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Speciation of Cd and Pb in dust emitted from sinter plant

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ABSTRACT

Many studies have provided evidence of the impact of heavy metals in atmospheric emission. Sinter plants represent the first step in steel production, and are important emitters of Cd and Pb. The toxicity of these two metals depends above all on their speciation. Particles collected before and after the filtration system were analysed to determine the Cd- and Pb-bearing phases, using analytical tools such as XRF, EXAFS or ICP-AES and chemical leaching (sequential extractions adapted to steel dusts). Results show that Pb is associated with carbonate and Cd with chloride. These two types of speciation lead to high solubility under common environmental conditions, which may produce impacts on the environment and health.

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1. Introduction

The problem of atmospheric contamination by airborne particulate matter (PM) has worsened notably due to the increase in industrial activity. Emitted particles are considered to be an important health hazard (Dockery et al., 1993; Pope et al., 1995; Schwartz et al., 1996; Kyotani and Iwatsuki, 2002). Particulate matter (PM) has a direct influence on health through respiration because of the typically small size and composition of the particles, containing heavy metals and metalloids, which may interfere with biochemical mechanisms (Fernandez Alvarez et al., 2004). The toxicity of inorganic pollutants depends more on their chemical nature than their concentration (Hayes, 1997; Adamson et al., 2000), with the less soluble forms being generally regarded as less toxic. Consequently, a thorough analysis of the speciation of heavy metals is a prerequisite for a meaningful assessment of their environmental impact and potential toxicity (Baize, 1997; Fernandez et al., 2000).

The steel industry is an important emitter of atmospheric particulate matter. The sintering plant is the first step in the steelmaking process, where iron ore is prepared with additive materials to form sinter that is then transported to the next step in the production process. Dust generated by the sintering process is very fine compared with other dusts originating from blast furnaces (Menad et al., 2006), and the effective filtering of microscopic-sized particles and aerosols is a major long-standing problem, for which no solution yet exists (Formo et al., 2000). Moreover, Pb and Cd derived from introduced recycled materials are largely concentrated in atmospheric emissions. Cd and Pb are assumed to contribute to the toxic potential of atmospheric PM (Fortoul et al., 2005). Their toxicity depends above all on their speciation (INERIS, 2003, 2004). Generally, because of their high solubility, salts are often pointed out as being the more potentially toxic phases. However, insoluble Pb and Cd phases can be converted into water-soluble salts in nature under the influence of oxygen and acids in soils, thus leading to increased toxicity (Jonnalagadda and Prasada Rao, 1993).

Unfortunately, most studies concerning steel sintering plant emissions are focused on dioxin and other organic emitted compounds (Wang et al., 2003; Aries et al., 2004, 2006; Shih et al., 2008). There is a lack of research on heavy metal speciation in sinter plant emissions, although this type of plant is the most important emitter of particles in the steel industry. Indeed, it accounts for about 45% of all PM emissions and is also a major emitter of heavy metals (Menad et al., 2006).

In this study, a number of analytical tools and chemical protocols (XRD, EXAFS, chemical extractions) are used to determine the speciation of Pb and Cd in sinter plant emissions. To our knowledge, this study is the first to describe the speciation of Cd and Pb in sinter plant emissions.

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2. Material and methods

2.1. Studied site and sample collections

The studied steel plant is located in southern France and produces about 5 million tons of steel per year. It generates about 6000 tons of dust per year. The sintering process is a core part of the integrated iron and steel-making process route. In the sintering process, feed material, consisting of a moist agglomerate of fine-grained iron ores, revert materials, solid fuel (coke) and limestone, is distributed on a moving grate as a bed of uniform thickness. It is then heated at high temperature (about 1300 °C), sintered and calibrated to be acceptable for the blast furnace (Buekens et al., 2001; Anderson et al., 2002). The sinter final product is a porous but physically strong cake generally composed of four main phases occurring as iron oxides, ferrites, glasses and calcium silicates (Scarlett et al., 2004). The off-gases and dust particles generated by this process are led through a multiple field electrostatic precipitator (ESP) for cleaning before being discharged via a stack (Buekens et al., 2001). This filtration system involves the application of three successive electric fields to trap the majority of particles with low resistivity. Other particles not retained by the ESP are emitted to the air by the sinter stack.

