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Immobilization Mechanism of Arsenic in Waste Solidified Using Cement and Lime

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The material studied, a waste fly ash from the metallurgical industry, contains the toxic element As in high concentrations, ranging from 23% to 47% (wt %). Besides As, Sb and Pb are present in the waste material. The waste was solidified with inorganic materials such as cement and pozzolanic materials in order to reduce the leachability of the contaminants from the waste. The optimal solidification recipe lowered the As concentration in the leachate of the extraction test DIN 38 414 S4 from ca. 5 g/L to ca. 5 mg/L. In this paper, it was shown that this enormous reduction in As concentration was due to the formation of $CaHAsO_3$ in the leachate, in the presence of $Ca(OH)_2$. Formation of $CaHAsO_3$ alone cannot lower the arsenic concentration beneath ca. 55 mg/L, as was calculated with the speciation program MINTEQA2.

Introduction

Large quantities of arsenic trioxide, As_2O_3, are available worldwide as a concentrated byproduct from various metal extraction and refining operations, mainly Cu extraction and refining. Although a considerable amount of byproduct arsenic trioxide is used commercially, mainly in products used in agriculture, a worldwide excess of arsenic trioxide exists. It is improbable that any significant reduction in the amount of arsenical wastes generated could be achieved by changes in processing techniques (prevention) (*1*). Recycling of the waste or recovery of arsenic from the waste is from an economic point of view not very interesting since supplies already exceed demands. Moreover, incineration of arsenic-bearing wastes is obviously not possible nor useful. Landfill disposal seems therefore the only suitable alternative for arsenic-bearing wastes, but treatment of the waste before landfilling may be necessary to meet landfill regulations. Solidification/stabilization (S/S) processes are widely applied to treat hazardous waste in order to make it comply with current landfill disposal requirements (*2*). In this paper, inorganic S/S processes are studied, using inorganic binders such as cement, lime, and pozzolanic materials (*3, 4*).

The waste material studied is a fly ash, resulting as a waste product from a Cu refining process. The major elements in the waste are As, Sb, and Pb. All waste material studied originates from the same metallurgical process, but samples were obtained at different times. In these samples, the concentrations range from 23% to 47% (wt %) for As, from 16% to 35% for Sb, and from 8% to 23% for Pb. In Belgium, this waste material is produced in quantities of several thousand tons per year, and since it is classified as a hazardous waste, it has to be treated as such.

The starting point of this research was the 'Soliroc' process for stabilization of hazardous wastes containing metals (*5*), which neutralises harmful elements by using silicate reagent and additives to create inert metal silicates incorporated in a concrete resembling matrix. The process involves the formation of a mixture of an amorphous and a crystalline silicate structure, and it is claimed that, for arsenic-containing wastes, As is bound as a silica−alumina−arsenate.

At the start of this research (*6*), a solidification recipe was applied from a licensed process from Esdex (*1*), based on the Soliroc process. The solidification of the waste was carried out by first adding waste acid from the galvanic industry (5 M HCl containing Zn and Fe concentrations of ca. 60 g/L and a Pb concentration of 150 mg/L), blast-furnace slag, and water to the waste. Later on, quick lime, cement, and water were added in order to obtain finally a solid with a sufficient strength and consistency after solidification. The detailed initial solidification procedure was as follows: per 10 g of waste material, 15 g of slag, 5 g of waste acid, and water (4 mL) are added to obtain a sludge. This mixture is set aside for 24 h to form silicon-containing acids. After the 24-h waiting period, 10 g of lime and 11 g of cement are added together with water (20 mL). This mixture is vigorously stirred and starts to set shortly thereafter. Before the solidification product is subjected to the extraction test used to examine the effectiveness of the immobilization of the contaminants after solidification, the S/S material is allowed to harden for 2 weeks.

