

Parameters Influencing The Leachability Of Antimony From Hardened Concrete

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Abstract

The interest in the environmental impact of cement based materials has been growing in recent years. The possible leaching of inorganic compounds when concrete is in contact with water is one of the main concerns. It is well known that cements and concrete mineral additions can contain traces of several heavy metals, whose immobilisation pathways are not yet completely understood. The use of antimony compounds as reducing agents in cements has been recently proposed in order to fulfil the requirements of the European Union regarding the elimination of soluble chromates. This poses the need to assess the long term leaching behaviour of antimony from concrete and cement based-products in aqueous environment. Even though a reference standard is not yet available, a number of leaching test methods are used worldwide. However, their relevance to concrete placed in the environment can be questioned. In this paper the results of a study on antimony leaching from hardened concrete are presented. Several parameters such as cement composition, initial concentration of antimony, curing age and carbonation have been taken into account. Considering the importance of pH in immobilisation/release mechanism, particular attention has been given to the effect of pH on antimony leaching. On the basis of the data collected, some hypothesis on the behaviour of antimony in hydrated cement systems are discussed.

Originality

Several papers deal with concrete where the heavy metals content is increased by the use of solid wastes as alternative fuels. During clinker burning metals are usually bound in silicate matrix and the leaching behaviour follows some rules already described and studied. Since the European Community introduced some years ago the obligation to eliminate soluble chromates, the addition of inorganic reducing agents such as tin, iron or antimony salts during cement grinding has become a common practice. In this case, the inorganic element is not bound, but simply dispersed in cement. In our opinion the originality of this paper lies in the fact that only a few works are dedicated to investigating the possible antimony leaching from concrete, and all of them take into consideration only the metal bound in clinker minerals.

Chief contributions

The majority of cements produced and imported in Europe contain several parts per million of tin, iron or antimony used as reducing agent. Notwithstanding the advantages of the elimination of hexavalent chromium, for a global evaluation of the environmental impact of reducing agent it is indeed important to study its leaching behavior. The main contribution of this paper is to allow the assessment of the real possibility of antimony release under several conditions.

Keywords : leaching, antimony

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1. Introduction

Heavy metals are commonly contained in traces in Portland cements. Their origin can be directly related to materials used for raw meal production or can be linked to the use of alternative fuels or secondary mineral additions. It is commonly reported that there is no a direct relationship between the bulk heavy metals content and the leachable fraction of these elements (Marion et al, 2005). Many elements are embedded in clinker matrix during clinker production or immobilized in hydration products of cement. Among other heavy metals, antimony is reported to be naturally present in some Portland cements. In Germany, the investigation on more than 400 commercially available cements showed an average antimony content of 2,9 ppm (part per million, mg/kg) but higher values (in the range 5-30 ppm) are quite common (VDZ, 2001). A specific study on the impact of waste incineration on heavy metals in clinkers evidenced an average content of 6 ppm Sb, coming from primary raw materials and from secondary fuels (Achterbosch et al., 2003).

Antimony recently gained importance due to the fact that it had been identified as one of the most effective reducing agent for soluble chromates, whose elimination is required for all the cements produced or imported in the European Union. In industrial practice, antimony is usually added during cement grinding at an indicative dosage of 5-10 ppm for each ppm of Cr(VI) to be reduced (Magistri et al., 2008). Considering the average Cr(VI) content of commercial cements, usually 20-150 ppm Sb can be added. These amounts are higher than Sb natural content and the different nature of the addition (an antimony compound interground with cement and not bound in clinker matrix) poses the necessity to assess its leaching from concrete. The aim of this paper is to study the parameters that influence the leaching of antimony (added during cement grinding as antimony trioxide) from concrete and to identify possible pathways of antimony immobilization in cement based products.