The emitted particles studied here correspond to the ESP dust that is not retained by the electrostatic field. They were collected at the bottom of the stack onto 85-mm diameter Teflon air filters using a sampling probe just after the ESP and before emission into the atmosphere. Samples were collected during four sampling events to obtain sufficient particles for analysis.

The mineralogy of particles determined by X-ray diffraction is mainly composed of sylvite (KCl), hematite (Fe_2O_3), calcite ($CaCO_3$) and halite (NaCl) derived from introduced materials (coke, limestone, recycled products, etc.).

The size distribution of the emitted particles is assessed by a low-pressure DEKATI cascade impactor mounted just after the filtration system. 75% of the total mass of particles has a size below 2.5 μm (with 58% below 1 μm), indicating that the sinter plant emits a majority of fine particles (Scarlett et al., 2004; Ahn and Lee, 2006). The mass above 10 μm is only 7%.

2.2. Chemical composition

Filters of emission dust were cut into eight pieces. Four pieces of each filter were dissolved by acid digestion with aqua regia added to fluorhydric acid (4 mL HCl, 4 mL HNO_3 and 2 mL HF). Solutions were heated at 120 °C for 9 h, and then made up to 25 mL with 2 mL boric acid and 13 mL pure water. The prepared solutions were filtered to 0.2 μm and then analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES Optima 30, Jobin Yvon, France). Elements analysed were Cr, Cd, Zn, Pb, Mn, Fe and K.

2.3. Solubility of Cd and Pb

The chemical extraction method used here was developed to fractionate the different chemical species of heavy metals from sediments using multiple extraction steps with a variety of chemical reagents, reaction times, temperature and pH conditions (Tessier et al., 1979). Sequential extractions provide a pragmatic approach for determining heavy metal chemical fractionation and solubility.

In our study, the protocol of sequential extractions was adapted and optimized for heavy metals contained in steel plant emissions (Sammut et al., 2008). Table 1 gives details of the different steps and experimental conditions.

To interpret the results and apply our optimized protocol to industrial dust, the procedure was first calibrated on samples prepared from pure compounds of Pb and Cd (sulphates, chlorides, carbonates, oxides and sulphides). These compounds have been found in particles emitted from industrial sites (Fernandez et al., 1992; Sobanska et al., 1999) and may be present in the dust from steel plants.

Table 1
Speciation scheme for steel plant air particulate matter.

Step	Fraction	Reagents	Experimental conditions	Extracted metals
S1	Exchangeable	60 mL of H_2O ultrapure pH 7	Stirred for 3 h at 60 °C	Soluble metals in water
S2	Carbonate	20 mL of 1MCH_3COONa in 2 mL CH_3COOH at pH 5	Stirred for 3 h at ambient temperature	Carbonated metals and insoluble salts
S3	Oxide	25 mL of 0.25 M NH_2OH. HCl at pH 5.5	Stirred for 4 h at ambient temperature	Metals bound to reducible phases
S4	Reduced	7.5 mL of 30% H_2O_2 + 15 mL of 2.5 M NH_4AcO at pH 3	Heated at 95 °C until evaporation and 3 h at ambient temperature	Metals bound to phases easily soluble under oxidizing conditions such as sulphides
S5	Residual	4 mL of HNO_3 + 4 mL of HCl + 2 mL HF at pH 1	Heated at 120 °C for 3 h	Metals present in crystalline structure of primary and secondary minerals, soluble under strongly acidic conditions

Sequential extractions on dust samples were performed with the same liquid/solid ratio as used for the reference compounds. Four replicates of each filter were used for the sequential extractions. After each extraction, samples were centrifuged at 4000 rpm for 20 min. The supernatant was filtered at 0.2 μm and collected for soluble ion analysis. Concentrations of heavy metals in solution were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). For each element, the sum of five extraction steps is compared with the total concentration obtained by acid digestion. The element recovery rate obtained is situated between 80% and 117%.

2.4. Determination of Pb and Cd speciation

2.4.1. X-ray diffraction

To ensure dissolution of the most soluble phases and detect minor phases, we chose to apply the technique to washed dust. The dust particles were rinsed with pure water to dissolve soluble salts (KCl and NaCl), and then dried at an ambient temperature of 30 °C. Particles were analysed with a Philips PW 3710 X-rays diffractometer using Co Kα radiation at 40 kV and 40 mA, over a range from 10° to 90° with a step of 0.05° and 5 s counting time per step. Then, the proportions of all detected mineralogical phases were estimated by Rietveld refinement of the experimental difractogram (Rietveld, 1969). The method consists of fitting the diffraction spectra using the structural parameters of mineralogical compounds. The relative proportions of mineralogical phases were determined using the Fullprof software (Rodriguez-Carvajal, 2005).