As shown in an earlier publication from this laboratory (*6*), solidifying the raw waste material with this solidification procedure lowers the concentration of As in the leachate, as determined by the extraction test DIN 38 414 S4 (*7*) (see Experimental Section), from ca. 5 g/L to ca. 5 mg/L, which means a reduction by a factor of 1000. It was found empirically (*6*) that the main factor in reducing the concentration of As in the leachate is the addition of quick lime to the waste; all the other additives had only a negligible influence. The S/S recipe could thus be simplified considerably: per 10 g of waste material, 8 g of lime, 6 g of cement, and 20 mL of water were added. The results described (*6*) reflected the formation of a hardly soluble calcium−arsenic compound, since the concentration of As as well as the concentration of Ca leached reach a constant value as soon as a sufficient amount of lime is added. At that moment, the leachate pH has reached a value of ca. 12.5.

Moreover, the Soliroc theory, which was the starting point of this research, was seriously questioned, since even without the use of cement and with lime as the only additive in the solidification recipe the concentration of As in the leachate of the extraction test also reduced to ca. 5 mg/L.

As discussed in a subsequent publication (*8*), As was present in the leachate in the As(III) oxidation state. Therefore, if the concentration of As in the leachate decreases significantly by the formation of an insoluble compound containing As and Ca, this must be a compound containing As(III). Since no values were found in the literature regarding the solubility product K_S of any Ca−As(III) compound, it was investigated experimentally (*8*) as to which insoluble compound could be formed in an aqueous solution containing Ca and As(III). The solubility product K_S of this compound was determined. In aqueous solutions, As(III) occurs in

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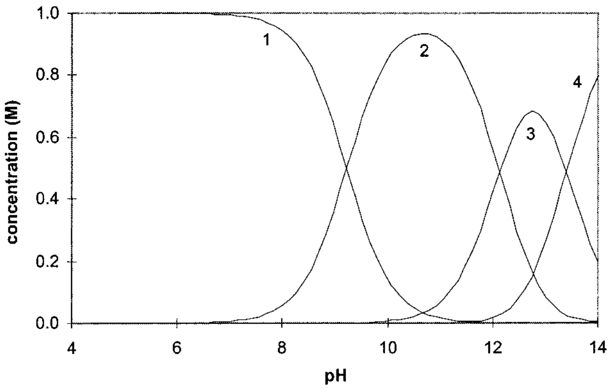

FIGURE 1. Different forms of As(III) in aqueous solutions as a function of pH; $K_1 = 6$ E−6; $K_2 = 7.5$ E−13; $K_3 = 4$ E−14.1, H_3AsO_3; 2, $H_2AsO_3^-$; 3, $HAsO_3^{2-}$; 4, AsO_3^{3-}.

different forms depending on the pH: H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} (Figure 1). In the pH range (11.91−12.75) where a precipitate was detected, in synthetic Ca−As(III) solutions, a large fraction of As(III) occurs as $HAsO_3^{2-}$. Also, on the average, close to 1 mol of Ca precipitated/mol of As. These two arguments point at the formation of $CaHAsO_3$ [which might also be denoted $CaAsO_2OH$ (*9*) or $Ca(OH)_2{\cdot}Ca(AsO_2)_2$ (*10*)] in a synthetic solution containing Ca and As(III). The solubility product of $CaHAsO_3$ was determined as 1.07 E−7.

The obvious question is now whether this compound is also formed in the course of the 24-h shaking period of the extraction test, performed on the solidified arsenic-bearing waste material. In other words, is the concentration of As in the leachate of the extraction test limited by the solubility of the compound $CaHAsO_3$ rather than by incorporation in a silica−alumina−arsenate as suggested by the theory of the Soliroc process? The present paper will answer this question and will elucidate the immobilization mechanism of As, giving a concentration in the leachate of ca. 5 mg/L, the minimum As concentration found as a result of a wide variety of S/S procedures (*6*, *8*, *11*).

In general, extraction tests are used to determine the maximum or saturated leachate concentrations under a given set of test conditions. The underlying assumption in this type of test is that steady-state conditions are achieved by the end of the extraction test (constant concentration of constituents by the end of the test) (*12*). This may be verified by varying the extraction period. It is commonly believed that extraction tests are a simulation of a 'worst case' scenario. If a component precipitates in the leachate of the extraction test by the formation of an insoluble compound with another component leached from the sample (e.g., $HAsO_3^{2-}$ with Ca^{2+}), however, no worst case scenario is simulated, since the concentration during the test may have been higher than the measured concentration at the end of the test.

