Solidification/stabilisation of hazardous arsenic containing waste from a copper refining process

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Abstract

An industrial waste, originating from a metallurgical process in which copper is refined and containing large amounts of arsenic (42 wt%), was studied. A suitable treatment method, solidification/stabilisation (S/S), allowing a reduction of the leachability of arsenic from the waste was studied and optimised by measurement of the influence of all additives (waste acid, blast-furnace slag, slaked lime, cement) used in the process. The S/S process could thus be simplified considerably. The addition of lime to the waste was the most important factor in reducing the arsenic concentration in the leachate by formation of a hardly soluble calcium–arsenic compound. To reduce the arsenic concentration in the leachate even further, by formation of other insoluble compounds, the addition of aluminium and barium salts was investigated.

1. Introduction

Hazardous inorganic and radioactive wastes are produced in enormous quantities. In some cases, these hazardous wastes cannot be destroyed or reused and therefore controlled disposal in a landfill is necessary. No universal method to treat all kinds of waste exists. A realistic goal, however, is to minimise the risk by treatment and disposal of hazardous waste by transformation of the contaminants into less hazardous compounds.

Solidification/stabilisation (S/S) technology [1] is used to transform potentially hazardous liquid or solid waste into less hazardous or nonhazardous solids before disposal in a landfill. S/S technology is mostly used to treat waste containing toxic, inorganic components. It has been used for many years to treat industrial waste, and

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more recently also for contaminated soils [2], combustion residues and incinerator ash. S/S is particularly useful for arsenic containing waste, as recovery of arsenic is of no economic interest because of the limited number of uses for this element and since incineration is limited because of volatilisation of As-containing compounds.

The broad objective of S/S technology is waste containment, thus preventing waste from entering the environment [3]. Containment may be realised by several methods according to the type of binder material used. Inorganic S/S processes use inorganic binders such as cement or pozzolanic materials. Organic binders are used in organic S/S processes such as micro-encapsulation by thermoplastic materials, macro-encapsulation, organic polymerisation and S/S processes using organophilic clay. Organic S/S is more expensive than inorganic S/S, and yields a smaller increase of the waste volume. Organic/inorganic S/S technology combines the use of cement and polymers. Vitrification involves the heating of a mixture of waste and silica in order to form a glass.

Regardless of these differences, all S/S methods have the following common objectives: (1) production of a monolithic solid mass; (2) limitation of the solubility of the contaminants in the leaching water by formation of insoluble compounds; (3) reduction of transfer or loss of contaminants by decreasing the surface area; (4) improvement of the handling and physical characteristics of the waste. Ideally, toxic compounds are transformed into a nontoxic form, which implies a chemical transformation with formation of new compounds, but little evidence of chemical transformation has been reported in the literature.

In this paper only inorganic S/S processes are studied based on cement and lime. These processes are used commercially and have been successful in reducing the leachability for many types of waste. Contaminants are made as insoluble as possible and their mobility is further restricted by encapsulation in the resultant matrix. In this paper, most attention is given to the study of the limitation of the solubility of the contaminants of interest in the leaching water by the formation of insoluble compounds (objective (2)).

For metals present as cations, such as Cr^{3+}, immobilisation is usually quite successful. For negatively charged metal compounds, e.g. AsO_3^{3-} and AsO_4^{3-}, immobilisation is generally less effective. Quality standards for arsenic in groundwater and surface water are set in Belgium at 50 μg/l. The maximum allowed concentration of arsenic in the effluent waters of an industrial landfill is 1 mg/l. From July 1, 1995, the absolute emmission standard for ground- and surface water will be lowered to 30 μg/l [4]; thus providing the motivation for this study. The waste studied originates from a metallurgical process in which copper is set free from its ore. In this process, fly ashes are produced with a high concentration of arsenic which was originally present in the ore.

The toxicity of arsenic is related to the oxidation state of the element. Elementary arsenic is not toxic, As(III) is 25 to 60 times as toxic as As(V) and several hundred times as toxic as methylated arsenic compounds, arsine is the most toxic compound of arsenic. It is therefore important to identify the oxidation state of arsenic in the treated waste materials.