1.1 *The behavior of antimony in cement-based systems*

The chemistry of antimony in aqueous media is dominated by III and V oxidation states. Both species have amphoteric nature: antimony oxides/hydroxides are dissolved in alkaline media with formation of antimonites and antimonates (Sb(OH)_4^- and Sb(OH)_6^-) (Cornelis et al., 2008). The interactions between antimony and cement hydration products has not received too much attention in scientific literature. Solubility product of calcium antimonate $\text{Ca[Sb(OH)}_6\text{]}_2$ was calculated and is $K = [\text{Ca}^{2+}] \cdot [\text{Sb(OH)}_6^-]^2 = 10^{-12.55}$ (Annette Johnson, 2005). Cornelis et al. investigated the antimony leaching from incinerator solid waste in function of pH and carbonation and the adsorption of antimony on some mineralogical phases commonly found in Portland cements pastes. They concluded that at alkaline pH the Sb leaching is lower than what expected on the basis of the solubility product of calcium antimonate. Calcium bearing minerals (particularly portlandite and ettringite) play an important role in controlling Sb leaching (as demonstrated by specific adsorption experiments) and the modification of these phases given by carbonation modifies their immobilization properties towards antimony (Cornelis et al., 2006).

1.2 *Leaching test for concrete*

Leaching from concrete can be governed by diffusion, dissolution (the element is released due to its solubility in the conditions of the test) or decomposition of phases (an hydrated phase decomposes allowing the release of an element previously immobilized). The leaching of a specific element can be driven by different mechanisms depending on conditions.

A number of leaching test method are used in the world, but an European standard for leaching from concrete still does not exist. The most suitable test for laboratory simulation of the behavior in use is the tank test, in which the release is usually considered to be diffusion-controlled (Marion et al., 2005, Van Der Sloot, 2008). Size reduction of sample (e.g. crushing or grinding) or the use of artificially aggressive leachants can be suitable in assessing the release of elements in severe conditions, not

commonly encountered in concrete life cycle. The relevancy of these tests to concrete placed in the environment should be questioned (Hillier et al., 1998). The leaching of antimony from concrete was evaluated in the following conditions:

- tank test on monolithic material;
- leaching from crushed concrete;
- leaching in conditions of accelerated carbonation;
- leaching at different pH.

2. Experimental part: samples preparation and leaching tests

In this study three different types of cements were reproduced by grinding clinker, gypsum and mineral additions in a lab ball mill. Cement compositions were chosen in order to verify if leaching can be influenced by a different clinker content and/or by the presence of mineral additions. Two different dosages of a commercially available product for Cr(VI) reduction based on antimony trioxide were added directly in the mill. Considering that in industrial practice the antimony trioxide is dosed at around 10 ppm for each ppm of Cr(VI), the quantities chosen can be regarded as an average and an exceptionally high antimony content (respectively for 5 and 20 ppm of hexavalent chromium to be reduced). Details on cement compositions and dosages of antimony are reported in the table 1. For each cement reproduced, concrete (340 kg/m³, class XC4 according to EN-206) was mixed and casted in several 10x10x10 cm cubic specimen. Water cement ratio was kept constant (W/C=0,5) and a standard acrylic based superplasticizer was used. Cubes were cured for 24 h and (wrapped in plastic foil as a form of protection against accidental contamination) for 56 days at 20 ± 2 °C and >90% RH.

Table 1: details on cement composition

Cement type according to EN 197-1	Cement composition	Antimony trioxide (ppm)	Sb (ppm)	Blaine (m ² /kg)	Residual 40 μm (%)
CEM I	95% clinker 5% gypsum	0	0,0	454	9,4
		60	49,8		
		200	166,0		
CEM II/B-L	71% clinker 4% gypsum 25% limestone	0	0,0	489	15,2
		60	49,8		
		200	166,0		
CEM III/A	52% clinker 3% gypsum 45% blast furnace slag	0	0,0	383	10,9
		60	49,8		
		200	166,0		

2.1 Leaching tank test on monolithic and crushed material

Tank test was conducted using an internal method based on Dutch standard NEN 7345 (Determination of the leaching of inorganic components from building materials with the diffusion test). Concrete cubes were immersed in tap water (liquid volume / surface area of cube 80 l/m²) and kept in static conditions at 23 ± 2 °C. Six leachates (after 1, 3, 7, 16, 32 and 56 days) were collected: the water was separated, the pH measured then acidified and stored for analysis, then replaced with the same amount of fresh water. Leaching in accelerated carbonation conditions was tested with a similar procedure, with the continuous bubbling of CO₂ into water. Leaching from crushed material was evaluated by placing 15 g of the concrete (crushed until all the material is passing through a 1 mm sieve) in 150 ml distilled water and magnetically stirred. After 7 and 48 h the suspension is filtered and the filtrate analyzed for antimony content. pH is measured directly in the suspension at 1, 7 and 48 h

