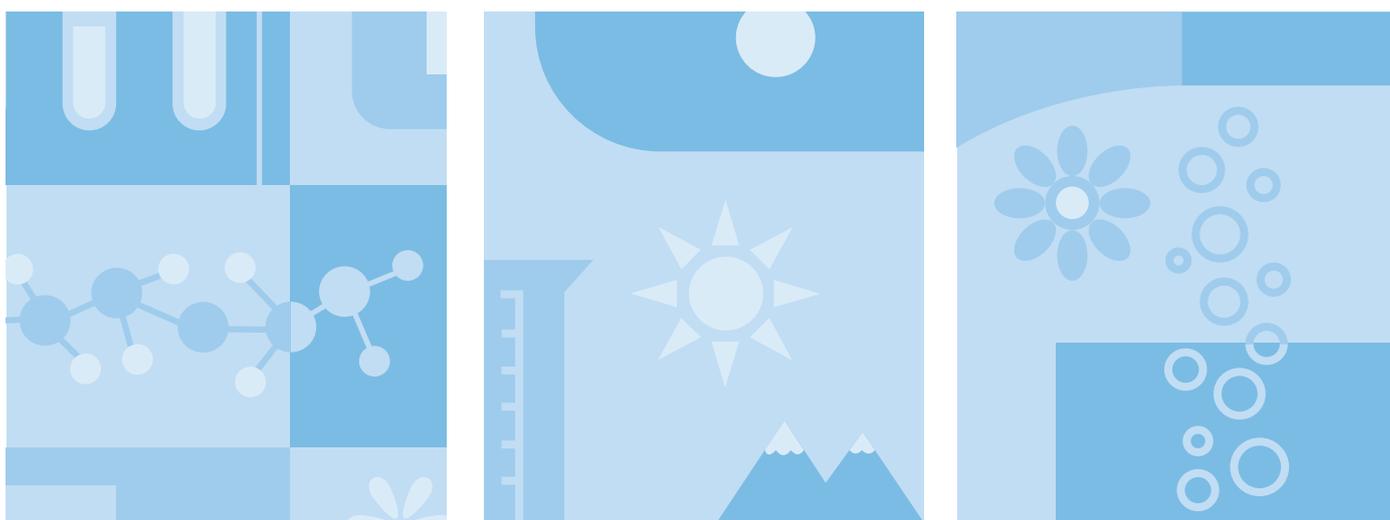


# Soil chemical behaviour of cadmium pigments from paints



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Department of Land and Water Resources Engineering, KTH Royal  
Institute of Technology



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## **Foreword**

This report was commissioned to Professor Jon Petter Gustafsson at the Royal Institute of Technology (KTH), Sweden, by the Swedish Chemicals Agency (KemI). The task was to describe the solubility and availability of a number of cadmium-containing substances, used in paints.

The responsibility for the report contents rests entirely with the author. The views here shall not necessarily be taken to reflect the official opinion of Swedish Chemicals Agency.



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## Abstract

A review focusing on the thermodynamic stability and dissolution rates of Cd-containing sulphides and selenides from paints is presented. In the surface horizon of Swedish agricultural soils, cadmium sulphide, CdS(s), and cadmium selenide, CdSe(s), are shown to be thermodynamically unstable. The presence of electron acceptors such as oxygen gas and iron(III) will lead to gradual dissolution of these compounds. The dissolution rate of Cd-containing sulphides is dependent on the amount of crystalline zinc sulphide in contact with the cadmium, as zinc will be dissolved preferentially from a mixed cadmium zinc sulphide mineral. In the absence of crystalline zinc sulphide, Cd will be dissolved completely after 1-3 years. The presence of crystalline zinc sulphide can extend the life span of CdS to 1-2 decades; however, sewage sludge contains mostly amorphous ZnS that will dissolve more quickly. In conclusion, if a time frame of several decades is applied, it is very likely that Cd from Cd pigments has a similar solubility and bioavailability as an easily soluble Cd salt such as cadmium chloride.

