



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

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Abstract

This work aimed to assess the retention in the mortars of the heavy metals fed in a cement kiln with natural raw materials, fossil fuels or waste derived fuels. Industrial cement has been studied, along with laboratory samples enriched during clinkering with lead, zinc and chromium. The relevant mortars were tested for metal release through leaching studies in various chemical contexts. Zinc appeared to be insoluble in the pH range 7–13. Lead is released only in alkaline medium above pH 12.5. Hexavalent chromium, whose salts are usually very soluble, is retained though in an hydrated phase, that is stable in the chemical environment ensured by the cement matrix. Lead and chromium releases are linked to the metal levels in the mortars. The solubility studies of a chromium + sulfate ettringite revealed that chromium release is linked to its proportion in the crystal. A selective dissolution of the chromium part of ettringite has been pointed out. This leads to a lowering of the chromium level in such a solid contacted with water. These results improved the understanding of the release mechanisms of chromium by the mortar blocks. © 2000 Elsevier Science Ltd. All rights reserved.

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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 fossil 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 (16 December 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], except 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 which is fairly abundant in

some used oils, and zinc in old tyres; that is 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 explained 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:

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- Laboratory samples have been enriched in metals during clinkerisation. 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.

1. Experimental

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 synthesised 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.

A third set of clinkers was made in a laboratory furnace from an industrial raw metal that had been enriched in chromium, zinc and lead before the clinkerisation. Three metal levels were chosen, up to 10 times the maximum concentrations usually encountered

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

mg/kg	Cr	Pb	Zn	Cr(VI)
I Industrial	101	32	200	33
I Replicate	98	6	192	32
II Industrial	58	2	224	15
II Replicate	62	13	228	21
III Industrial	118	24	246	42
III Replicate	155	14	248	54

in industrial samples (Table 2). The levels of hexavalent chromium have also been checked afterwards.

These three sets of samples have been crushed after addition of gypsum so that 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 moulded in cylindrical bars; after 28 days of maturation at 20°C and 98% relative humidity, they were cut into disks of 1.4 cm high and 8 cm in diameter (volume 70.4 cm³, surface 132 cm², weight 152 ± 2 g). 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 = 5 cm (i.e. 660 dm³ of leachant; liquid to solid mass ratio = 4.33)
- Immersions:
 - either 10 sequential contacts of 1-1-1-4-7-7-14-28-30 days (total 100 days),
 - or 1 continuous contact, during which aliquots are withdrawn at the times above mentioned.
- Leachant: deionised water excepted otherwise stated.

1.1. Complementary experiments

- Sequential leaching tests had been carried out as described 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 100 µm* were contacted until 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 by additions of HNO₃ or NaOH.

2. Results

The leachates have been analysed by ICP AES or graphite furnace SAA. The detection limits are 4 µg/l

Table 2
Heavy metal contents of the enriched laboratory cements

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

for chromium, 10 µg/l for lead and 3 µg/l for zinc. Hexavalent chromium determinations have been carried out by ionic chromatography.

2.1. Comparison of industrial samples and laboratory replicates

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.

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 the laboratory furnace provides samples whose leaching behaviour is representative of industrially-made clinkers.

2.1.1. 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.

2.1.2. Chromium

The chromium release is also quite low, and sometimes under the detection limits. The cumulative chromium extracted over the test duration can, however, 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) have no influence. This result has been confirmed by the extraction tests on crushed material, as shown in Table 4.

Concerning chromium, the samples made from laboratory clinkers exhibit a leaching behaviour very

Table 4
Solubilisation of chromium from crushed material

	Deionised water (µg/l)	pH 7 (µg/l)	% Cr ⁶⁺ extracted at pH 7 ^a
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

^a Amount of chromium extracted at pH 7, related to the amount of Cr(VI) in the mortar, taking into account the L/S ratio (10) and the dilution factor of the cement in the mortar (4.5).

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 only the enriched laboratory clinkers.

2.2. Release mechanisms studied on enriched laboratory samples

The mortars made from enriched clinkers exhibit measurable metal releases (Table 5), the first extracts being the more concentrated. The amount of lead and zinc leached is 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 10 times the usual content in industrial samples), the concentrations in the leachates reach 150 µg/l in the experimental conditions here applied.