The possible formation of $CaHAsO_3$ in the leachate can be evaluated by comparing the ion product of the Ca^{2+} and $HAsO_3^{2-}$ concentrations measured in the leachate with the (experimentally determined) K_S value. To easily interpret these results, a saturation index is defined:

$$\mathrm{SI} = \log\left(\frac{\text{ion product}}{K_S}\right) \qquad (1)$$

No precipitate will form in a state of undersaturation (SI < 0). When SI = 0, there is a state of chemical equilibrium, and the solution is saturated, in equilibrium with the precipitate. When the saturation index has a positive value, the solution is oversaturated and the precipitate will tend to form (*13*).

To investigate if the As concentration in the leachate is limited by solubility, a number of experiments were carried out:

Variation of the Liquid to Solid Ratio in the Extraction Test. The leachate concentration of a species (e.g., Na, K) is inversely proportional to the liquid to solid ratio if it forms no slightly soluble compounds. However, if the concentration of a given species is limited by the solubility of a slightly soluble compound, the final concentration is independent of the L/S ratio and simply equals the maximum solubility.

Variation of the Amount of Lime in the Solidification Recipe. Waste material was solidified using only lime, and the amount of lime was varied. The amount of lime used in the recipe determines the concentration of Ca^{2+} ions in solution and thus the value of the saturation index of the compound $CaHAsO_3$.

Experimental Section

The extraction test DIN 38 414 S4 (*7*), 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 As-containing waste material (10 g of raw waste material per solidified waste sample) is incorporated in the test, regardless of the amount of additives used in the solidification procedure.

First, experiments were carried out to verify if the 24-h shaking period is long enough to reach steady-state conditions. S/S samples all prepared with the same optimal recipe [whereby per 10 g of waste material, 8 g of CaO, 6 g of cement (Cem II/A-M 32.5 R, a Portland composite cement), and 20 mL of water were added] were extracted (DIN 38 414 S4; L/S = 10 L/kg) for different leaching periods: 5, 10, 19, 24, and 48 h, whereafter the leachate was filtered and analyzed (concentrations of Ca, As, Sb, and Pb) by ICP−MS (inductively coupled plasma−mass spectrometry). The ICP−MS used was a PQ^{2+} from VG-Elemental. Before the measurements, the samples were diluted 10 times, HNO_3 acid was added to obtain a final concentration of 2%, and In (50 μg/L) was added as an internal standard. As a standard, a 1000 μg/L solution of As (with HNO_3 and In) was used. The reproducibility of the results was 2−3%. Because of the relatively high As concentration, interferences from ArCl polyatomic ions were negligible.

Solidified waste samples (all prepared with the same optimal recipe) were leached according to the extraction test. The liquid to solid ratio was varied from 2 to 200 L/kg in order to investigate if the concentration of As in the leachate is limited by solubility. The waste material was extracted for a period of 24 h, whereafter the filtered leachate was analyzed for As and Ca and the pH was determined.

Finally, the waste material was solidified with different amounts of lime (CaO) added to the waste without the addition of cement. The amount of CaO varied from 0.2 to 16 g/10 g of raw waste material. The S/S samples were subjected to the extraction test, and the concentration of As and Ca and the pH value of the leachate were determined.