## 1. Objective

This review has been carried out for the Swedish Chemicals Agency. The task was to describe the solubility and availability of a number of cadmium-containing substances used in paints. These substances include the following:

CAS number	Name
1306-23-6	Cadmium sulphide
8048-07-05	Cadmium zinc sulphide yellow
12656-57-4	Cadmium sulphoselenide orange
58339-34-7	Cadmium sulphoselenide red
12442-27-2	Cadmium zinc sulphide
12626-36-7	Cadmium sulphoselenide

The objective of this report is to supply information on the solubility of these cadmium compounds and compare to a reference compound with higher solubility, such as cadmium chloride. From this an assessment may be made on the availability for plant uptake in a scenario in which these compounds end up in a sewage sludge that is then applied to agricultural land. The time frame considered is 50 years (after application of the sludge).

The review does not cover the processes determining the overall solubility and bioavailability of cadmium ions in soils, as these have already been studied extensively in connection with the EU risk assessment for cadmium (European Chemicals Bureau, 2007)

## 2. Introduction

Cadmium-containing sulphides and selenides give rise to a range of different clear colours. Cadmium sulphide pigments are synthesized using either a wet or a dry process using cadmium oxide or cadmium metal as a starting material. From the 1840s, cadmium pigments have been commercially available and quickly became popular among the 19<sup>th</sup> century artists. The bright yellow colour, its wide applicability and suitability for mass production were three reasons. In addition, CdS was thought to be highly stable in oil paint and water colours (Curtis and Wright, 1954; van der Snickt et al., 2009), which was an advantage over other available alternatives such as chrome yellow (PbCrO<sub>4</sub>). The CdS pigments also have excellent heat stability, and can withstand temperatures higher than 3 000°C (Cepriá et al., 2005). Artists who made frequent use of the yellow CdS pigments include Claude Monet, Vincent van Gogh, Juan Miró, and Pablo Picasso.

By partial substitution of cadmium in the crystal lattice of CdS by selenium, a range of additional clear colours can be obtained, such as orange, red and maroon. Further, by substituting part of the Cd ions for Zn, intermediate colors in the lemon-yellow to maroon range of cadmium colors can be obtained (Cepriá et al., 2005). During the 20<sup>th</sup> century, the use of Cd pigments was expanded to include colouring of plastics etc.

Today, the use of Cd pigments in Europe is decreasing, and the reasons for their decline may include the following:

- Due to increased environmental awareness, a number of restrictions limit the use of Cd pigments in the European Union. For example, the use of Cd in certain plastics (except for in recycled PVC) has been banned (European Union, 2012).
- The long-term stability of Cd pigments is now known to be lower than was originally believed, especially in cases when the paint is exposed to light and humidity. Paintings from the 19<sup>th</sup> century show clear signs of fading of the yellow CdS pigment colours (Leone et al., 2005; van der Snickt et al., 2009). These authors have convincingly demonstrated that the reason is that CdS with time is dissolved because of sulphide oxidation. Fading, however, is not unique for CdS; other frequently used pigments, such as chrome yellow (PbCrO<sub>4</sub>) also fade with time. In this case the reason is reduction of chromate to chromium(III) (Monico et al., 2011). These findings should have important implications for methods of conservation of a long list of famous paintings by, e.g., van Gogh and Picasso.

In the following, a review is made on the general chemical properties of cadmium sulphide and selenide. Of these, cadmium sulphide is the one most well studied; a number of observations can be made also from studies of zinc sulphide. All these compounds are similar to one another in many respects, as cadmium and zinc, as well as sulphur and selenium, are similar to one another and readily substitutes for one another in the pigments.

