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Oxidation of arsenic bearing fly ash as pretreatment before solidification

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Abstract

When a waste fly ash, containing large amounts of As_2O_3, is solidified using cement and lime, the arsenic concentration in the leachate (extraction test DIN 38 414 S4) is determined by the solubility of $CaHAsO_3$ and can be lowered to a value of ca. 5 mg/l, in a saturated solution of $Ca(OH)_2$. One of the criteria for landfilling of hazardous waste is, however, that the arsenic concentration in the leachate must be lower than 1 mg/l. In this paper, it is shown that oxidation of the waste before solidification, whereby As(III) is oxidised to As(V) using H_2O_2, lowers the leaching of arsenic, and other contaminants, from the solidified product. With the speciation program MINTEQA2, it is calculated that the solubility of As(V) in the presence of a pure $Ca_3(AsO_4)_2$ precipitate is lower than the solubility of As(III) in the presence of a pure $CaHAsO_3$ precipitate. The arsenic concentration in the presence of both a $Ca(OH)_2$ and a $Ca_3(AsO_4)_2$ precipitate can even be lowered to 0.47 mg/l (pH 12.5). The As concentration in the leachate of the extraction test on an oxidised S/S sample was indeed lowered to ca. 0.5 mg/l, which is a reduction by a factor of 10 compared to the concentration of ca. 5 mg/l, obtained in the leachate of the extraction test on a non-oxidised S/S sample. This is in very good agreement with the calculated value of 0.47 mg/l. Also, the pretreatment decreased the cumulative fraction of arsenic released over the entire test period of a semi-dynamic leach test by a factor of 7. At all times

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during the test, the As concentration did not exceed the norm of 1 mg/l.

1. Introduction

In Belgium, several thousand tons of arsenic bearing fly ash are produced every year, as a waste product from the copper refining industry. The major elements in the waste are arsenic, antimony and lead. In the waste material, arsenic is present as As_2O_3, and the As concentration ranges from 23% to 47% (wt.%). In Flanders, Belgium, this waste is classified as a 'hazardous waste' [1], because it 'contains more than 500 mg arsenic or soluble arsenic compounds per kg of dry solid (expressed as As)'. Hazardous waste can be landfilled in a 'category 1' landfill, for the 'disposal of industrial and comparable wastes of mostly inorganic material', after proper treatment to meet the criteria for landfill disposal, as mentioned in VLAREM II [2]. The criterion of major interest for the waste material studied, is that the leachate concentration of arsenic (determined according to the extraction test DIN 38 414 S4 [3]) of the disposed material must be lower than 1 mg/l. Before 1995, however, this regulation was less severe, and followed the KB '76 norm [4], which for arsenic was set at 500 mg of soluble arsenic per kg of dry solid, corresponding to 50 mg/l in the leachate of the extraction test DIN 38 414 S4. The older norm was thus 50 times less severe than the norm used since 1995. To meet the criteria for landfill disposal, inorganic solidification/stabilisation technology is used as treatment method for the arsenic bearing waste material.

In an earlier publication from this laboratory by Dutré and Vandecasteele [5], the solidification procedure was optimised, in order to lower the leachate arsenic concentration, using the extraction test DIN 38 414 S4 as regulatory test, resulting in the following recipe: 0.6 g of cement (Cem II/A-M 32.5 R) and 0.8 g of quick lime (CaO) were added per g of waste material. The concentration of As(III) in the leachate is hereby reduced from ca. 5000 mg/l, in the leachate of the raw waste material, to ca. 5 mg/l after solidification. The leachate pH reaches a value of ca. 12.5. A variety of different recipes [5–7] did not succeed in lowering the arsenic concentration below 5 mg/l. In a subsequent publication by Dutré and Vandecasteele [8], it was shown, both experimentally and theoretically, that the arsenic concentration is determined by the solubility of $CaHAsO_3$ in the leachate: the As concentration is lowered to ca. 5 mg/l due to the precipitation of $CaHAsO_3$ in a saturated solution of $Ca(OH)_2$, whereby the Ca^{2+} ions are supplied by the lime added during solidification of the waste material.