2.2.1. Zinc

Fig. 1 shows the extraction of zinc from crushed mortar at various pH values. Zinc appears to be insoluble for a pH higher than 8. Its concentrations in the leachates are lower by 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.

Table 3
Metal release from the industrial samples and the laboratory replicates^a

	Cumulative release in 100 days (µg/kg cement)		
	Cr	Pb	Zn
I Industrial	NS ^b	NS	NS
I Replicate	NS	NS	NS
II Industrial	NS	NS	NS
II Replicate	NS	NS	NS
III Industrial	0.9	NS	NS
III Replicate	1.0	NS	NS

^a 10 immersions, total duration 100 days.

^b NS, non-significant because too many leachates concentrations < detection limit.

Table 5
Metal release from the laboratory enriched samples^a

Enriched samples	Cumulative release in 100 days (µg/kg cement)		
	Cr	Pb	Zn
B	1.0	NS ^b	NS
M	7.3	1	0.8
H	13.6	3	0.7

^a 10 immersions, total duration 100 days.

^b NS, non-significant because too many leachate concentrations < detection limit.

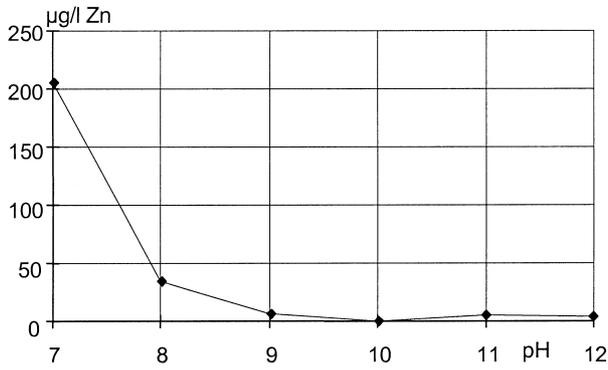


Fig. 1. Extraction of zinc from crushed material — sample H.

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 releases in 10 immersions (total length 100 days) are between 0.4 and 0.75 mg/kg; there is no significant influence, neither of the chemical conditions of leaching, nor of the metal content in the solid.

2.2.2. Lead

The solubilisation curve of lead from crushed mortar is presented in Fig. 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].

The various experiments undertaken have clearly shown 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 (Fig. 3).

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. Comparison of the two previous curves shows that lead release is strongly influenced by a solubilisation process controlled by the pH value.

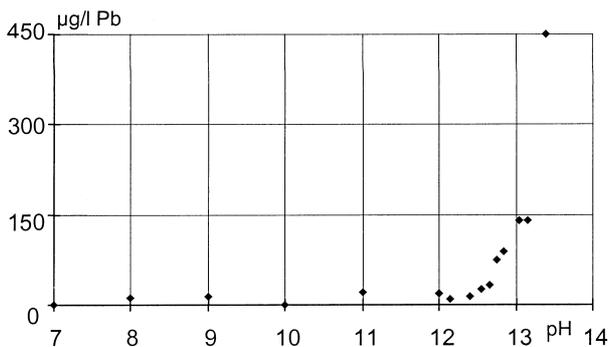


Fig. 2. Extraction of lead from crushed material at various pH — Sample H.

2.2.3. Chromium

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

- As foreseen with the non-enriched samples (Section 2.1), the chromium in the leachates is solely in its hexavalent state (no significant difference between total chromium by ICP and hexavalent chromium by ionic chromatography). Hence trivalent chromium is not released in our experiments.
- The total amount of chromate of the sample is extracted for pH values under 10.
- Chromate, though usually soluble, is bound in the solid in the pH range ca. 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].