### **3. Cadmium sulphide, CdS(s) – Equilibrium chemistry**

#### **3.1. Solubility of cadmium sulphide**

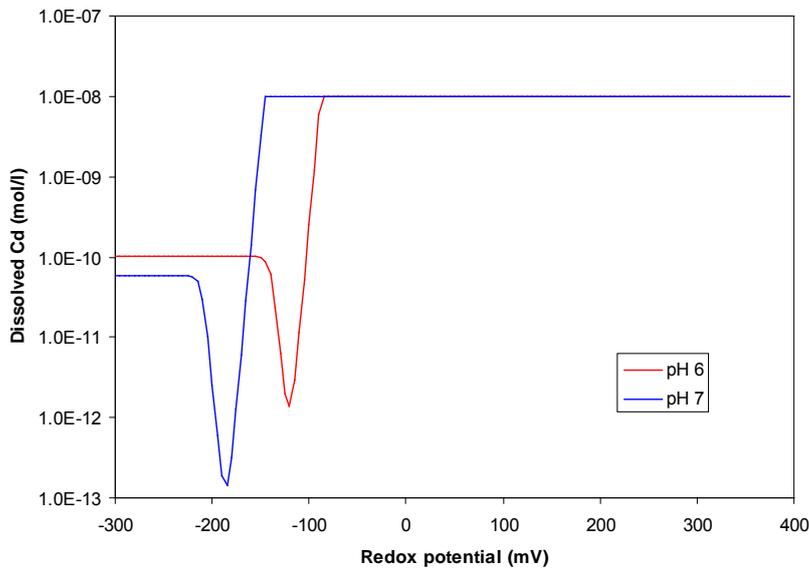
Cadmium sulphides can exist as different forms. In nature, pure CdS minerals are relatively rare. Greenockite and hawleyite are the two recognized natural CdS minerals. Much more commonly, CdS occurs as a minor constituent of other sulphide minerals such as sphalerite, ZnS(s). CdS(s) can also be synthesized on the laboratory. Freshly precipitated CdS(s) has a low degree of structural order, and it also has a solubility that is about two magnitudes higher than that of

crystalline forms, such as the mineral greenockite (Daskalakis and Helz, 1992). In general, the dissolution reaction of CdS(s) can be written as follows:



In equation 1, the solubility constant  $*K_s$  is defined according to  $*K_s = \{\text{HS}^-\} \{\text{Cd}^{2+}\} / \{\text{H}^+\}$ . The  $\log *K_s$  value of for crystalline CdS minerals is in the range of -14 to -14.5 (e.g. Daskalakis and Helz, 1992; Gustafsson, 2012). It should be noted that equation 1 does not provide the full picture to the solubility of  $\text{Cd}^{2+}$  in sulphide-containing systems, as  $\text{Cd}^{2+}$ , once dissolved, will also form a number of soluble complexes with  $\text{HS}^-$ . In any case, the solubility of CdS(s) is low in systems where both cadmium and sulphide ions occur. However, in the presence of electron acceptors such as  $\text{O}_2(\text{g})$  and Fe(III), CdS(s) becomes less stable due to the oxidation of sulphide ( $\text{HS}^-$ ) ions to sulphate ( $\text{SO}_4^{2-}$ ) ions.

The *redox potential* is often used to indicate the electrochemical conditions of different environments. In other words, the redox potential indicates the availability of electron acceptors, which are present in soils and waters. A high redox potential will cause the oxidation of sulphide into sulphate, and thereby lead to dissolution of CdS.



**Fig. 1.** Solubility of Cd in equilibrium with greenockite, CdS(s) as a function of redox potential, at two different pH values, 6 and 7. Conditions: 0.001 M NaCl, 20°C, dissolved S = 0.1 mM.

With a geochemical model such as Visual MINTEQ, it is possible to relate the solubility of CdS(s) to the redox potential. In the simulation shown in Fig. 1, the solubility of  $1 \cdot 10^{-8}$  mol/l CdS(s) (about 1.45  $\mu$ g/l) is shown as a function of the redox potential at environmentally realistic conditions. Two pH values, 6 and 7 have been chosen as they represent typical conditions in the surface horizon of agricultural soils. At low redox potentials, Cd solubility will be small. A minimum solubility occurs between -200 and -100 mV. This can be explained on the basis of the stability of dissolved Cd-HS complexes, which dominate Cd speciation at low redox potential, but these begin to dissolve at higher redox potential. At between -100 to -150 mV, the lines flatten at  $1 \cdot 10^{-8}$  mol/l Cd; this is because under these conditions, CdS(s) is completely dissolved.