2.4.2. X-ray absorption fine structure (XAFS) at Cd–K edge

Cd–K edge (26 600 eV) XAS spectra were obtained on the XAS CRG BM 30B French beamline (FAME) at the ESRF radiation source (European Synchrotron Radiation Facility, Grenoble, France). The

storage ring operated at 6 GeV and the beam size was 300 μm × 200 μm. XAS spectra were recorded with a Si (220) monochromator on ground particles mixed with 30% BN to ensure pellet resistance, using fluorescence mode with a high-purity Ge 30-element fluorescence detector. The sample pellets were placed at an angle of 45° to the incident beam. All spectra were calibrated in terms of energy against the edge position of a thin Cd foil. Spectra were recorded from −100 eV to 800 eV around the threshold energy, with a step of about 1 eV. Seven crystalline standards were also analysed, containing Cd with different atomic environments.

2.4.2.1. EXAFS treatment. EXAFS spectra were processed using a standard edge step normalization procedure. A standard procedure for data reduction was used to analyse the EXAFS measurements using a series of programs developed by Michalowicz (Michalowicz, 1991). The analysis of XAFS spectra is well described in the literature (e.g. (Brown et al., 1988; Koningsberger and Prins, 1988). The EXAFS region ($\chi_{(E)}$), is converted into reciprocal space and then subjected to a Fourier Transform to calculate a radial structure function (RSF), which is a one-dimensional representation of the local structure surrounding the absorbing element. The inverse Fourier Transform extracted from each peak of the RSF represents the contribution of one or several atomic shells.

2.4.2.2. EXAFS modelling. The speciation of Cd in emitted particles was determined by EXAFS modelling. The inverse Fourier Transform extracted from the first peak of the RSF was modelled. Amplitude and phase-shift functions used to recalculate partial EXAFS spectra were extracted from the FEFF 8.0 code (Ankudinov et al., 1998). Modelling parameters were extracted from data on reference components. The accuracy on R_i (distance between Cd and neighbouring atoms) and N_i (numbers of neighbours) is found to be 0.02 Å and 20%, respectively.

3. Results

3.1. Chemical composition

Fe is the main element contained in the emitted particles. The presence of Fe species (hematite) after this type of filtration system indicates the failure of the ESP to trap all Fe compounds (Ahn and Lee, 2006), despite its efficiency being higher than 90% for Fe.

K represents about 15% of the bulk composition of the emitted particles, which is lower than the proportions generally measured for other sinter plants (Oravisjarvi et al., 2003). These differences in percentages may be due to variations in the composition of the introduced material (Lee and Pacyna, 1999; Moreno et al., 2004). Cd and Pb are abundantly present (955 and 20 519 ppm, respectively) in the emitted particles. The sintering plant is the greater single emitter of Cd and Pb from steel works, since it accounts for about 98% and 96% of the total Cd and Pb emission from the overall steel-making process (Oravisjarvi et al., 2003).

3.2. Solubility of Cd and Pb

Sequential extractions were performed on Pb and Cd reference compounds to observe their behaviour during successive steps (Fig. 1).

Chemical extractions applied on reference compounds show that $CdCl_2$, $CdSO_4$ and $PbCl_2$ are solubilized in water (S1), while $PbSO_4$ is extracted in the same fraction as $PbCO_3$ (S2). The difficulty of dissolving $PbSO_4$ is due to its low solubility product ($K_{PbSO_4} = 10^{-7.85}$) whereas $K_{CdSO_4} = 10^{-0.11}$. Half of the $PbCO_3$ is dissolved in the second step. PbS and CdS require more drastic conditions to be solubilized; CdS is totally extracted during S4, while PbS