2. Materials and methods

2.1. Waste characterisation

All waste material studied originates from the same metallurgical process, but was obtained at different times. Each of the three samples received was analysed using an acid destruction technique whereby the waste material is dissolved in a boiling mixture of HNO_3 and HCl. The filtrate is then analysed by ICP-MS (inductively coupled plasma mass spectrometry), a multi-element analytical technique with high sensitivity, using a PQ_e spectrometer from Fisons Instruments. For each of the three different samples, the destruction was carried out on two replicates. The results of these destructions are summarised in Table 1, giving the mean values for the two replicates. Preliminary tests showed that each replicate has an accuracy and precision of 2–6%.

2.2. Solidification/stabilisation

The solidification of the waste was carried out by adding waste acid (5 M HCl with Zn and Fe concentrations of approx. 60 g/l and a Pb concentration of 150 mg/l), blast-furnace slag, slaked lime, cement (PPZ30) and water to the waste in order to obtain a solid with a sufficient strength and consistency after solidification. The initial solidification procedure, based on a previous study with another waste material, is as follows: per 10 g of waste, 15 g of slags, 5 g of waste acid and water are added to obtain a sludge. This mixture is set aside overnight because it is believed that silicon containing acids (H_2SiO_3) are formed, due to a reaction between the acid and the silicate compounds of the binder materials, which are responsible for further polymerisation on a long-term basis. These polymers are believed to capture leachable metals. After 24 h 10 g of lime and 11 g of cement are added together with water. This mixture is vigorously stirred and starts to set shortly after. This procedure will be called the '2 day process'. When Al- and Ba-salts are used in the procedure, an aqueous solution of these salts is added to a mixture of only waste material and cement. Before the solidification product is subjected to any leach test it is allowed to harden for one week. Every leach test is carried out on two S/S samples with the same recipe.

Table 1
Waste characterisation (wt%)

	As	Sb	Pb
Sample 1	42.2	34.7	14.1
Sample 2	46.5	24.4	8.0
Sample 3	39.3	17.7	20.6

2.3. Extraction test

An appropriate way to examine the effectiveness of the immobilisation of the contaminants after solidification of the waste, is to perform extraction tests. A variety of different extraction procedures are currently available. In all these tests the solidified material, either pulverised or in a monolithic block, is added to a leaching medium in a chosen ratio of mass of waste material to volume of leachant and the mixture is shaken for a certain period of time. At the end of the leaching period, equilibrium is in general reached between the leachant and the solidified material. Therefore, extraction tests are commonly used to determine the maximum leachable concentration under the chosen conditions [3].

In this study, the extraction procedure used is the DIN test, DIN 38414: 1 l of distilled water is added to 100 g of dried substance, after which it is shaken for a 24 h period using a shaking machine. In the DIN test however the sample is crushed whereas in our study the monolithic sample is subjected to the extraction test. At the end of the shaking period, the monolithic sample has fully or partially disintegrated. After filtration, the leachate is analysed using ICP-MS.

3. Results and discussion

3.1. Leaching of raw waste material

The leachability of the contaminants from the raw waste material was examined by submitting the waste to the extraction test. 10 g of waste material was added to a volume of 100 ml of distilled water, at various pH-values, and shaken for a period of 24 h. The different pH-values were obtained by adding NaOH or H_2SO_4 to distilled water. The results are summarised in Table 2, giving the mean values of two extraction tests.

Arsenic is clearly the most easily leachable element, with concentrations in the leachate up to more than 5 g/l. At low pH-values, a fairly large amount of Zn is leached. Pb and Sb are more effectively leached at higher pH-values. When the untreated waste is leached in distilled water, without pH-adjustment, the pH of the leachates varies between 3 and 3.5, which indicates the acid character of the waste.

3.2. Oxidation state of arsenic in the raw waste material

It is important to identify the oxidation state of arsenic in the waste, not only because of differences in degree of toxicity, but also because of differences in the formation of arsenic compounds. Two forms of arsenic are considered: As(III) and As(V).