### **3.2. Stability of CdS in the environment**

Because the redox potential in the surface horizon of agricultural soils is a lot higher, between 200 and 500 mV (Nilsson, 1988; Macsik, 2000), CdS(s) in paints is thermodynamically unstable in agricultural soils. However, due to its crystal structure, it is very likely that dissolution is not instant, but controlled by kinetically constrained dissolution (“weathering”), c.f. section 5 below.

The importance of the redox conditions for CdS(s) solubility is important to consider when interpreting the results from leaching tests that are reported, e.g. in the ECHA database. As indicated above, when dissolving pure CdS(s) in water in a closed batch system, the availability of electron acceptors is very small (the presence of sulphide will buffer the redox potential to a low value), leading to very low values of dissolved Cd as CdS(s) is relatively stable under these conditions. When purging with O<sub>2</sub>(g), however, the availability of electron acceptors increases drastically, leading to an increased redox potential and hence to sulphide oxidation. Under these conditions, CdS(s) will be converted gradually to CdSO<sub>4</sub>(s), which is very soluble.

In other words, when geochemical modeling is used to predict leaching of Cd from pigments (using codes such as, e.g., Visual MINTEQ or HSC 7.0), it is important to include the effect of the redox potential in the environment to allow sulphide oxidation; otherwise the results obtained will be irrelevant for the real situation in the field.

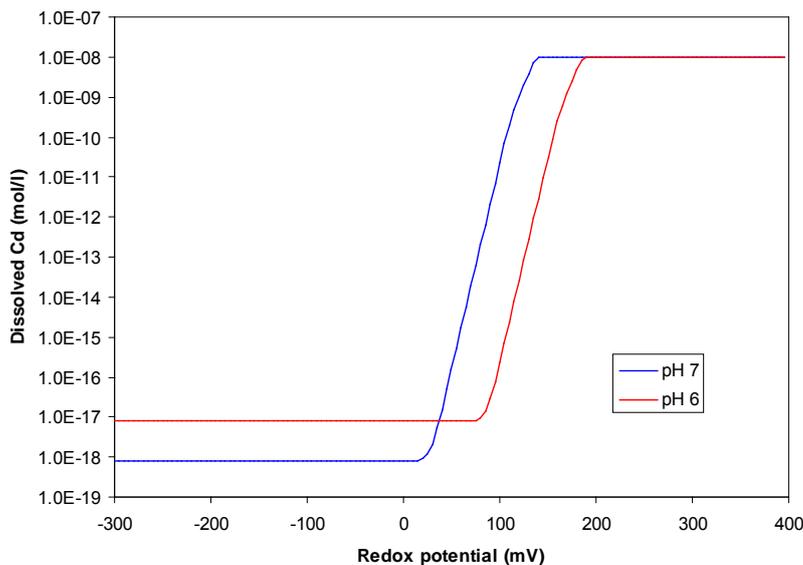
## **4. Cadmium selenide, CdSe(s) – Equilibrium chemistry**

The general properties of cadmium selenide are expected to be rather similar to cadmium sulphide because of the similar properties of sulphur(-II) and selenium(-II). However, the solubility of cadmium selenide is quite low, much lower than that of cadmium sulphide. For the dissolution reaction:



In equation 2, the solubility constant  $\log *K_s$  (see text under equation 1 for definition) is equal to -20.2 at 25°C, according to the Visual MINTEQ thermodynamic database (Gustafsson, 2012). Therefore in the absence of electron acceptors, under reducing conditions, cadmium selenide will be stable and the release of cadmium ions very small.

However, similarly to the case for cadmium sulphide, the stability of cadmium selenide is very sensitive to the redox potential, as selenide is oxidized to higher oxidation states. In the case of selenium, there are several oxidation states that may be formed at higher redox potential, i.e. Se(0), Se(IV) and Se(VI). Fig. 2 shows the result from a geochemical model simulation of the Se solubility in a similar way as Fig. 1, i.e. using an initial concentration  $10^{-8}$  mol/l cadmium selenide. The value used for dissolved Se in the simulation,  $5 \cdot 10^{-10}$  M, is representative of Swedish waters (Örnemark and Olin, 1995).