2.2 Leaching test at different pH

The standard CEN/TS 14429 (Characterization of wastes – Influence of pH on leaching) describes a method to assess the leaching from waste materials at different pH. Crushed sample are dispersed in water, the pH corrected with nitric acid or sodium hydroxide and the suspension is stirred for 48 h. Equilibrium conditions are supposed to be reached during the test and a constancy of the pH for the whole period is requested. This method seems not applicable in our case, for the following reasons:

- cement paste in hardened concrete is mainly composed by portlandite and calcium silicate hydrates (C-S-H). Both compounds have strong alkaline properties and rapidly react with acids. It is nearly impossible to stabilize the pH of water containing ground concrete using a strong acid since this react and quickly decomposes cement paste. Experimentally it can be seen that the pH after the addition of nitric acid rapidly increases as faster as finer is the material ground or as higher is stirring speed.
- The use of a strong oxidizing agent such as nitric acid can modify the leaching behavior of a strong reducing agent such as antimony trioxide.

The leaching at different pH was measured with the procedure already described for tank test on monolithic material, but using specific buffer solutions at pH $4,0 \pm 0,5$ (acetic acid 0,2 M and sodium acetate 0,2 M 80:20 v/v) and pH $6,0 \pm 0,5$ (acetic acid 0,2 M and sodium acetate 0,2 M 5:95 v/v) in place of water. In this way the pH is stabilized over a long period (several weeks) and the behavior of Sb^{3+} is not influenced by oxidizing agents.

2.3 Analysis of leachates

For the analysis of antimony and other elements content in leachates Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP/AES Varian Vista MPX Axial) was used. The lower detection limit of the instrument for antimony in this matrix can be considered 0,01 ppm (mg/l). It should be pointed out that antimony is normally present in Portland clinkers and in many other industrial applications. Several materials such as plastic and coatings contain antimony trioxide as synergistic component of flame retardant systems or antimony compounds have been used as catalyst for polymerization. Objects made of polypropylene, polyethylene, PVC can contain 4-10% antimony trioxide. Sb content up to 200 ppm are reported in polyethylen therephthalate (PET) used for bottles manufacturing (Westerhoff et al., 2008). Contaminations of samples due to leaching from other sources (plastic buckets used for tank test, plastic moulds for concrete casting) are possible. For each test performed, a blank test (using the same cement composition in the same conditions but without the addition of antimony) was run. Tap water was used for all the tests (with the exception of leaching on crushed material and at different pH). At any change of eluent, water was analyzed with ICP/AES in order to exclude the presence of antimony.

3. Results

3.1 Leaching from monolithic and crushed material

In monolithic tank test the pH of eluates is close to 12 (after 1 day leaching) and progressively decreases to $8,6 \pm 0,2$ (pH of water used as eluent). No detectable antimony is present in leachates, regardless to the concrete curing time, type of cement, antimony content and leaching time.

Leachates referring to crushed material present high constancy of pH ($12,5 \pm 0,1$ for CEM I and CEM II and $12,3 \pm 0,1$ for CEM III), probably related to the buffering effect of calcium hydroxide. No antimony is detectable, regardless the type of cement and the antimony content.

3.2 Leaching test in accelerated carbonation conditions

Test conditions can be definitely considered very aggressive, since carbonation in real systems is slower. Continuous bubbling of CO₂ produces a saturated solution of carbonic acid that buffer the pH of all leachates at $6,6 \pm 0,3$. The Sb concentration in leachates referring to concretes with the highest content of antimony is reported in Fig. 1 (cumulative concentration). The extraction is faster during the first 7 days, then the concentration of antimony becomes similar in all leachates and comprised in the range 0,15-0,21 ppm (this correspond to 0,014% of the total leachable antimony, calculated considering that if all the antimony added were extracted the concentration in water would be 1520 ppm). A final value of around 1 ppm (0,066% of the calculated total Sb) is reached. Limestone cement presents a lower extraction of antimony. This can be probably related to the high carbonate ion activity due to the high content of calcium carbonate. Concretes with lowest content of antimony show final values of around 0,17 ppm. The concentration of calcium, silicon and sulphur in leachates was evaluated and corrected subtracting the concentrations of the same elements in absence of carbonation. Results are summarized in Fig. 2 and 3. The leaching of all elements has a trend similar to antimony, with a faster extraction during the first 7 days. This suggest that the release of antimony is related to the decomposition of cement paste, basically the conversion of portlandite and ettringite to calcium carbonate and monocarbonate (Eglington, 1998).