The oxidation state of arsenic in the leachate of the raw waste material was determined using two different titration methods. First, raw waste material was leached in distilled water and the leachate was filtered and analysed for its total
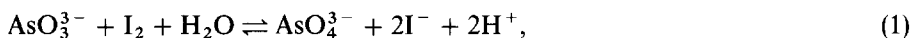
Table 2
Concentration in leachate of raw waste

pH leaching solution	As (g/l)	Sb (mg/l)	Pb (mg/l)	Zn (mg/l)
2	2.98	3.07	1.31	335
4	5.16	15.8	3.26	78.4
6	4.24	4.07	3.04	60.2
8	4.86	20.0	2.75	55.7
10	4.52	13.8	2.45	74.2
12	1.62	78.8	4.76	1.6

Table 3
Oxidation state of As in the leachate of the raw waste

Total As conc. (mg/l)	As(III)–I_2 (mg/l)	As(III)–$KBrO_3$ (mg/l)	% As(III)
455	428	436	94.8
547	522	534	96.5
885	820	821	92.8
1268	1206	1207	95.2
3399	3268	3268	96.1
6269	5902	5901	94.1
6487	6049	6036	93.1
7022	6711	6692	95.4
7280	6817	6755	93.2

arsenic concentration (As(III) + As(V)) using ICP-MS. To determine the concentration of As(III), a titration was carried out on the filtrate, based on the oxidation of As(III) to As(V) with iodine or potassium bromate:

$$AsO_3^{3-} + I_2 + H_2O \rightleftharpoons AsO_4^{3-} + 2I^- + 2H^+, \tag{1}$$

$$BrO_3^- + 3AsO_3^{3-} \rightleftharpoons Br^- + 3AsO_4^{3-}. \tag{2}$$

Both results were compared. From the total arsenic concentration, the percentage of As(III) in the leachate can then be calculated. Table 3 gives the results for nine extraction tests carried out on the raw waste material. The leach time was varied from 14 to 144 h resulting in an increase of the concentration of As in the leachate. Both methods give similar results, and indicate that on the average 94.6% of the total arsenic in the leachate is in the As(III) state. Because the waste contains small amounts of Fe, Fe(III) could oxidise As(III) to As(V). The As(III) percentage would then however only increase with 1–1.5%. These results indicate that the waste contains mostly the more toxic As(III), probably as As_2O_3.

3.3. Optimisation of the solidification procedure

Because arsenic is the most hazardous constituent in the waste material, the solidification procedure is optimised based on the measured concentration of arsenic in the leachates of the solidified materials, submitted to the extraction test. Every extraction test is carried out on two S/S samples with the same recipe. First, the extraction test was carried out several times on the untreated waste. The arsenic concentration found in the leachates ranged from 0.5 to 7 g/l (15 experiments). Solidification of the waste, according to the 2 day process described earlier, lowered the arsenic concentration in the leachate to approximately 5 mg/l. The concentration ranges for As, Sb and Pb in the leachate are given in Table 4.

The concentration of lead is clearly higher in the leachate of the solidified waste than in the leachate of the untreated waste, due to the high pH-value after solidification, established by the addition of lime.

The influence of all additives (slags, waste acid, water and slaked lime) on the immobilisation of arsenic was then studied systematically. It appeared that the addition of waste acid and slags and the amount of water added had only a negligible influence. Slags are added to increase the silicon content in the resulting product, thereby promoting the polymerisation during setting of the cement. However, the hardening process takes weeks or months and cannot be investigated in these one-week tests. To measure the influence of slags, long term tests are necessary. The addition of slags on a short-term basis had no significant influence on the concentration of the contaminants in the leachate. The addition of waste acid to the mixture lowered the concentration of arsenic from 10 to 5 mg/l. This slight difference is negligible compared to the enormous decrease in leachate concentration from the unsolidified to the solidified waste (7 g/l to 5 mg/l). Thus, the waste acid cannot be seen as a key component in the reduction of the leachability of arsenic.