However, the norm [2] of less than 1 mg/l As was not reached. Therefore, in this paper, a study is made of the pretreatment of the considered waste in order to attain this norm after solidification.

In the literature on solidification/stabilisation technology, much attention is given to the use of additives to lower the concentration of the contaminants in the leachate by formation of hardly soluble compounds between the contaminants and some elements

from the additives. Little attention however has been given to the modification of the waste itself (the form in which the contaminants occur in the waste) before it is solidified. Obviously, such pretreatment has to bring the contaminants in a more stable (less soluble) state, and maximum stabilisation is obtained when an element is present in its most stable (natural) mineral phase. Bringing the considered element in its most stable form should indeed be the essence of the stabilisation process. In this way, the problem is dealt with at the source whereas in the other techniques a slightly soluble compound is formed in the leachate after the components of interest were already leached from the waste.

Because $Ca_3(AsO_4)_2$ ($K_S = 6.8 \times 10^{-19}$ [9,10]) is less soluble than $CaHAsO_3$ ($K_S = 1.07 \times 10^{-7}$ [6]), an obvious pretreatment consists in oxidising As(III) to As(V). Moreover, As(V) is less toxic than As(III) [11]. H_2O_2 was used as oxidising agent. After oxidation, the waste can be solidified as before, with lime and cement, providing Ca^{2+} ions and the right pH environment to form $Ca_3(AsO_4)_2$.

2. Materials and methods

2.1. Oxidation with hydrogen peroxide, H_2O_2

The oxidation–reduction chemistry of hydrogen peroxide in aqueous solution is characterised by:

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O \quad E° = 1.77 \text{ V} \tag{1}$$
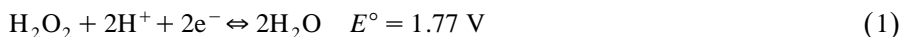
Dilute or 30% hydrogen peroxide solutions are widely used as oxidants. In acid solution, oxidation reactions with hydrogen peroxide are most often slow, whereas in basic solution they are usually fast.

Oxidation of As(III) to As(V) in aqueous solution occurs according to the following half reaction:

$$HAsO_2 + 2H_2O \Leftrightarrow H_3AsO_4 + 2H^+ + 2e^- \quad E° = -0.56 \text{ V} \tag{2}$$
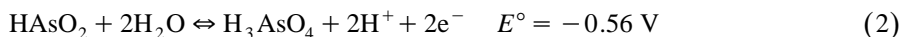
so that As(III) can be oxidised with H_2O_2:

$$HAsO_2 + H_2O_2 \Leftrightarrow H_3AsO_4 \tag{3}$$

Decomposition of H_2O_2 according to the reaction:

$$2H_2O_2 \Leftrightarrow 2H_2O + O_2 \quad \Delta H = -23.6 \text{ kcal/mol} \tag{4}$$

occurs most rapidly in basic solution; hence excess H_2O_2 after oxidation of As(III) may best be destroyed by heating in basic solution [12].

2.2. Optimisation of the S/S procedure

Hydrogen peroxide (30%) was added to 10 g of waste material in increasing amounts (from 0 to 12 ml per 10 g waste). The mixtures were stirred until a reaction between the waste and H_2O_2 was observed, which occurred almost immediately. Then, these

mixtures were heated until the possible excess of H_2O_2 was destroyed. During heating of these mixtures, water had to be added in order to avoid evaporation to dryness. Then, lime (8 g of CaO) and cement (6 g of Cem II/A-M 32.5 R) were added, together with a sufficient amount of water, to finally obtain a solidified product. The solid waste specimens have a diameter of ca. 4.5 cm and a height of ca. 3 cm.

The solidified waste samples were leached according to the DIN 38 414 S4 extraction test in a volume of 270 ml of distilled water, whereafter the leachate was filtered and analysed (concentrations of Ca, As, Sb and Pb) by ICP-MS (inductively coupled plasma-mass spectrometry), and the leachate pH was measured.