**Fig. 2.** Solubility of Cd in equilibrium with cadmium selenide, CdSe(s) as a function of redox potential, at two different pH values, 6 and 7. Conditions: 0.001 M NaCl, 20°C, dissolved Se =  $5 \cdot 10^{-10}$  M.

As Fig. 2 shows, cadmium selenide is stable up to a redox potential of around 100 mV. Above about 150 mV, dissolved Cd reaches  $1 \cdot 10^{-8}$  mol/l, which means that all CdSe(s) has dissolved and that cadmium selenide can be considered unstable. This means that cadmium selenide, as well as cadmium sulphide, are expected to be thermodynamically unstable in the A horizon of most agricultural soils.

## 5. Dissolution kinetics of Cd-containing sulphide (and selenide) minerals

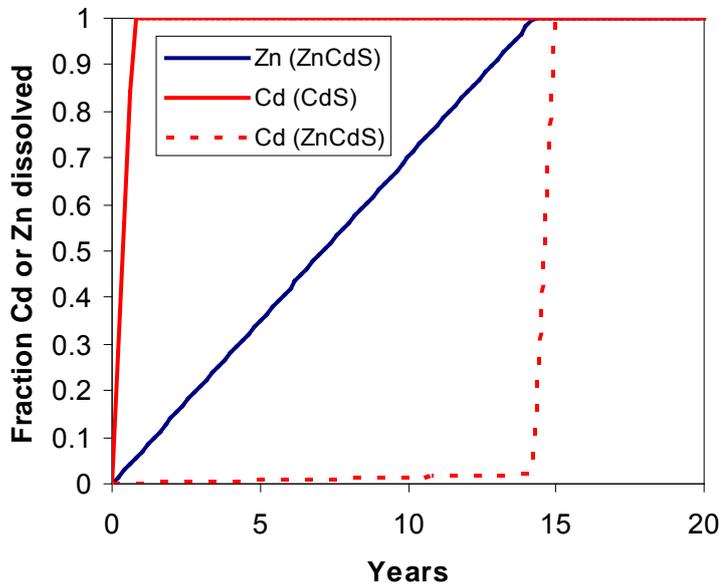
### 5.1 Summary of literature findings

As shown in preceding sections, cadmium sulphide is expected to be thermodynamically unstable in agricultural soil environments. The release of cadmium ions to the environment and the bioavailability of this cadmium would therefore be dependent on the dissolution rate of the cadmium sulphide supplied to this environment through sewage sludge.

The dissolution of sulphide minerals, if deposited through sludge, will be more or less slow due to a number of factors: (i) the crystallinity and surface area of the minerals; (ii) the diffusion rate of electron acceptors, which for soils are mainly  $O_2(g)$  and Fe(III) (see, e.g., Barrett and McBride, 2007); (iii) surface reactions with other dissolved substances in soils, which may either retard or enhance dissolution. There has been relatively little research into factors determining the dissolution rates of Cd-containing sulphides. Some highlights are listed below:

- Pure cadmium sulphide is much more sensitive to oxidative dissolution compared to a zinc sulphide mineral such as sphalerite. Therefore, the dissolution rate of pure CdS may be up to 20 times that of sphalerite (Barrett and McBride, 2007).
- The dissolution rate of Cd (as for Zn) sulphide is pH-dependent, although different samples behave differently (Salmon and Malmström, 2006; Barrett and McBride, 2007). An estimate based on published results is that the dissolution rate of sphalerite will decrease with a factor 5 for a pH increase of 2 units.
- When Cd occurs as mixed ZnCdS, the dissolution rate of Cd is much lower than that of Zn as long as the Zn/Cd ratio is higher than 1 (Barrett and McBride, 2007; Stanton et al., 2008; de Livera et al., 2011). Based on the results obtained by these authors, it can be estimated that the Cd dissolution rate will be a factor 30 to 300 lower than that of Zn as long as there is an excess of Zn in the dissolving sulphide mineral. The reason for the preferential dissolution of Zn is not precisely known, but it is generally thought to be a result of the lower solubility of CdS as compared to that of ZnS (e.g., Barrett and McBride, 2007).
- Short-term toxicity tests carried out for Cd sulphides generally show rather small toxic effects; this is particularly the case for ZnCdS when Zn occurs in excess (National Academies, 2004); the likely reason is the low dissolution rate of Cd in these minerals, as mentioned above.