Lime is added to reach a high pH-value necessary for the cementation reactions and it also buffers the pH of the solidified product. The addition of lime has an important influence as shown in Fig. 1. The concentration of arsenic in the leachate is lowered considerably when more lime is added to the raw waste. From an amount of 6 g Ca added per 10 g of waste, where the pH has reached a value of 12.6, the concentration of As is lowered to a constant value of approximately 5 mg/l. It is however not the high pH-value of the solidified product, due to the lime addition, that keeps the arsenic from leaching. An experiment was carried out where a mixture of waste, cement and NaOH was solidified. NaOH was added to reach a high pH-value after solidification:

Table 4
Concentration ranges (µg/l) in leachate of solidified waste 2 day process (14 experiments)

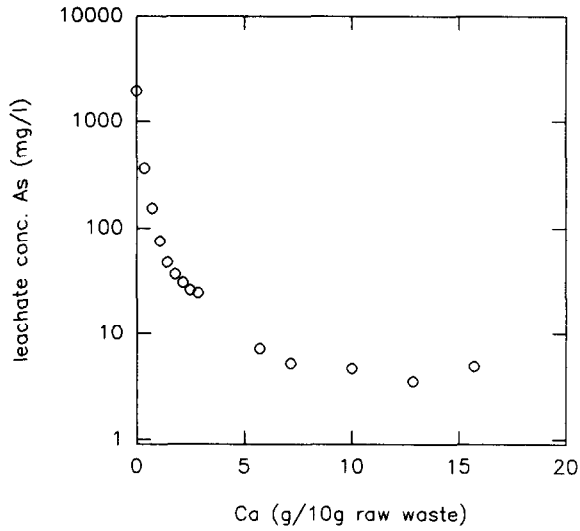|	
As	5020–6180
Sb	8980–9570
Pb	12,520–17,800
pH	12.6–12.7

Fig. 1. Concentration of As in leachate of S/S waste as a function of calcium (CaO) added (2 day process).
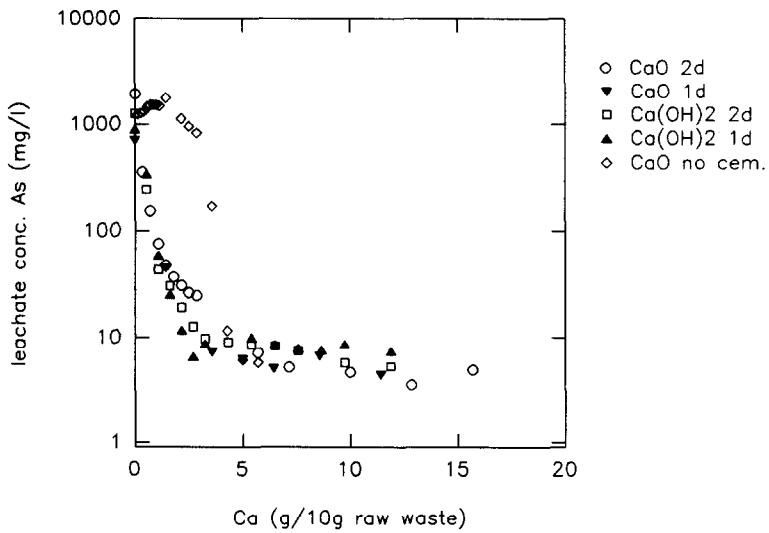

Fig. 2. Concentration of As in leachate of S/S waste as a function of calcium added for different S/S procedures.

the leachate had a pH-value of 12.4. The amount of As leached (ca. 3 g/l) was however comparable with results for S/S products without lime addition and thus low pH-values. Therefore, it is suggested that a hardly soluble calcium–arsenic compound is formed in the leachate. Since waste acid and slags were shown not to have an influence

on the leaching behaviour of arsenic, waste samples were prepared without addition of these materials. Solidification can thus be performed in 1 day ('1 day process') instead of 2 days as described earlier: waste, lime and cement are mixed together with water. As shown in Fig. 2, leaching of these solidified waste samples prepared without addition of waste acid and slags yielded comparable results as for the 2 day process. Using quick lime ($Ca(OH)_2$) instead of slaked lime (CaO) gave similar results, both for the 2 day and for the 1 day process. It is also of interest to notice that even without the addition of cement to the waste-lime-water mixture, the concentration of arsenic in the leachate was reduced to the same concentration. However, the concentration starts only to decrease after addition of a larger amount of calcium, as the amount of calcium otherwise present in the cement has to be added additionally (Fig. 2).