The release of chromium by the mortar bars is shown in Fig. 5. Just like in extraction tests, we showed that 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

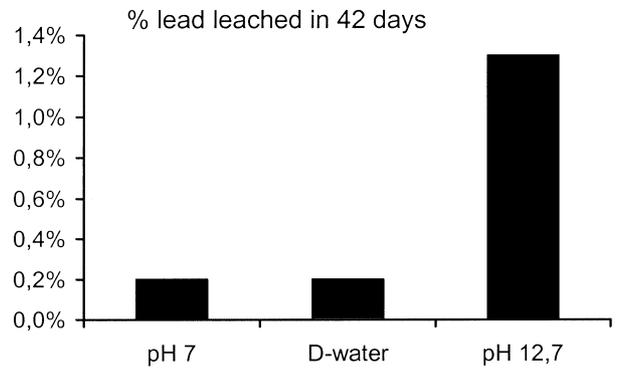


Fig. 3. Percentage of lead leached from mortar blocks in various leaching conditions.

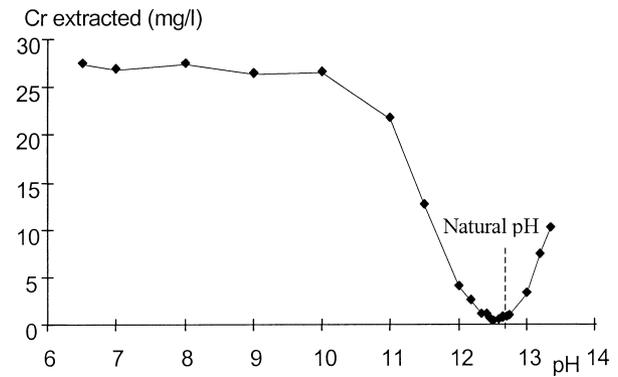


Fig. 4. Extraction of chromium from crushed material at various pH — Sample H.

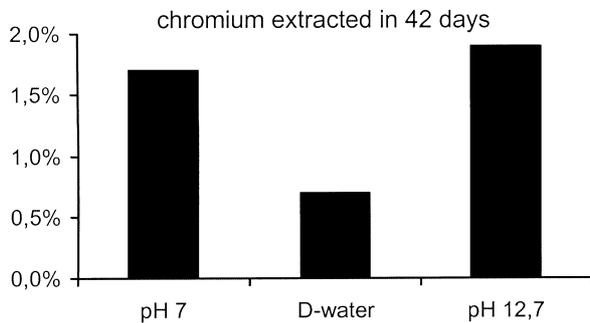


Fig. 5. Percentage of chromium leached from mortar blocks in various leaching conditions.

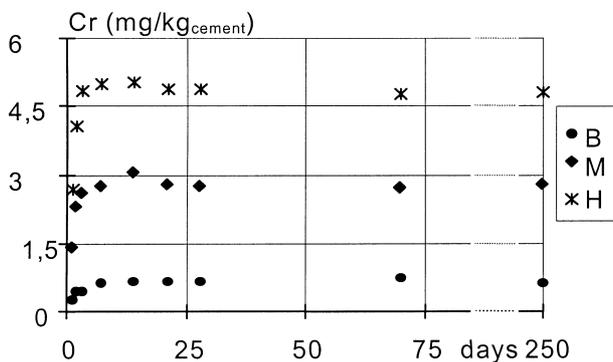


Fig. 6. Amount of the chromium released in the leachant during a unique prolonged contact.

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 explained taking into account only the influence of the pH.

3. Discussion

The release of zinc by the monoliths contacted with deionised water is very low (in our tests, less than 25 μg 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 ensures an elevated pH in the mortar bars even if the surrounding solution is fairly aggressive: this remark explains why the zinc released 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 on the pH conditions applied to the material. This metal being bound in the matrix for 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 in 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.

Another 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 consideration of the specific chemical properties of such chromate-ettringite, and especially its solubilisation mechanisms.

As an example, Fig. 6 presents the evolution of chromium concentration during a unique continuous contact. The metal level rises 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.

4. Conclusions

The first part of our study has shown that the trace metals occurring in Portland cement clinker are retained in the relevant mortar bars when they are submitted to deionised water. The metal concentration in the leachates is consistently under or close to the detection limits. Furthermore, samples enriched in metals up to 10 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 been extended to leachants in the pH range 7–13.
- Lead is nearly unreleased in deionised water: we have shown 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 values.
- 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 to be the limiting factor.

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