2.3. Extraction test

The extraction test DIN 38 414 S4 [3], used in this study, is a German standard method for the 'determination of the leachability of sludge and sediments by water'. In this agitated extraction test, 1 l of distilled water is added to 100 g of dried substance (grain size < 10 mm) and mechanically shaken for a period of 24 h at room temperature. In this study, the entire solidified sample prepared in the laboratory is used in the extraction test, so that the total amount of the arsenic containing waste material (10 g of raw waste material per solidified waste sample) is incorporated in the test. The samples were brittle so that no special equipment was necessary to crush the samples to < 10 mm.

2.4. Semi-dynamic leaching

Leaching of contaminants out of monolithic cement-based waste forms is mostly a diffusion controlled process. With the assumption of a constant diffusion coefficient, it can be shown that the cumulative fraction of a substance that has been released at time t (CFR) is given by:

$$\text{CFR} = \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{D_e t} \qquad (5)$$

with D_e = effective diffusion coefficient (cm^2/s), t = leach time (s), S = surface area of specimen (cm^2), and V = volume of specimen (cm^3). The effective diffusion coefficient can thus be calculated from the slope of the plot of CFR as a function of the square root of time.

Semi-dynamic leach tests, whereby the leachant is replaced periodically after intervals of static leaching, are used for this purpose. In this study, the timing of the leachant renewal is based on Eq. (6), the test is therefore called the N^2 leach test:

$$t_n = n^2 t_1 \quad \text{with } t_1 = 1 \text{ h and } n = 1,2,3,4,5,\ldots \qquad (6)$$

where t_n = duration of nth leaching interval [13].

The raw waste material was treated with 10 ml of H_2O_2 (30%) and then solidified, following the procedure described in 'optimisation of the S/S procedure'. Two S/S samples, pretreated with H_2O_2 before solidification, were subjected to the semi-dynamic leach test. Another S/S sample, solidified following the initial optimised recipe (0.8 g

of lime (CaO) and 0.6 g of cement (Cem II/A-M 32.5 R) per gram of waste material), was also leached as a non-pretreated reference sample and is referred to as 'DW closed'. The monolithic (non-crushed) samples were leached in distilled water as a leaching medium, in a volume of 600 ml. A total of 21 renewals were performed over the 3-week testing period. The solid waste specimens have a diameter of ca. 4.5 cm and a height of ca. 3 cm.

2.5. Hydride generation coupled to ICP-MS

Hydride generation is used to determine the oxidation state of arsenic in aqueous solutions. It makes use of the properties of some elements, like As, to form hydrides. Generally, the method is based on the conversion of arsenic to gaseous AsH_3 using $NaBH_4$ as a reducing agent in an acid environment. The reaction of As(III) with $NaBH_4$, leading to arsine, can be represented as follows:

$$3BH_4^- + 3H^+ + 4H_3AsO_3 \rightarrow 3H_3BO_3 + 4AsH_3 + 3H_2O \tag{7}$$
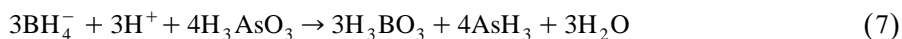
When basic borohydride is added to an acidic solution, excess hydrogen is also produced according to:

$$BH_4^- + 3H_2O + H^+ \rightarrow H_3BO_3 + 4H_2 \tag{8}$$

Sodiumborohydride is the preferred reducing agent because it gives fast hydride formation and is simple to use. NaOH is normally added to the $NaBH_4$ solution for stabilisation, and HCl is used for acidification. A membrane gas–liquid separator is used to separate chloride containing aerosol from the gas stream (arsines) before introduction in the ICP-MS. The system used for this study was a modified continuous flow hydride generator from FISONS INSTRUMENTS [14].

It appeared, as was shown in a study by Van den Broeck et al. [15], that the use of 0.1 M $NaBH_4$ in an acid environment (2 M HCl) is powerful enough to reduce also pentavalent arsenic to AsH_3. The reduction of As(V) to As(III) however is very slow compared to the hydride forming reaction. Higher acid concentrations can improve the prereduction velocity, but the use of special prereductants is recommended [16]. To determine only As(III), an acetic acid/sodium acetate buffer (pH = 5) is used instead of HCl. At this pH, As(V) is not reduced and only As(III) forms hydrides.

The detection limit for arsenic is normally about 10 times lower than the detection limit for ICP-MS without hydride generation, which is ca. 0.1 $\mu g/l$.