Results and Discussion

Variation of the Leach Time of the Extraction Test. The results for the extraction tests with different leach times are shown in Figure 2, giving the leachate concentration for the elements As, Sb, Pb, and Ca (mg/L) as a function of the leach time. The leachate pH values for the five extraction tests

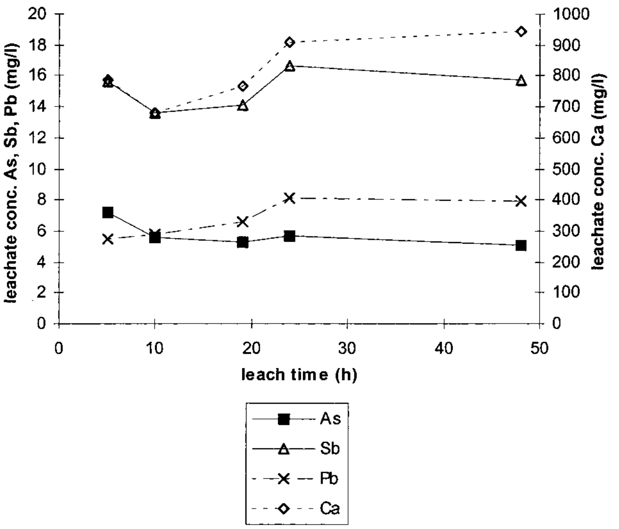

FIGURE 2. Leachate concentration of S/S waste as a function of the leach time (extraction test).

TABLE 1. Concentration of As and Ca (mg/L) and Leachate pH at Various L/S Ratios

L/S	pH	As	Ca
2	12.58	4.44	800
10	12.61	5.51	783
20	12.64	6.79	840
40	12.44	10.35	710
70	12.39	19.12	391
100	12.31	15.81	428
150	12.22	19.48	388
200	12.16	15.93	261

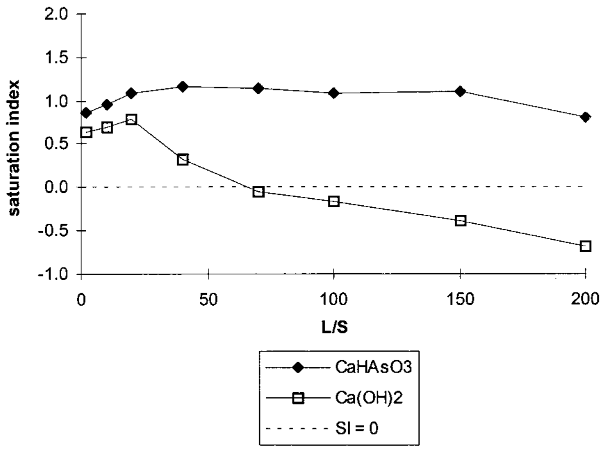

FIGURE 3. Saturation indices of the compounds $CaHAsO_3$ and $Ca(OH)_2$ as a function of the L/S ratio.

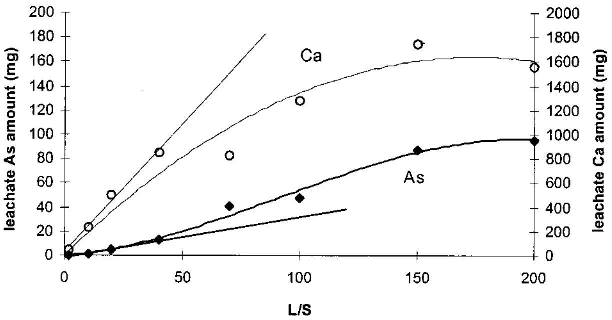

FIGURE 4. Leachate amounts of As and Ca (mg) as a function of the L/S ratio.

were 12.51, 12.52, 12.56, 12.56, and 12.59. These experiments indicate that after a period of 24 h steady-state conditions are achieved.

Variation of the Liquid to Solid Ratio of the Extraction Test. The results of the extraction tests at various L/S ratios are given in Table 1. It appears that at increasing L/S ratios the pH of the leachate decreases, the concentration of Ca decreases, and the concentration of As increases in general.