## 5.2 Simulation of Cd and Zn dissolution rates



**Fig. 3.** Dissolution of Cd or Zn (expressed as the fraction of total applied) as a function of time after application, depending on the form of metal added. Assumptions: Specific surface area  $3 \text{ m}^2/\text{g}$ , Zn dissolution rate  $2.3 \cdot 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ , for ZnCdS the initial ZnS/CdS ratio was 100, Cd dissolution rate 50 times lower than Zn in ZnCdS when  $\text{Zn} > \text{Cd}$ , otherwise Cd dissolution rate is 20 times higher than Zn.

In Fig. 3 the results from a simulation is presented that shows the dissolution of Cd and Zn sulphides as a function of time, assuming that these are added to a surface horizon of an agricultural soil with a pH value of 6. It should be stated that the dissolution rates are based on the estimates of sphalerite weathering rates provided in the above references, but nevertheless they are uncertain with maybe a factor 3-10. It is, however, encouraging that the simulation produced Zn dissolution rates similar to those obtained in field trials with sphalerite added to soils (Voegelin et al., 2011). In the latter study, between 26 and 75 % of the added ZnS had been dissolved during four years (compared to 25 % in Fig. 3).

Therefore Fig. 3 may serve as an indication of the time scales involved for the dissolution of Cd and Zn sulphides once added to an agricultural soil environment. According to the simulation, cadmium when added as pure CdS will dissolve completely within only one year. The cadmium dissolved will then add to the reactive Cd pool in soils and behave in an equivalent manner as if cadmium chloride had been added to the soil.

When, however, there is an excess of zinc sulphide (as compared to cadmium sulphide), in this case a factor 100, the dissolution of Cd progresses much more slowly, and after 13 years still only 2 % is dissolved. However, once ZnS has been dissolved completely, the remaining Cd will dissolve as for CdS, leading to quick dissolution of the remainder. In other words, applied Cd may have a rather low short- and medium-term availability if it is supplied together with an excess amount of sphalerite.

It should be noted that the simulation in Fig. 3 uses the assumption that the surface area is around  $3 \text{ m}^2/\text{g}$ , as was the case for spheralite fragments with a particle size of  $10 \text{ }\mu\text{m}$  (Stanton et al., 2008). Usually, cadmium pigments have smaller particle sizes, in the range of  $0.1$  to  $3.5 \text{ }\mu\text{m}$  (USEPA, 1988), which most likely means a higher surface area and quicker dissolution. Therefore it is possible that the time scales shown in Fig. 3 is longer than the real ones.

### 5.3. Availability of ZnS in sewage sludge components

The zinc sulphide needed for cadmium stabilization may originate either from the pigments themselves, or from other sludge components. However, even though zinc sulphide is one of the most common zinc species in fresh sewage sludge (Donner et al., 2011), the zinc sulphide for most part will dissolve already during the initial drying and stockpiling (which lasted from 6 to 24 months). The reason is probably that most of the ZnS in sludge is non-crystalline; this ZnS will dissolve faster than the crystalline sphalerite used in the simulation of Fig. 3. In conclusion, long-term stabilization of Cd in applied sludge is possible only if there is an excess of *crystalline* ZnS components. However, the amount of crystalline ZnS in sewage sludge applied to agricultural land is not known.

