaching tests in sealed polyethylene bottles
- Ratio : volume of leachant / sample surface = 5cm
  (i.e. 660 dm^3 of leachant ; liquid to solid mass ratio = 4,33)
- Immersions :
  – either 10 sequential contacts of 1d - 1d - 1d - 4d - 7d - 7d - 7d - 14d - 28d - 30d (total 100d),
  – or 1 continuous contact, during which aliquots are withdrawn at the times above mentioned.
- Leachant : deionised water excepted otherwise stated.

Complementary experiments

- Sequential leaching tests had been carried out as described here above, though using an alkaline leachant (pH 12.7) which is typically non aggressive for the cement matrix, or in pH conditions regulated at 7 by nitric acid additions.

- Extraction tests : Mortar samples **crushed to 100µm** were contacted till equilibrium with solutions of various pH (liquid to solid mass ratio = 10). The influence of the pH of the leachant upon the effectiveness of the fixation has been established, by using contact solutions maintained at various pH values between 6 and 13.

Results

The leachates have been analysed by ICP AES or graphite furnace SAA. The detection limits are 4µg/l for chromium, 10µg/l for lead and 3µg/l for zinc.

1-Comparision of industrial samples and laboratory replicates

The table 3 presents the total release of metals by the mortar bars contacted with deionised water. Most of the leachates exhibit metal levels below the detection limits.

	cumulative amount leached in 100d (µg)		
	Cr	**Pb**	**Zn**
I Industrial	NS	NS	NS
I Replicate	NS	NS	NS
II Industrial	NS	NS	NS
II Replicate	NS	NS	NS
III Industrial	29	NS	NS
III Replicate	33	NS	NS

table 3 : Metal release from the industrial samples and the laboratory replicates (10 immersions, total duration 100d)
NS : non significant because too many leachates concentrations < detection limit

The metal release being non measurable in deionised water, these two sets of samples have been tested in conditions more aggressive for the cement matrix, to make sure that the clinkerisation in laboratory furnace provides samples whose leaching behaviour is representative of industrially-made clinkers.

Lead and zinc

For the industrial samples and their laboratory replicates, the lead and zinc concentration in the leachates are consistently under or close to the detection limits, whatever the conditions applied : sequential leaching of monoliths in deionised water (table 3), in alkali, at pH 7 regulated, or even during the tests of extraction from crushed material at various pH values. Hence there is no measurable difference between the two sets of samples, considering the release of lead and zinc.

Chromium

The chromium release is also quite low, and sometimes under the detection limits. The cumulative chromium extracted over the test duration can though be worked out. In the different chemical conditions tested, the metal release from the monoliths appeared to be directly linked to the **chromate** content of the solid. The clinkering conditions of the sample (industrial kiln or laboratory furnace) has no influence. This result has been confirmed by the extraction tests on crushed material, as shown in table 4 :

	deionised water (µg/l)	pH 7 (µg/l)	% Cr^{6+} extracted at pH7
I industrial	50	791	108
I replicate	31	789	110
II industrial	15	355	106
II replicate	22	489	105
III industrial	66	1005	108
III replicate	84	1036	110

table 4 : Solubilisation of chromium from crushed material

Concerning chromium, the samples made from laboratory clinkers present a leaching behaviour very similar to the corresponding industrial samples. Concerning lead and zinc, and within experimental accuracy, the laboratory samples do not exhibit any obvious discrepancy from the industrial ones.
The study has therefore been pursued using solely the enriched laboratory clinkers.

2- Release mechanisms studied on enriched laboratory samples

The mortars made from enriched clinkers exhibit a measurable metal release (table 5), the first extracts being the more concentrated. The amount of lead and zinc leached are still very low ; the corresponding concentrations in the leachates are in the µg/l range. The chromium levels are somewhat higher. For the sample H (enriched to ten time the usual content in industrial samples), the concentrations in the leachates reach 150µg/l, in the experimental conditions here applied.

Enriched samples	Cumulative amount leached (µg)		
	Cr	Pb	Zn
B	34	NS	NS
M	245	34	26
H	459	101	23

table 5 : Metal release from the laboratory enriched samples (10 immersions total duration 100 d)
NS : non significant because too many leachate concentrations < detection limit

Zinc

The figure 1 shows the extraction of zinc from crushed mortar at various pH values. Zinc appears to be insoluble for the pH higher than 8. Its concentrations in the leachates are lower by of orders of magnitude than the solubility of the common zinc compounds such as hydroxides or carbonates, thus indicating a chemical bounding in the solid phase.