In Figs. 3 and 4, the results for Sb and Pb are presented. As can be seen from Fig. 3, more Pb is leached when more Ca is added. Leaching begins at a pH-value of approximately 12.6. All curves follow similar trends, but for the 1 day process leaching starts to increase at lower Ca values. This is due to the fact that pH-values are higher for the same amount of Ca added because no waste acid is added that has to be neutralised. The concentration is also lower for the 1 day process, because no Pb is added to the solidified product through waste acid addition. When no cement is added, more Pb is leached. The leaching of Sb is practically not influenced as a function of the amount of Ca added as can be seen from Fig. 4.
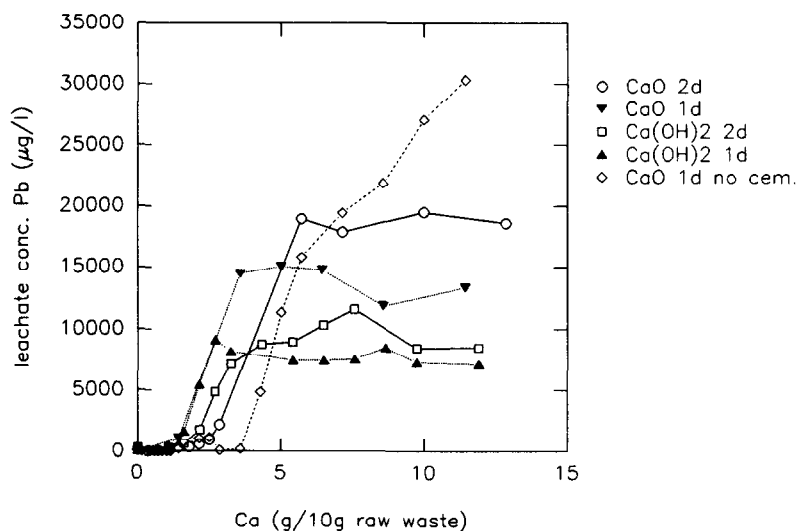

Fig. 3. Concentration of Pb in leachate of S/S waste as a function of calcium added for different S/S procedures.
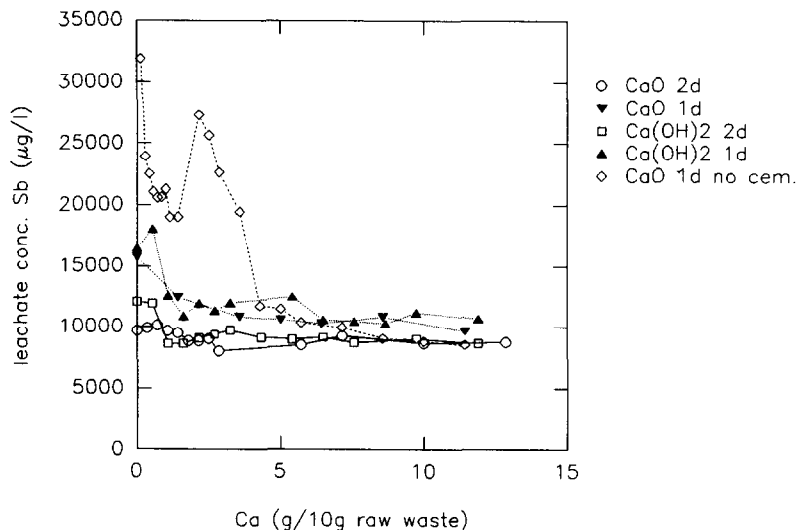
Fig. 4. Concentration of Sb in leachate of S/S waste as a function of calcium added for different S/S procedures.

Table 5
Solubility of arsenates and arsenites

Arsenate: AsO_4^{3-}	Solubility	Arsenite: AsO_3^{3-}	Solubility
$AlAsO_4$	a	–	
$Ba_3(AsO_4)_2$	w	–	
$Ca_3(AsO_4)_2$	w	$Ca_3(AsO_3)_2$	w

a: insoluble in water and only sparingly soluble in acids.
w: sparingly soluble in water but soluble in acids.