Upon addition of water to lime, $Ca(OH)_2$ is formed, which may easily dissolve and give OH^- and Ca^{2+} ions, thus having an effect on the pH of the leachate. From the experiments it is to be noticed that the pH and the Ca concentration follow the same trend. For the first three L/S ratios, pH, As and Ca concentrations remain fairly constant. From L/S 40 on, the pH and Ca concentrations decrease and the As concentration increases. This behavior of Ca (constant for low L/S and decreasing for higher L/S) seems to indicate that the concentration of Ca is limited initially by solubility, probably as $Ca(OH)_2$. In literature (*14*), the following values are reported for the solubility in water of $Ca(OH)_2$: 1.85 g/L at 0 °C and 0.77 g/L at 100 °C. This corresponds with a value of 1.00 g/L Ca at 0 °C. The pH corresponding with this amount of $Ca(OH)_2$ in solution can be calculated and is 12.4. With the speciation program MINTEQA2 (*15*), the concentration of Ca in equilibrium with $Ca(OH)_2$ can be calculated at various pH values (at 25 °C): 1500 mg/L at pH = 12.3; 914 mg/L at pH = 12.4, and 585 mg/L at pH = 12.5.

At a pH of 12.4, the concentration of Ca in water is ca. 900 mg/L. As appears from Table 1, the Ca concentration and the pH value in the leachates of the extraction tests performed at L/S ratios 2, 10, 20, and 40 are fairly close to these values. At higher L/S ratios, the Ca concentration decreases, as if the maximum solubility is no longer reached. To further verify this, using the measured Ca concentration and pH, the saturation index for $Ca(OH)_2$ can be calculated according to

$$\mathrm{SI} = \log\left(\frac{[\mathrm{Ca}^{2+}][\mathrm{OH}^{-}]^{2}}{K_{\mathrm{S}}}\right) \qquad (2)$$

Some literature values for the solubility product of $Ca(OH)_2$ are 7.94 E−6 (*16*); 9.1 E−6 (*17*); 5.5 E−6 (*18*); 6.5 E−6 (*19*). The most recent value, 6.5 E−6 (*19*), was used. Also, the saturation index of $CaHAsO_3$ was calculated. Both SI values are shown in Figure 3 as a function of the L/S ratio.

As can be seen from Figure 3, the saturation index of $CaHAsO_3$ is positive for all the L/S ratios considered, indicating that $CaHAsO_3$ will precipitate. In fact, when equilibrium with a pure precipitate is reached, the saturation index should be zero. The calculated SI values here are however higher than zero, probably due to the fact that in the leachate there is a continuous source (the S/S sample) supplying calcium and arsenic to the leaching solution next to the $CaHAsO_3$ precipitate. The saturation index of $Ca(OH)_2$ is positive at the first four L/S ratios and then turns negative. When SI is positive, a $Ca(OH)_2$ precipitate is formed in the leachate, explaining the nearly constant pH value and Ca concentration. At higher L/S ratios, the Ca concentration decreases and the solubility product of $Ca(OH)_2$ is no longer exceeded. The pH value, however, is still in the region where $HAsO_3^{2-}$ is formed, and there is a sufficient amount of Ca present in the leachate to form $CaHAsO_3$. As a consequence of the lower Ca concentration in the leachate, the As concentration in equilibrium with the $CaHAsO_3$ precipitate increases.

In Figure 4, the total amount of As and Ca (mg) in the leachate is presented as a function of the L/S ratio. For the first 4 L/S ratios, the amount in the leachate of Ca as well as As is proportional to the L/S ratio, indicating a constant concentration of Ca and As, respectively, in the leachates of

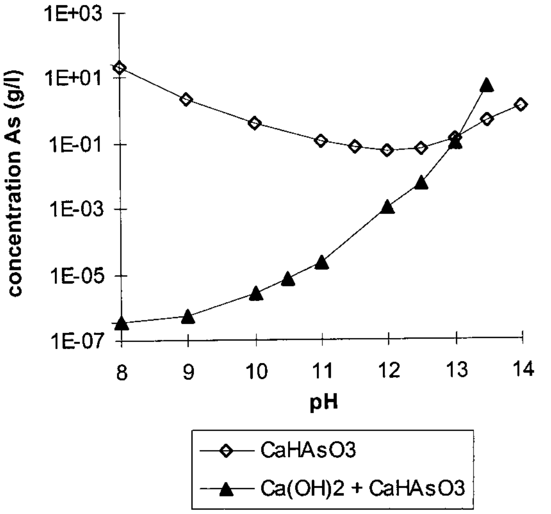

FIGURE 5. Solubility of As (g/L) versus pH for $CaHAsO_3$ and $Ca(OH)_2$ + $CaHAsO_3$ in equilibrium with water at 25 °C/1 atm.

these tests and thus a limitation of the concentration by solubility. From a L/S ratio of 70 on, the total amount in the leachate no longer follows this linear trend: the concentration of Ca in the leachate is lower than the one determined by the solubility of $Ca(OH)_2$.