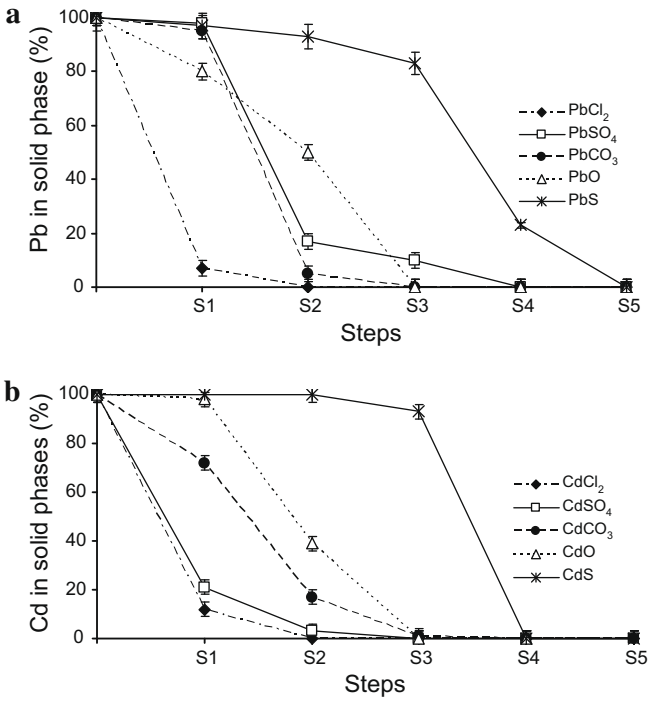


Fig. 1. Solubility of reference compounds according to sequential extractions. (a) Pb references, (b) Cd references.

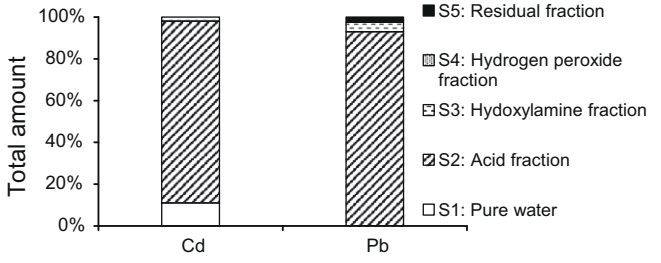


Fig. 2. Cd and Pb distribution according to the five sequential extraction steps for particles emitted from sinter plant.

is totally dissolved in the last step (S5). We also note that CdO and PbO are partially dissolved in the second fraction (S2), but the totality of these two phases is extracted with the third fraction (S3).

Calibration of this protocol provides some information about the behaviour of Cd and Pb as a function of their speciation. Moreover, this test on reference compounds allows us to obtain a better knowledge of the specificity of each extraction. Thus, the protocol was applied to samples of the sintering particulate emissions (Fig. 2).

Sequential extractions applied to the sintering emissions show that the majority of Pb contained in dust is soluble, since it is extracted in the second step. According to the sequential extractions performed on the Pb reference compounds, this second step is specific for the dissolution of $PbSO_4$ and $PbCO_3$.

In the same way as Pb, Cd is also extracted with the second fraction in dust. According to the sequential extractions on pure compounds, the second step dissolves a small amount of the $CdCl_2$ and $CdSO_4$ not dissolved by the first step, along with most of the $CdCO_3$.

3.3. Speciation of Pb

XRD was performed on water-washed particles to identify the minor compounds masked by the more intense signal due to salts.

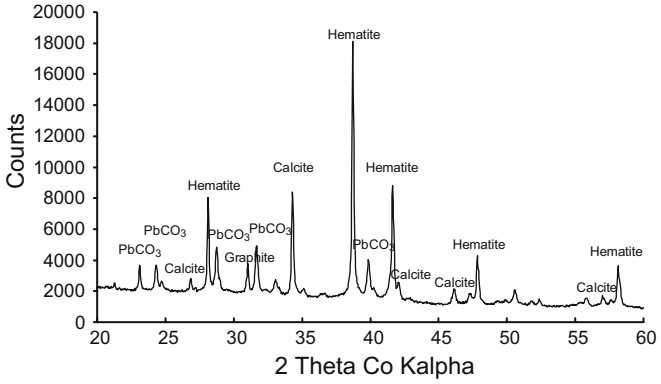


Fig. 3. Diffractogram of water-washed emitted particles from a sinter plant.

In this way, we detected the diffraction peaks of a Pb compound (Fig. 3).