3.4. Addition of Al and Ba salts

Although the oxidation state of arsenic in the leachate of the untreated waste is mostly As(III), this does not necessarily mean that it is the same for the leachate from the solidified waste. Initially, we believed that calcium formed with arsenic the hardly soluble calcium arsenate, $Ca_3(AsO_4)_2$. From results of leach tests, where different solidified samples were leached in different volumes of leachant, it appeared that the amount of arsenic leached was limited by the solubility product of a calcium–arsenic compound, but it could not be determined which compound was formed: calcium arsenate or calcium arsenite. To further identify the oxidation state of As, other additives were sought which form a hardly soluble compound with either As(III) or As(V). We selected Al and Ba. Some information regarding the solubility of their compounds with arsenic is given in Table 5.
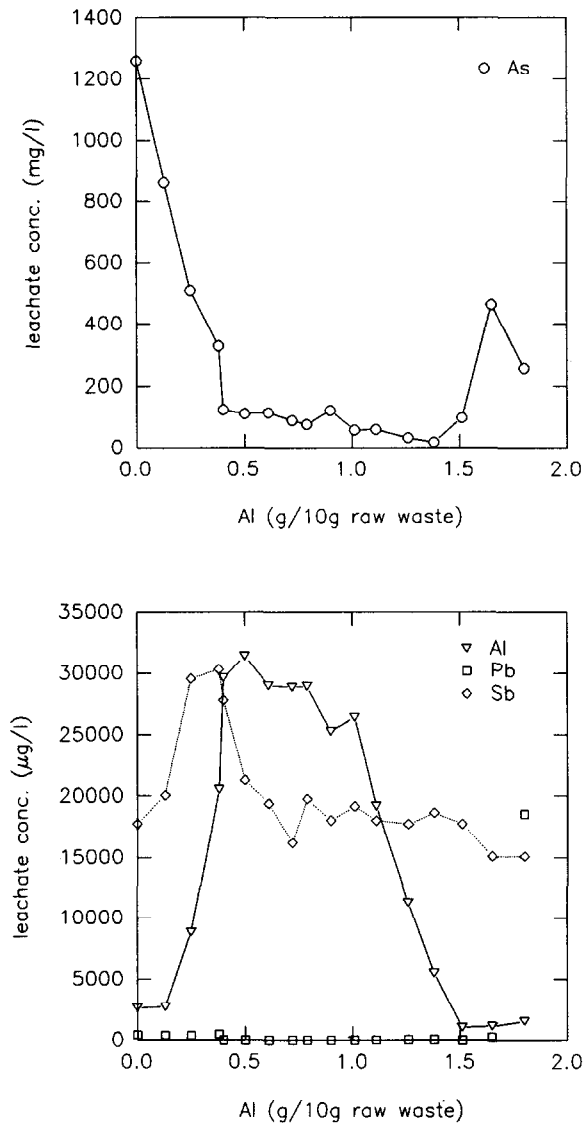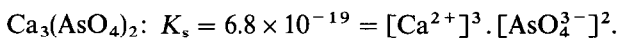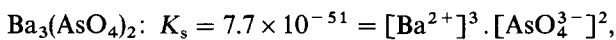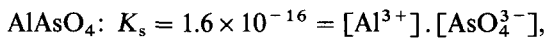
Fig. 5. Concentration of contaminants in leachate of S/S waste as a function of aluminium added.