That a kinetic effect is not responsible for the lower concentration of Ca in the leachates at higher L/S ratios was proven by carrying out the extraction test at L/S 100 for different leaching periods: 10, 24, 48, and 96 h. Analysis of the leachates indicated a As concentration of ca. 15 mg/L for the four leachates. The lower Ca concentration is thus indeed due to the fact that an insufficient quantity of Ca is available to achieve saturation for the high L/S ratios.

With the speciation program MINTEQA2 (*15*), calculations were made to determine the concentration of As in equilibrium with an 'infinite' amount of $CaHAsO_3$, at 25 °C. The solubility product K_S for the compound $CaHAsO_3$ was not available in the database of the speciation program, so that the experimentally determined value (*8*) was incorporated in the database. Also, the concentration of As in equilibrium with both infinite amounts of $Ca(OH)_2$ and $CaHAsO_3$ was determined [the solubility product for the compound $Ca(OH)_2$ in the MINTEQA2 database is 4.73 E−6]. The results of these calculations are graphically presented in Figure 5. With only $CaHAsO_3$ present, the minimum concentration of arsenic that can be reached is ca. 55 mg/L at a pH of approximately 12. When both $Ca(OH)_2$ and $CaHAsO_3$ are present, the concentration of As decreases considerably below a pH value of ca. 13. At a pH of 12.5 (the approximate pH value in the leachate of the extraction tests), the As concentration is 5.4 mg/L, in almost perfect agreement with the results of the extraction tests [i.e., the leachate As concentration of ca. 5 mg/L, the minimum arsenic concentration found as a result of a variety of S/S procedures (*6, 8, 11*)].