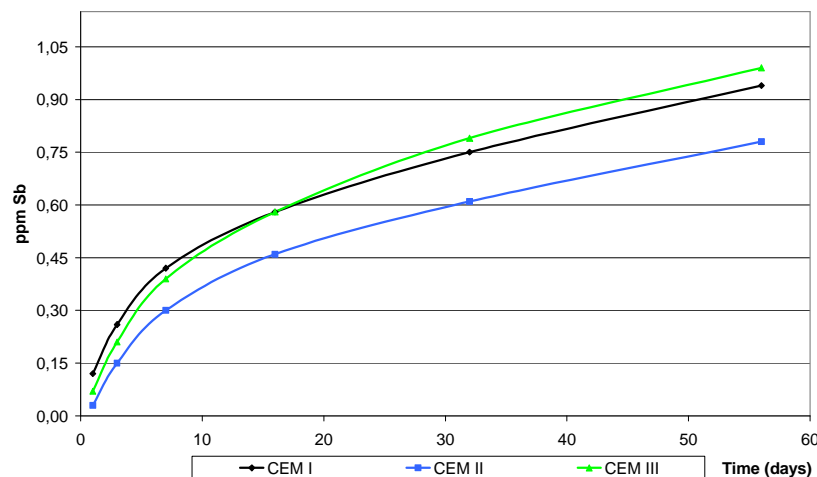


Figure 1: antimony leaching in accelerated carbonation conditions. Data refers to leaching from concrete made with highest Sb content cements

3.3 Leaching at different pH

The pH value alone does not give much information, since different acids with similar strengths can have different influence. Anyway, due to the complexity of interactions between organic acids and concrete, the pH remains the most common criterion. Acids initially decompose the lime in cement paste, then attack all the other hydrated phases leading to a progressive dissolution. This results in extraction of antimony, as evidenced in Fig. 4. The leaching is higher at lower pH, reaching 0,66 ppm in the case of concrete made with CEM II at high content of antimony. At pH 4, concrete made with limestone cement seems to be more easily attacked by acids. It is interesting to compare the Sb leaching at pH 6 with the leaching in accelerated carbonation. Although the pH is similar, higher amounts of antimony are extracted in presence of carbon dioxide. This suggests that hydrated phases sensitive to carbonation are possible pathways for Sb immobilization. Analysis of calcium, silicon, sulphur, aluminium, iron and magnesium in leachates show a general release of all the elements coherent with the progressive decomposition of all the samples. As expected, the lower the pH, the faster is the dissolution of concrete. Again, Sb extraction is related to decomposition of cement paste.