3. Results and discussion

3.1. MINTEQA2

With the speciation program MINTEQA2 [17], calculations were made to verify whether the concentration of arsenic in equilibrium with a $Ca_3(AsO_4)_2$ precipitate instead of a $CaHAsO_3$ precipitate could be lowered beneath the norm of 1 mg/l. As the solubility product K_S for the compound $CaHAsO_3$ was not available in the database of
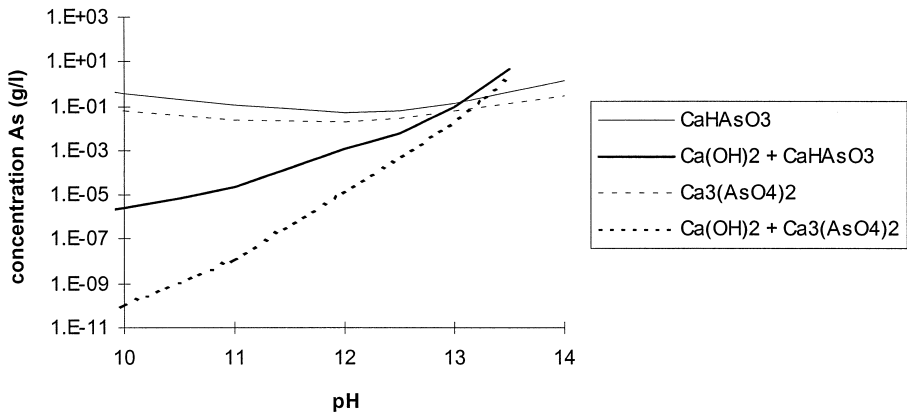
Fig. 1. Solubility of As (g/l) versus pH for $CaHAsO_3$, $Ca(OH)_2 + CaHAsO_3$, $Ca_3(AsO_4)_2$ and $Ca(OH)_2 + Ca_3(AsO_4)_2$ in equilibrium with water at 25°C/1 atm.

the speciation program, the experimentally determined value [6] was incorporated in the database. The calculations were made with an infinite amount of the solids present. In Fig. 1, the As concentration versus pH curves are given for a $CaHAsO_3$ and a $Ca_3(AsO_4)_2$ precipitate in equilibrium with water at 25°C, calculated with the speciation program MINTEQA2, together with the As concentrations obtained when these precipitates occur in the presence of a $Ca(OH)_2$ precipitate. In Table 1, the As and Ca concentrations (mg/l) in a solution in equilibrium with the mentioned compounds are given for a pH of 12.5 (the approximate pH value in the leachate of the extraction test performed on a S/S sample prepared according to the optimised S/S recipe). The arsenic concentration is reduced from 65.4 mg/l to 5.4 mg/l if a $Ca(OH)_2$ precipitate is also present next to $CaHAsO_3$. If, however, As(V) would be present instead of As(III), the As concentration is even further reduced: from 30.3 mg/l, if only a $Ca_3(AsO_4)_2$ precipitate occurs, to 0.47 mg/l in the presence of both a $Ca(OH)_2$ and a $Ca_3(AsO_4)_2$ precipitate.

Thus, if the waste material is first pretreated to oxidise As(III) to As(V), and then solidified with the same materials as before (lime, cement, . . .), the arsenic concentration in the leachate is expected to meet the regulatory limit mentioned in VLAREM II.

Table 1
Calculated As and Ca concentrations (mg/l) at pH 12.5

Compound	As	Ca
$CaHAsO_3$	65.4	35.0
$Ca(OH)_2 + CaHAsO_3$	5.4	585
$Ca_3(AsO_4)_2$	30.3	24.3
$Ca(OH)_2 + Ca_3(AsO_4)_2$	0.47	585

Table 2
Leachate pH and leachate concentration (mg/l)

Sample	H_2O_2 (ml)	pH	Ca	As	Sb	Pb
1	0	12.58	1012	4.88	12.2	9.41
2	3	12.52	685	21.5	12.6	2.11
3	4	12.56	949	8.09	12.8	2.67
4	5	12.55	842	8.51	9.41	3.14
5	6	12.58	911	2.56	3.44	4.72
6	8	12.48	615	0.44	1.11	2.35
7	12	12.56	701	0.21	0.62	1.29