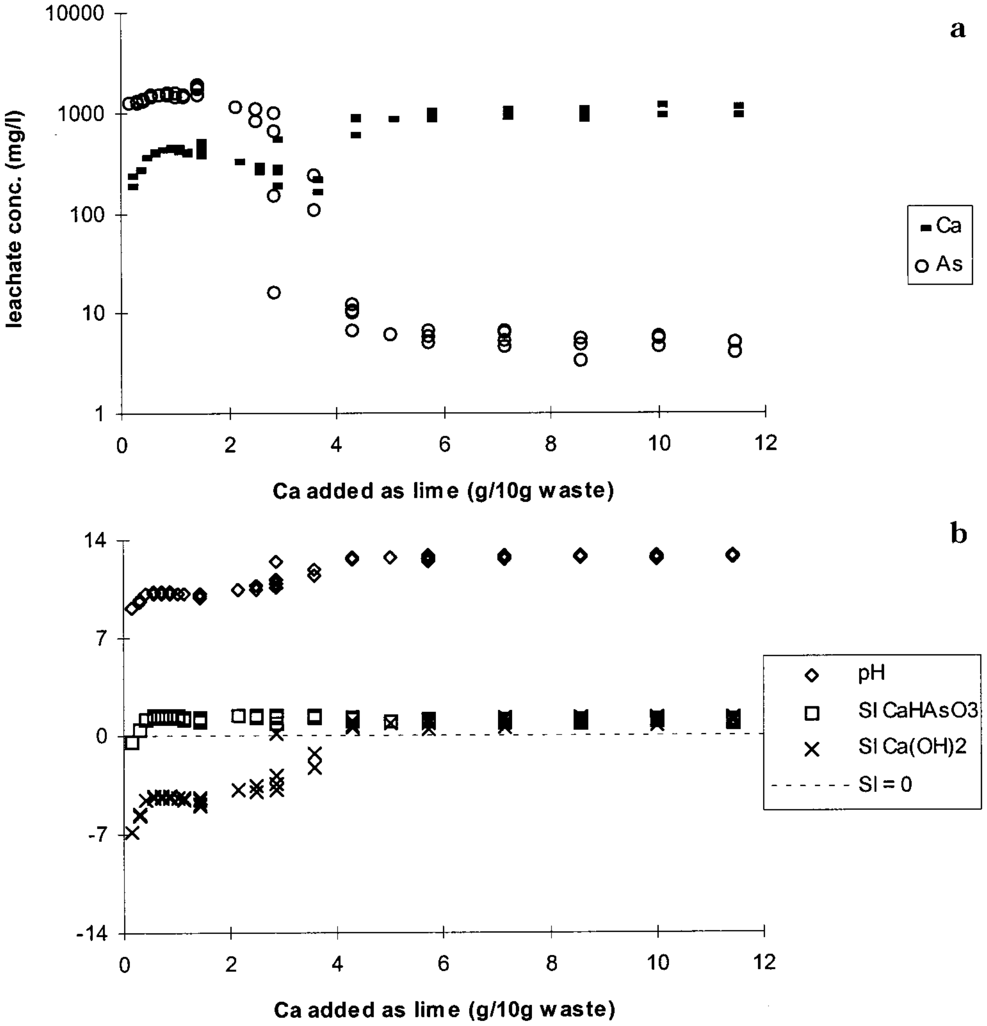

FIGURE 6. Leachate concentrations of As, Ca, leachate pH, and saturation indices as a function of the amount of lime (CaO) added to the waste (no cement added).