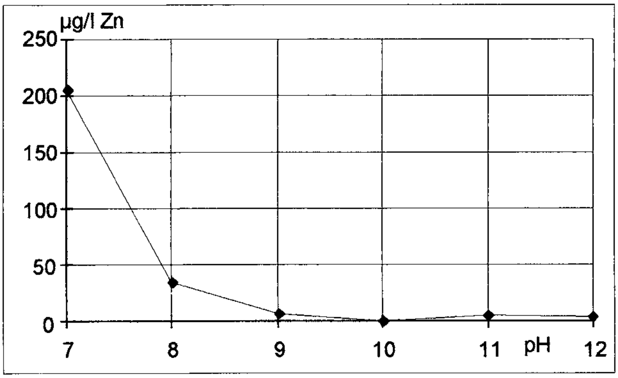

figure 1 : Extraction of zinc from crushed material - sample H

Such a low solubility strongly limits the release of zinc by the mortar monoliths : The level of zinc in the leachates of mortars blocs are consistently in the µg/l range. The cumulated amount leached in 10 immersions (total length 100 days) are between 15 and 25 µg ; there is no significant influence, neither of the chemical conditions of leaching, nor of the metal content in the solid.

Lead

The solubilisation curve of lead from crushed mortar is presented figure 2. Lead is partly extractable from the mortar in strongly alkaline conditions, but it is bound in the solid for pH values under 12.5. Just like for zinc, the equilibrium concentrations against pH are far lower than the expected solubility of lead compounds[6,7].

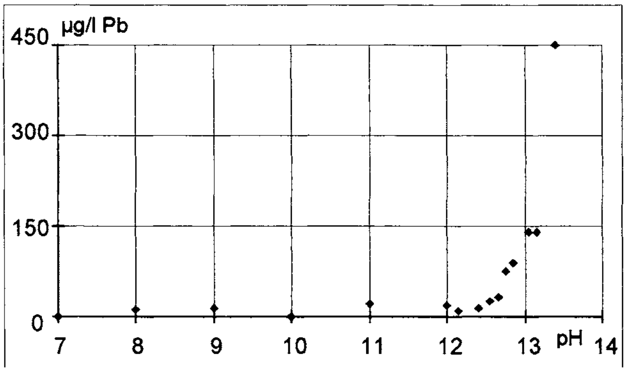

figure 2 : Extraction of lead from crushed material at various pH - Sample H

The various experiments undertaken have pointed out the **proportionality** between lead release and its level in the mortars. The results of lead released from monoliths are therefore expressed as percentages of the metal content of the solid (figure 3) :

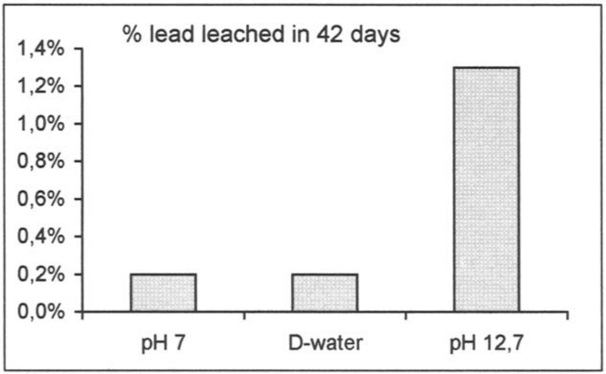

figure 3 : Percentage of lead leached from mortar bars, in various leaching conditions

The mortar bars exhibit a good retention of lead when they are contacted with neutral or moderately alkaline solutions (the leachant pH rose up to about 11 during the tests in deionised water) ; but when the leachant pH is very high, lead is partly released by the mortars.
The comparison of the two previous curves shows that lead release is strongly influenced by a solubilisation process controlled by the pH value .

Chromium

Whatever the leaching conditions, the release of chromium is directly proportional to the chromate content of the sample. The extraction test at various pH (figure 4) provided important results :

- As foreseen with the non-enriched samples (§ 2.), the chromium in the leachates is solely in its hexavalent form. Hence the trivalent chromium is never solubilised.
- The total amount of chromate of the sample is extracted for pH values under10.
- Chromate, though usually soluble, is bound in the solid in the pH range 11-13 ; we point out the fact that this range corresponds to the pH domain in which the ettringite phase is stable according to Damidot and Glasser[8].

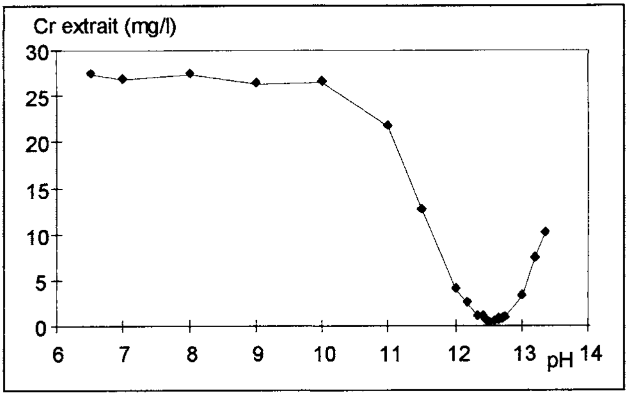

figure 4 : Extraction of chromium from crushed material at various pH - Sample H

The release of chromium by the mortar bars is shown figure 5. Just like in extraction tests, only hexavalent chromium is leached.

The mortars contacted with deionised water release less metal than in aggressive conditions such as pH 7 regulated. Surprisingly, the release is quite high in an alkaline solution of pH 12.7, although the extraction test proved that the solubilisation of chromium is minimal for a pH value of 12.5.