3.2. Optimisation of the S/S procedure using H_2O_2 as oxidising agent

The results of the extraction tests are presented in Table 2 as the leachate pH and the leachate concentrations (mg/l) of Ca, As, Sb and Pb, for seven samples. Sample 1 was prepared following the original solidification procedure, with only lime and cement addition (0.8 g CaO and 0.6 g Cem II/A-M 32.5 R per gram of waste). Again, as expected, the concentration of As (sample 1) is ca. 5 mg/l. For the samples 2 to 7, an amount of H_2O_2 (30%) was added to the waste before solidification, varying from 3 to 12 ml per 10 g of raw waste material.

As can be seen from Table 2, the leachate pH hardly changes from sample 1 to sample 7. The increase in arsenic concentration in samples 2, 3 and 4 (compared to sample 1) is somewhat correlated with the varying calcium concentrations: a high Ca concentration relates to a low As concentration and vice versa. The arsenic concentration decreases rapidly from sample 5 to sample 7. In the leachate of sample 6 (8 ml H_2O_2), the arsenic concentration was reduced by a factor of 11 (compared to sample 1), and was even further reduced as more H_2O_2 was added to the waste. Also, the concentrations of antimony and lead were reduced considerably, when comparing the leachate concentrations of sample 1 and sample 7. It is, however, not clear why there is little difference in Pb-concentration between samples 2 through 7 and why the effect on lead would already start from sample 2. The concentration of Sb was reduced (from sample 1 to 7) by a factor of 20, the concentration of Pb by a factor of 7. Most probably, Sb (Sb(III) → Sb(V)) and Pb (Pb(II) → Pb(IV)) are oxidised as well. From the results in Table 2, it can be concluded that, after pretreatment of the waste, the leachate concentration of As answers to the norm of VLAREM II.

Table 3
Leachate concentration of As(III) and As_{tot} (mg/l) and percentage of As(III)

Sample	As(III)	As_{tot}	% As(III)
1	4.26	4.88	87.3
2	14.15	21.47	65.9
3	7.28	8.09	90.0
4	7.04	8.51	82.7
5	1.93	2.56	75.4
6	0.0044	0.44	1.0
7	0.00041	0.211	0.19