The speciation inferred by X-ray diffraction of sintering emission samples is hydrocerussite ($PbCO_3{\cdot}2H_2O$). The association of Pb with carbonates is not the most common Pb phase in industrial emissions. The formation of this species may be due to the high concentration of CO_2 emitted during the process. Indeed, in lead smelters, the off-gas is mainly SO_2, which explains the association of Pb with sulphates, sulphides or oxides (Clevenger et al., 1991; Sobanska et al., 1999). Batonneau et al., (Batonneau et al., 2004) showed that $PbCO_3$ is more typically present in industrial waste slag. Sequential extractions on Pb reference compounds show that only half of the $PbCO_3$ is dissolved with the second step, in conflict with the results obtained from sintering emissions where Pb is totally extracted in S2. The formation of hydrocerussite is suggested by the hydration of Pb carbonate in sintering emissions. Indeed, the solubility of cerussite ($Ks_{PbCO_3} = 10^{-3.2}$ at 25 °C) is lower than hydrocerussite ($Ks_{PbCO_3{\cdot}2H_2O} = 10^{-1.8}$ at 25 °C), thus explaining the total solubility of hydrocerussite in sequential extractions.

Sammut (2007) had shown that, in the same site, for samples taken after a bag-house with desulphurisation treatment of smokes by lime, the lead speciation is changed and hydrocerrusite is replaced by anglesite.

The abundance of mineralogical compounds estimated by Rietveld refinement show that hematite (40%) and sylvite (30%) are predominant, as indicated by the chemical analyses. The relative abundance of $PbCO_3{\cdot}2H_2O$ is estimated at 2%. This value corresponds to 20 g kg^{-1} of Pb, which is in remarkable agreement with the Pb concentration determined by ICP-AES (20 519 ppm). 40% of Fe_2O_3 corresponds to 140 g kg^{-1} of Fe, suggesting that other Fe compounds are present in sintering emissions, such as magnetite as detected by XRD. Otherwise, 30% of KCl corresponds to 157 g kg^{-1} of K. The K concentration given by ICP-AES is 147 g kg^{-1}, which is in very close agreement considering that the Rietveld estimation is semi-quantitative. The other mineralogical compounds are calcite (15%), quartz (5%) and halite (4%).

3.4. Speciation of Cd

Speciation of Cd was determined by X-ray Absorption Fine Structure at the Cd–K edge. The EXAFS spectra of Cd were extracted as explained above. We then modelled the inverse Fourier Transform extracted from the RSF peak (Fig. 4a).