Hence the release of chromium cannot be explain taking into account only the influence of the pH.

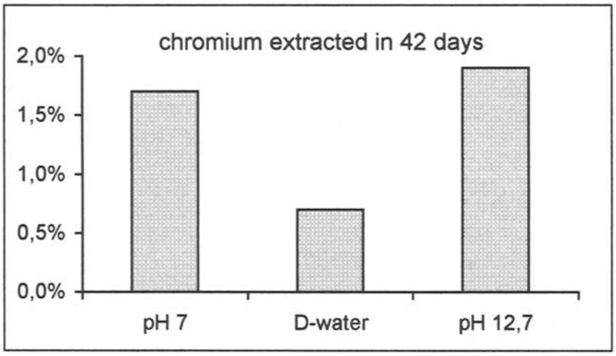

figure 5 : Percentage of chromium leached from mortar bars, in various leaching conditions

Discussion

The release of zinc by the monoliths contacted with deionised water is very low (In our tests, less than 25µg of zinc is extracted in 100 days of leaching, whatever the metal content of the mortars). It is due to the fact that this metal is bound in the solid as a compound which is insoluble in water.

This result can be extended to the various chemical conditions applied in our tests, as zinc is chemically retained in the matrix in the pH range 8-13. It must be highlighted that the elevated alkalinity of cement ensure an elevated pH in the mortar bars even if the surrounding solution is fairly aggressive : this remark explains why the zinc release by the monoliths is still low when the leachant is maintained at pH 7.

The release of lead from the monoliths is controlled by a solubilisation process strongly dependant of the pH conditions applied to the material. This metal being bound in the matrix for the pH lower than 12.5, its release is limited as long as the alkalinity of the leachant is not too elevated, which is the case of leaching in deionised water or at pH 7 regulated.
Very high values of pH would be reached only during a prolonged contact between the cement and the liquid, or when the mortar is submitted to an extremely alkaline solution. Such conditions of pH does not occur during the real utilisation of cement based materials.

An other part of this study[1] has proved that the chromate is chemically bound in the ettringite structure, in substitution for sulfate. The interpretation of the leaching results requires to consider the specific chemical properties of such chromate-ettringite, and especially its solubilisation mechanisms.

As an example, the figure 6 presents the evolution of chromium concentration during an unique continuous contact. The metal level rise up and becomes stable after a few days. This stationary value is directly proportional to the chromate content of the solid. The release of chromium is due to the partial dissolution of ettringite in which it is contained as an impurity. The stationary level of chromium is due to the quick saturation of the bulk with respect to ettringite. Depending upon the chromate level in the solid, the bulk is in equilibrium with ettringites containing different amounts of metal impurity. The partial dissolution of these phases liberates a corresponding amount of chromate into solution.

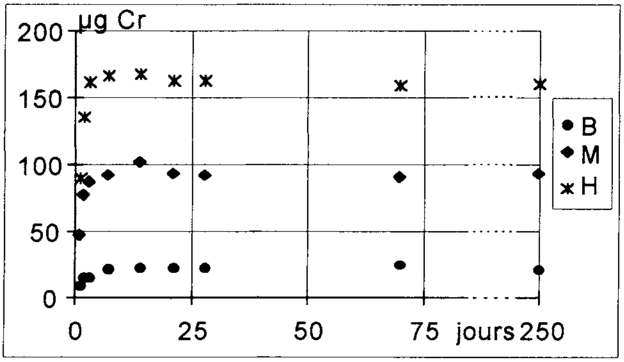

figure 6 : Amount of the chromium released in the leachant during one prolonged contact

Conclusions

The first part of our study has shown that the traces metals occurring in Portland cement clinker are retained in the relevant mortars bars when they are submitted to deionised water. The metal concentration in the leachates are consistantly under or close to the detection limits. Furthermore, samples enriched in metals up to ten times the levels usually encountered in industrial samples also exhibit very low metal release.

To explain these results, the work presented in this paper focused on the understanding of the retention mechanisms of the trace metals, and on the identification of the parameters controlling their release :

- Zinc is bound in the solid and is nearly insoluble in the chemical conditions applied ; therefore its release by mortar bars contacted with deionised water is very low. This result has be extended to leachants in the pH range 7-13.
- Lead is nearly not released in deionised water : we showed that this metal is insolubilised by the cement matrix, provided the leachant pH is under 12.5. It must be pointed out that in real conditions of use of cement materials, the contact water never reaches such elevated pH.
- The trivalent chromium is bound in the mortars. The soluble chromate ions are partly retained in the matrix owing to their fixation in the ettringite phase. Their release is linked to the dissolution mechanisms of this phase, and the quick saturation of the leachant with respect to ettringite appears as the limiting factor.

Acknowledgement

The authors would like to acknowledge the *Association Technique de l'Industrie des Liants Hydraulique (ATILH)* and the *Agence De l'Environnement et de la Maîtrise de l'Énergie (ADEME)* for supporting these studies.

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