In all the leachates of the 7 samples, the concentration of As(III) was then determined using hydride generation coupled to ICP-MS. To determine the As(III) concentration in the samples, the method of standard addition was used: the solution in which the concentration has to be determined is spiked with a fixed amount of As(III) and used as a standard. The results are presented in Table 3 where the total As concentration, As_{tot} (mg/l), and the As(III) concentration (mg/l) in the leachate of each of the seven samples is given.
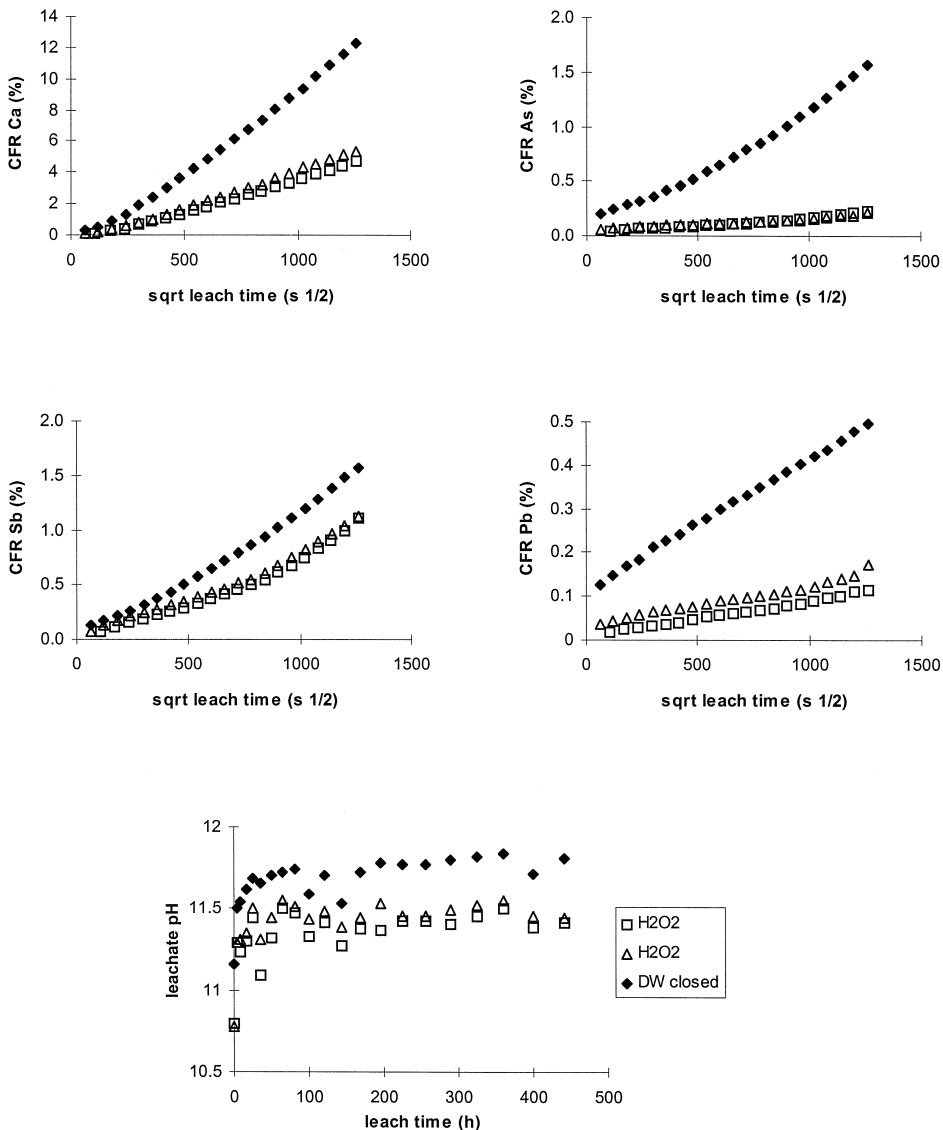

Fig. 2. CFR plots for the elements Ca, As, Sb and Pb and the leachate pH for 2 S/S samples with H_2O_2 pretreatment and a non-pretreated reference sample 'DW closed'.

Table 3 also gives the results as the percentage of the total amount of arsenic in the leachate which is present as As(III). These results indicate that an oxidation of the waste has taken place so that As(III) was oxidised to As(V). Samples 6 and 7, where, respectively an amount of 8 ml and 12 ml of H_2O_2 (30%) had been added to the waste, show an As(III) percentage of 1.00% and 0.19% compared to the total amount of arsenic present in the leachate. In the leachate of these samples, the total arsenic amount considerably decreased. In the leachates of samples 6 and 7, the As (almost entirely As(V)) concentration was 0.44 mg/l and 0.21 mg/l, and the leachate pH 12.48 and 12.56. These arsenic concentrations are in good agreement with the calculated solubility of arsenic in the presence of both $Ca(OH)_2$ and $Ca_3(AsO_4)_2$ at a pH of 12.5 (see Table 1).

3.3. Semi-dynamic leaching

The three S/S samples, prepared as described under '2.4 Semi-dynamic leaching' in Section 2, were subjected to the semi-dynamic leach test. After each interval of static leaching, the leachate pH was measured and the concentration of the elements (Ca, As, Sb and Pb) was determined.