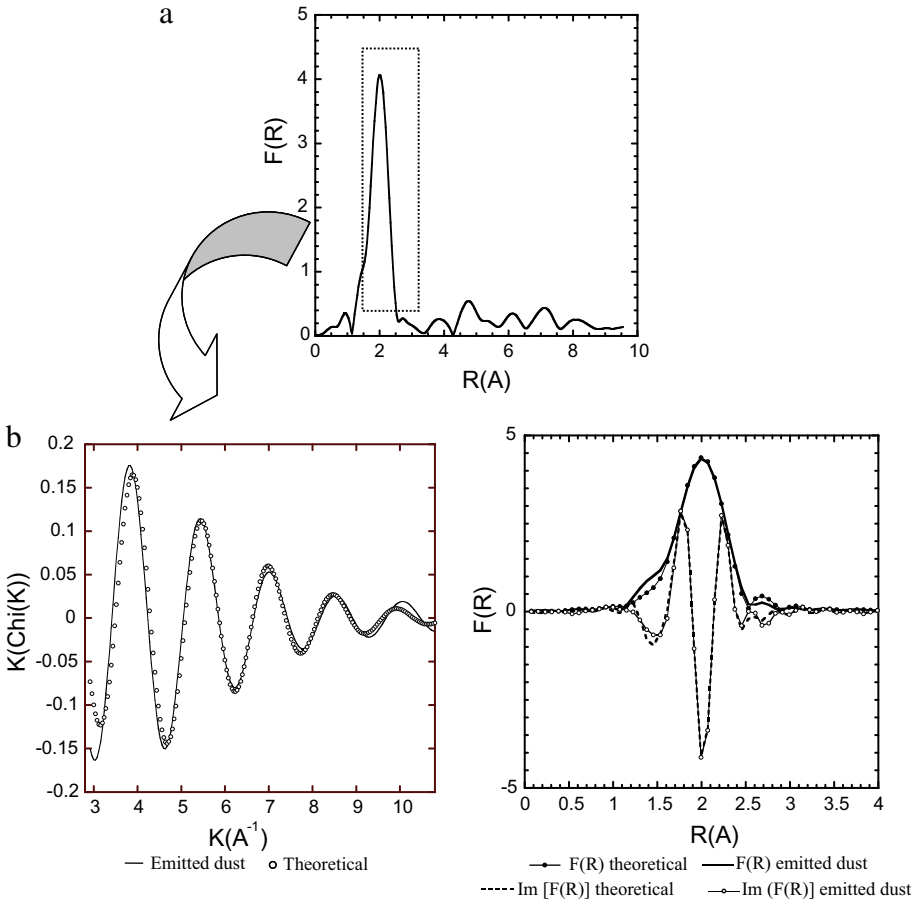


Fig. 4. (a) Radial structure function (RSF) of Cd in emitted dust; (b) real and imaginary components of emitted dust and theoretical spectra.

Table 2
Structural parameters of the first coordination sphere of cadmium in different compounds and in the studied sample.

Compound	Bond	N	R (Å)	σ	Residual
Cadmium chloride	Cd–Cl	6	2.65		
Cadmium sulphate	Cd–O	6	2.28		
Cadmium carbonate	Cd–O	6	2.28		
Cadmium oxide	Cd–O	6	2.34		
Cadmium hydroxide	Cd–O	6	2.34		
Cadmium sulphide	Cd–S	4	2.34		
This study	Cd–Cl	5.9	2.55	0.1	$8.36.10^{-2}$

The EXAFS modelling yields results concerning the first coordination sphere of the sintering emission PM. The experimental curve corresponding to the main peak of the RSF (Fig. 4b) is fitted with different atomic shells (Cd–O, Cd–S, Cd–Cd, Cd–Fe, etc.), but the best residual is obtained with the Cd–Cl atomic shell. Table 2 presents the structural parameters obtained for the weaker residual.

Structural parameters obtained by modelling the first coordination sphere of Cd present in the sintering emission particles are very close to values for the $CdCl_2$ reference ($CdCl_2$: dCd–Cl = 2.6 Å; $N = 6$), with 5.9 atoms of Cl at a distance 2.55 Å from the Cd atom. This confirms that Cd is mainly associated with chloride phases, and explains why it is not trapped by the ESP system (Ahn and Lee, 2006). $CdCl_2$ is a highly abundant compound in high-temperature processes such as waste incinerators or smelters, created by the presence of Cl (in a gaseous form) and Cd. Nevertheless, the occurrence of KCl associated with the particles identified by XRD may also explain the presence of $CdCl_2$ (Camerani et al., 2002). At high temperatures (above 300 °C), $CdCl_2$ is present in gaseous form. After cooling of the system, $CdCl_2$ (gas) precipitates as the same species, which accounts for the presence of $CdCl_2$ in sintering emissions. The speciation of Cd can lead to a toxic potential. Indeed, pure $CdCl_2$ is well known to generate a toxic (Valverde et al., 2000) or inflammatory response after inhalation. Moreover, as the bioavailability of this species depends on the solubility of Cd, the persistent high solubility may lead to a health issue.

4. Conclusion

In this study, we use different analytical tools to determine the speciation of Cd and Pb in dust emitted from sinter plant. Cadmium is found as chlorite and lead as carbonate. These speciations are different than those described in other industrial environment. Cadmium is found as carbonate and associated with hematite in basic oxygen furnace dusts (Sammut, 2007), as oxide, sulphate and sulphide in Pb/Zn smelter emissions (Sobanska et al., 1999) and as chloride, sulphate and oxide in MSWI fly ashes (Camerani et al., 2002). For lead, carbonate is suspected by Sammut (2007) for basic oxygen furnace dusts but the more important form is lead associated with hematite. Lead hydroxide and/or oxide are described by Sammut (2007) for electric steel plant. In the case of Pb/Zn smelter, sulphate, sulphide, chlorite and oxide are found (Sobanska et al., 1999; Choël et al., 2006). Oxide and chlorite are also described by Fernandez et al. (1992) for MSWI fly ashes.

Cadmium chlorite and lead carbonate have relatively low solubility products, compared to other forms as oxides or sulphide, and their environmental impacts for humans and ecosystems must take in account.

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