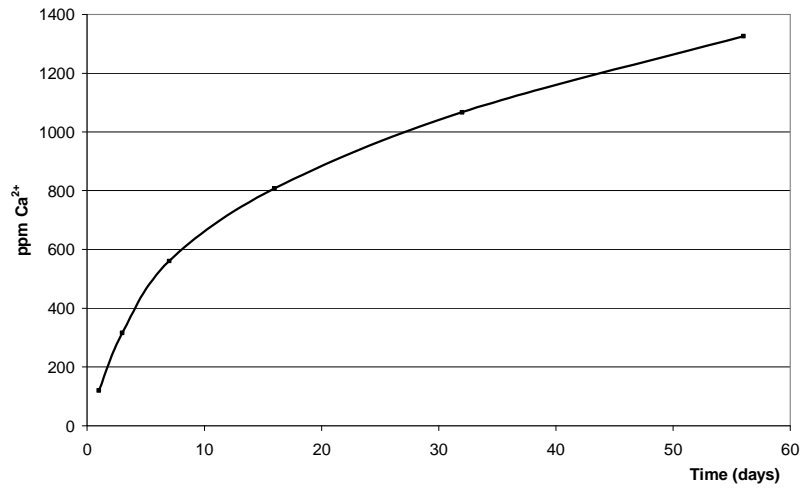


Figure 2: calcium leaching in accelerated carbonation conditions

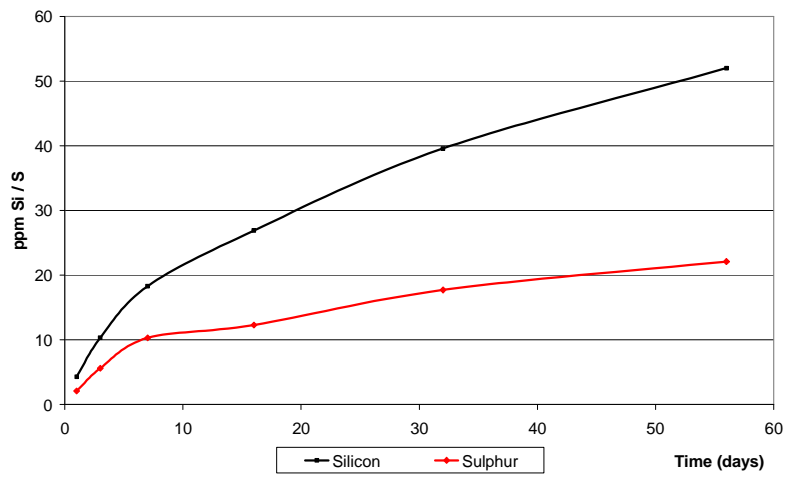


Figure 3: silicon and sulphur leaching in accelerated carbonation conditions

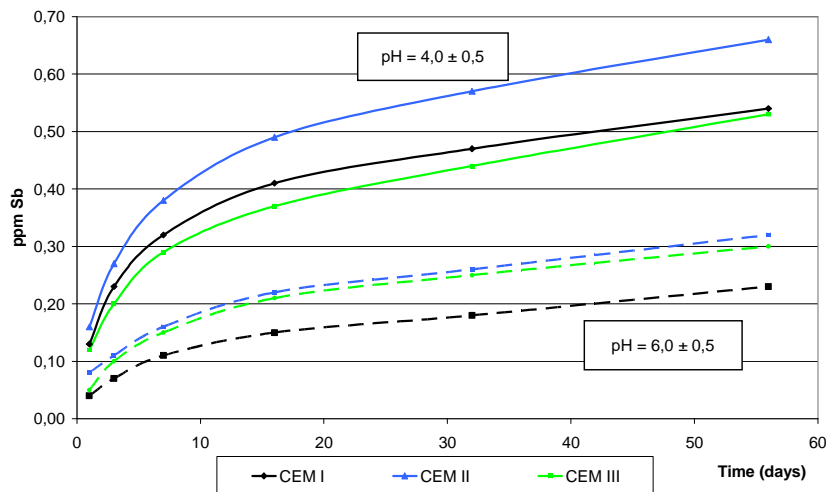


Figure 4: antimony leaching at different pH. Continuous lines refers to leaching at pH 4, dashed lines to leaching at pH 6. Leaching from concrete made with highest Sb content cements

4. Conclusions

No extraction of antimony was evidenced from concrete in test reproducing the conditions on site, even in case of increasing the diffusion process by crushing the material. In strong and aggressive conditions, a release of a minimal amount of the Sb previously added to cement is noticeable. Antimony leaching is always associated to the degradation of cement paste, due to carbonation or dissolution at acid pH. This suggests that although antimony is added as antimony trioxide interground with cement (and not embedded in clinker matrix), an inclusion in hydrated cement paste takes places and the real pathway of immobilization will be the subject of further studies. To refer to the bulk content of antimony as a criterion of environmental quality is unjustified and indeed restrictive, as already evidenced by other authors (Marion et al., 2005). On the basis of the data collected, the use of antimony based products for reduction of Cr(VI) do not pose risk of antimony leaching, provided that concrete is used in the proper conditions.

Aknowledgements

We aknoweledge the colleagues of Mapei Analytical lab (in particular Marilena Carrara and Zita Pellegatta) for ICP/AES analysis and colleagues of Mapei Concrete lab for concrete preparations.

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