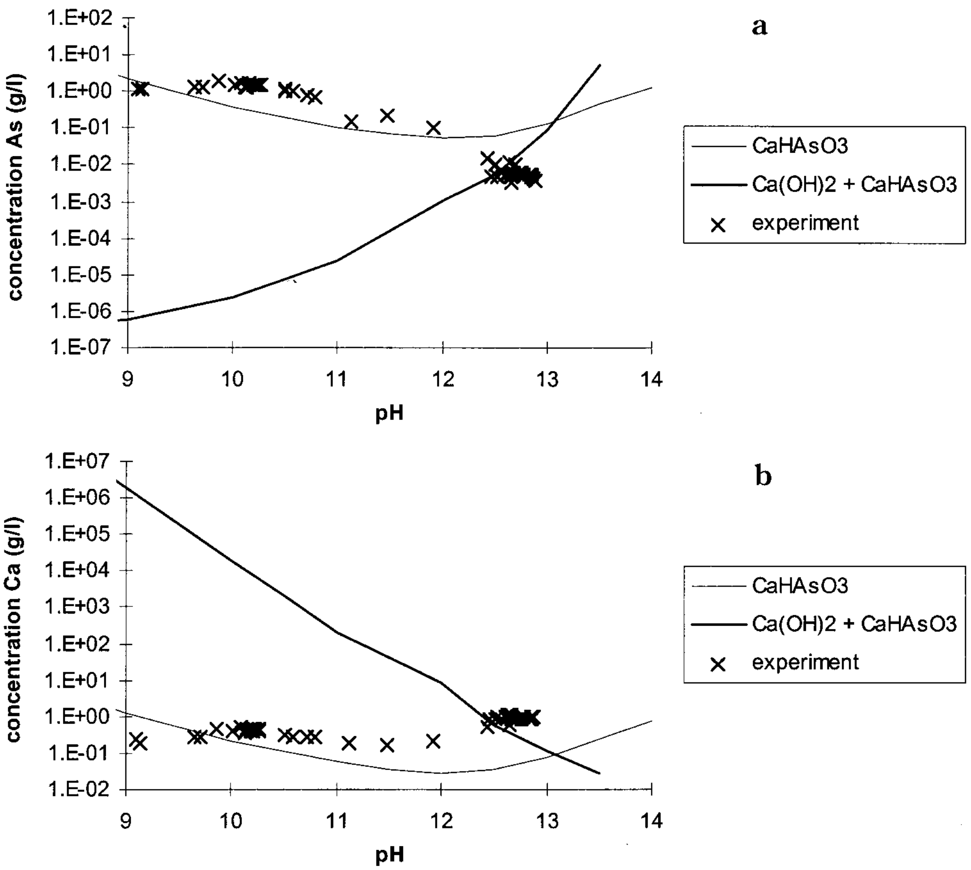

FIGURE 7. Calculated solubility of As and Ca (g/L) versus pH for the compounds $CaHAsO_3$ and $Ca(OH)_2 + CaHAsO_3$, in equilibrium with water at 25 °C/1 atm; together with experimental results, obtained using solidified/stabilized waste samples with addition of only lime.

Variation of the Amount of Lime in the Solidification Recipe. In Figure 6, the experimental results are presented as the concentration of As and Ca in the leachate as a function of the amount of lime added to the waste (no cement was added) together with the leachate pH and the saturation indices for $CaHAsO_3$ and $Ca(OH)_2$.

It appears from Figure 6 that the concentration of As in the leachate decreases as more lime is added in the solidification recipe of the waste material. From an amount of ca. 4 g of Ca/10 g of waste, the concentration of As reaches a minimum value of ca. 5 mg/L. The concentration of Ca in the leachate initially increases as more lime is added to the waste. From an amount of ca. 4 g of Ca/10 g of waste, the Ca concentration in the leachate remains nearly constant at a value of ca. 900 mg/L, and the leachate pH reaches a constant value of ca. 12.5. The saturation index of $Ca(OH)_2$ shows that from this point on $Ca(OH)_2$ precipitates in the leachate. The saturation index of $CaHAsO_3$ indicates precipitation of this compound from already very small amounts of lime addition. In the beginning of the curve, the As concentration however is still high because the Ca concentrations are lower than those in equilibrium with a $Ca(OH)_2$ precipitate and because of the low pH that results in only a small fraction of the As(III) being present as $HAsO_3^{2-}$ (Figure 1).

In Figure 7, the experimental values for the As and Ca concentration (g/L) are plotted together with the concentration versus pH curve for $CaHAsO_3$ and $Ca(OH)_2 + CaHAsO_3$ precipitates (calculated with MINTEQA2). For S/S samples where less than 4 g of Ca was added per 10 g of waste (leachate pH value less than 12), the As and Ca concentrations in the leachate closely follow the $CaHAsO_3$ curve. From an amount of ca. 4 g of Ca/10 g of waste, where the saturation index of $Ca(OH)_2$ is no longer negative (see Figure 6), the leachate As and Ca concentrations fall on the curve of $Ca(OH)_2 + CaHAsO_3$.

As proven by the above experiments and calculations with the speciation program MINTEQA2, an equilibrium is reached in the leachate of the S/S samples subjected to the extraction test DIN 38 414 S4 (L/S 10, 24-h shaking period) with precipitation of $CaHAsO_3$. It was found that also $Ca(OH)_2$ precipitates in the leachate of the extraction test (L/S 10), if a sufficient amount of lime was added during solidification. The concentration of Ca in the leachate is thus determined by the solubility of $Ca(OH)_2$, giving a Ca concentration of ca. 900 mg/L and a leachate pH value of ca. 12.5. Due to the presence of both $Ca(OH)_2$ and $CaHAsO_3$, the As concentration in the leachate is lowered to ca. 5 mg/L (at a pH of 12.5), whereas the minimum value of As that can be reached when only $CaHAsO_3$ is present is ca. 55 mg/L. The factor that determines this reduction in arsenic concentration is the excess of lime leading to the right pH and a high concentration of Ca^{2+} ions in solution. The concentration of ca. 5 mg/L, found earlier for a variety of different S/S recipes, is now fully understood.

Although S/S waste, solidified according to the initial Soliroc procedure, yielded the same results concerning the leachate As concentration, the theory regarding As immobilization as a silica–alumina–arsenate, as presented by the Soliroc process, must obviously seriously be questioned since it was proven in this paper that As is immobilized through the formation of $CaHAsO_3$.

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