The results are presented in Fig. 2 as the cumulative fractions released, and the leachate pH values. The pH value increased during the first intervals of leaching, but rapidly a nearly constant value was reached. For the leachates of the 2 S/S samples with H_2O_2 pretreatment, the pH reached a value of ca. 11.5. The reference sample reached a leachate pH value of ca. 11.7. The cumulative fraction of arsenic released over the testing period was considerably reduced when the waste is pretreated before solidification. The CFR value decreased from ca. 1.6% for the non-pretreated waste to ca. 0.22% for the pretreated waste, which is a reduction by a factor of 7.3. Similarly, the CFR values for the other elements also decreased, as is clear from Fig. 2. The CFR value for Ca decreased from 12.3% to 5.1% (a reduction by a factor of 2.4); for Sb from 1.6% to
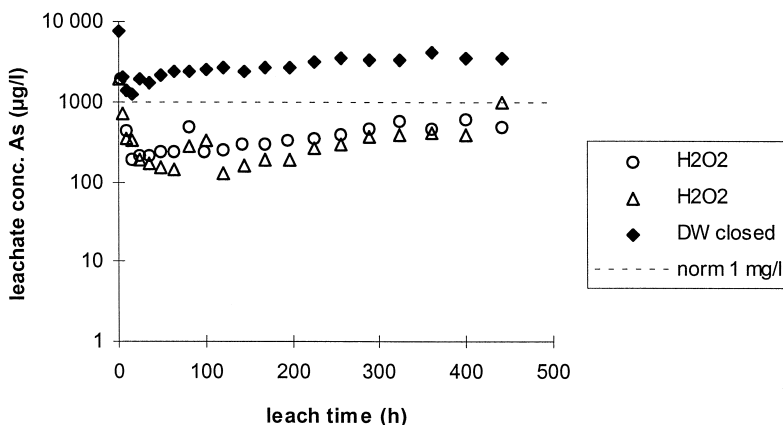

Fig. 3. Leachate concentration of As (μg/l) as a function of the leach time.

1.1% (a reduction by a factor of 1.5) and for Pb from 0.5% to 0.13% (a reduction by a factor of 3.8).

In Fig. 3, the leachate concentrations of arsenic are presented as a function of the leach time for the 3 S/S samples. As can be seen from the figure, the concentrations of arsenic released from the pretreated samples never exceed the norm of 1 mg/l. The arsenic concentrations of the non-pretreated sample on the other hand exceed this limit.

4. Conclusions

The raw waste material was pretreated with H_2O_2 (30%) before solidification in order to oxidise the As(III), present in the waste, to As(V). From an amount of 8 ml of H_2O_2 added to 10 g of waste material, As(III) was almost completely oxidised to As(V). Analysis of the leachates of the S/S samples, subjected to the extraction test, indicated that less than 1% of the total arsenic concentration in the leachate was As(III). Also, the total arsenic concentration in the leachate was reduced considerably: from ca. 5 mg/l in the leachate of the non-pretreated waste to below 0.5 mg/l in the leachate of the pretreated waste, a reduction by a factor of 10. The concentration of the elements Sb and Pb was also lowered, by a factor of 20 and 7, respectively. Pretreatment of the waste thus lowers the arsenic concentration in the leachate of the S/S sample, subjected to the extraction test, to below the 1 mg/l norm for As in the leachate for category 1 landfills.

The results of the semi-dynamic leach test also indicated a reduction in the released amounts of all the considered elements. The cumulative fraction of As released over the test period decreased by a factor of 7.3, compared with a non-pretreated sample. At all times, the concentration of As did not exceed the norm of 1 mg/l.

It can thus be concluded that pretreatment of the waste with H_2O_2 before solidification, improves the quality of the solidified product in respect to the leaching.

An additional advantage compared to solidification without prior oxidation is, as appears from Fig. 1, that with a decrease of the pH (which may occur at the edges of the waste), the solubility of As first decreases. Anyhow, the waste should after disposal be covered as much as possible in order to avoid incoming water and air and loss of buffer capacity.

It is to be noticed however, that the question of implementation to an industrial scale is still open. During mixing of the waste with H_2O_2, a reaction occurs with a rather high heat development. This heat development puts a restraint upon the amount of waste that can be treated in a batch reactor. Also, the installation would have to be adapted to control these high temperatures and possible emissions that may result. In order to obtain a solidified product with a sufficient strength, it might be necessary to heat the mixtures to destroy the possible excess of H_2O_2. However it is possible that in a large S/S mass the heat generated during mixing of the H_2O_2 into the waste, is sufficient. Moreover, the use of H_2O_2 to pretreat the waste increases the cost of the overall treatment. The costs will be higher due to an increase of the additives, a more complicated solidification procedure, and of course a more expensive installation. The process results in a significant increase of the amount of waste to be disposed, but this is also the case for solidification methods without prior oxidation of As(III).

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