Apul et al. (2010) reported that less Cd was dissolved from fresh sewage sludge than expected from geochemical modelling – this may be consistent with Cd binding in a ZnS component in the sludge. However, earlier studies focusing on Cd solubility in soils subjected to long-term applications of sewage sludge did not find evidence for a drastically reduced Cd solubility because of long-term sludge application (and possible binding to a ZnS component) (Bergkvist et al., 2003; Bergkvist et al., 2005). Indeed, the Cd sorption affinity did increase somewhat after sludge application, but this was attributed to the increased organic matter content causing increased Cd-organic matter complexation (Bergkvist et al., 2005); in fact, the increased Cd sorption was smaller than would have been expected as a result of the increase of organic matter only. This shows that ZnS, if anything of it remained in the sludge-amended soil, did probably not affect the behaviour of Cd in the soils. This in turn may be due either to (i) complete, or nearly complete, dissolution of the ZnS component within just a few years in agreement with Donner et al. (2011), and/or to (ii) heterogeneous distribution of the ZnS component, which may affect Cd only in certain pores, but not in the bulk material.

## 6. Implications for the soil environment

As shown above, cadmium sulphides and selenides in pigments are thermodynamically unstable in the surface horizon of agricultural soils. The presence of  $\text{O}_2(\text{g})$  and  $\text{Fe}(\text{III})$  will lead to the gradual dissolution of these compounds in the soil environment. Sulphide-bound Cd can persist in soils over a time scale of years only if there is an excess of sulphide-bound Zn. Therefore the dissolution rate of Cd is crucially dependent on the amount of crystalline ZnS that may be supplied through the sludge. However, available evidence show that most

of the ZnS supplied through sludge is non-crystalline in nature and will dissolve completely within just a few years.

The conclusions above apply for sulphide-bound Cd, for which there are direct evidence. Much less is known about the dissolution rate of selenide-bound Cd, but most likely the general trends are the same, as the compounds are rather similar.

Taken together, most evidence assembled suggest that Cd pigments will probably dissolve completely in soils over a time scale of years to decades. Therefore the long-term solubility and availability of Cd is likely to be the same regardless if the Cd is supplied in sulphide- or selenide-bound forms (as in pigments) or in easily soluble forms such as cadmium chloride.

Theoretically it seems that if a sufficient amount of crystalline ZnS is supplied to a soil on a regular basis, and mixed thoroughly with the soil material, dissolution of Cd could be substantially slower (in the order of centuries). However, the available literature evidence does not indicate whether this could be a realistic Cd stabilization method; it seems clear, however, from the studies of Bergkvist et al. (2003; 2005) that this does not happen in soils subjected to long-term applications of sewage sludge.

Because the Cd pigments will, most likely, dissolve rapidly in soils, the long-term behaviour of Cd dissolved from the pigments will be determined by retention mechanisms in the soil. Today the factors responsible for Cd solubility and bioavailability in soils are reasonably well understood. We know that organic matter is usually the most important sorbent for Cd, and the binding of Cd to organic matter is determined to a large extent by pH (dissolution of Cd increases with decreasing pH), and also by competition from Al and to a certain extent Ca. Soil chemical models have been developed that are able to successfully predict these processes (Gustafsson et al., 2003; Bonten et al., 2008; Khai et al., 2008).

## 7. Conclusions

- Cadmium-containing sulphides and selenides in pigments are not thermodynamically stable under the conditions that prevail in the surface horizons of Swedish agricultural soils.
- Under aerated conditions, the dissolution rate of pure CdS is comparably high. In a soil environment containing sufficient electron acceptors such as  $O_2(g)$  and Fe(III), pure CdS will be dissolved completely within one year.
- When sulphide-bound Cd is supplied to soils together with an excess amount of sulphide-bound Zn, the dissolution rate of Cd will slow down to low levels, as long as sulphide-bound Zn persists in the soil.
- Crystalline ZnS (such as sphalerite) can persist in soils for a time period of 1 to 2 decades, making CdS dissolution slow during this period. However, most evidence suggest that most of the ZnS added in sewage sludge is amorphous, and will dissolve completely within just a few years.
- Soil samples subjected to long-term applications of sewage sludge do not show a reduced Cd solubility because of the additions of ZnS through sludge.
- Based on the evidence assembled, it is concluded that Cd supplied in the form of sulphides or selenides should be considered fully available (similar to easily soluble cadmium chloride) when a time scale of 50 years is applied.

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