Another reason to search for other additives is to try to further lower the solubility of arsenic in the leachate from the solidified waste by formation of compounds with a lower solubility product. Some values are given below [5]:
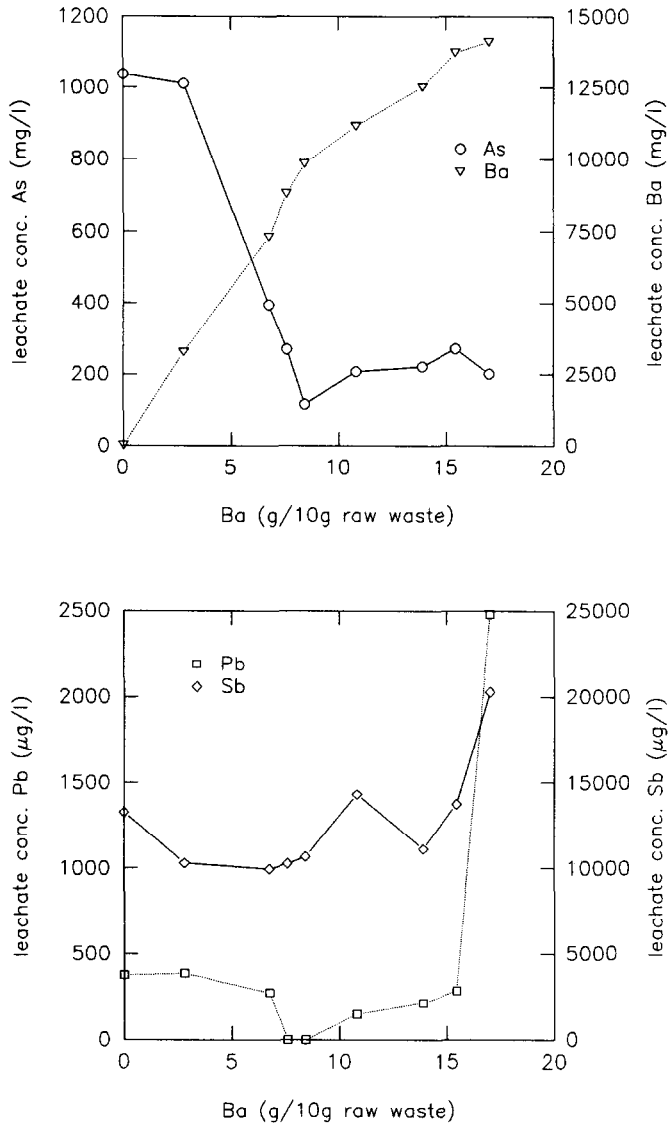
$$AlAsO_4: \quad K_s = 1.6 \times 10^{-16} = [Al^{3+}] . [AsO_4^{3-}],$$

$$Ba_3(AsO_4)_2: \quad K_s = 7.7 \times 10^{-51} = [Ba^{2+}]^3 . [AsO_4^{3-}]^2,$$

$$Ca_3(AsO_4)_2: \quad K_s = 6.8 \times 10^{-19} = [Ca^{2+}]^3 . [AsO_4^{3-}]^2.$$

Fig. 6. Concentration of contaminants in leachate of S/S waste as a function of barium added.

However, different values were found for the K_s-value of $Ba_3(AsO_4)_2$ [6]. The value was first determined by Chuklantsev [7], without taking ionic strength into consideration: 7.7×10^{-51} was found at 20 °C. Robins [8] and Essington [6] claimed that $Ba_3(AsO_4)_2$ was more soluble than originally thought. Robins found a K_s-value of 2.6×10^{-17} at 25 °C. Experiments where Essington took ionic strength into consideration, resulted in a mean K_s-value of 2.4×10^{-22}. The results of Chuklantsev were again

evaluated and showed that in his experiments, it was not $Ba_3(AsO_4)_2$ that was formed but $BaHAsO_4 . H_2O$ with a K_s-value of 2.29×10^{-25} [6].

Aluminium was added as an aqueous solution of aluminium nitrate to a mixture of waste and cement: the amount of Al ranged from 0 to 1.8 g per 10 g of waste. During the mixing, a foam was formed, which shrunk on continued mixing and even hardened. From an addition of 17.5 g of aluminium nitrate $(Al(NO_3)_3 . 9H_2O)$, the sample only partially hardened. The leachate of samples with 27 g of aluminium nitrate gave great difficulties in filtering. Therefore, the maximum amount of salt added was restricted to 25 g. The results from these tests are given in Fig. 5. It appears that Al decreases the leaching of arsenic but it is not clear whether this indicates the formation of $AlAsO_4$. The ion product for $AlAsO_4$ was calculated and was found not to be constant as a function of the amount of Al added. However, the formation of the foamy, jellylike structure could be an indication that an $Al(OH)_3$ gel is formed. Its ion product was calculated (mean value of 3.56×10^{-32}) and showed fair agreement with values found in the literature (2×10^{-32} [9] and 6.3×10^{-32} [10]). The positive influence of aluminium on the decrease in leaching of arsenic can thus probably be explained by adsorption of arsenic on the aluminium hydroxide gel and nothing can be concluded on the oxidation state of arsenic. The higher concentrations of As leached from the samples with the highest amount of Al can be explained from the fact that the sample was fully disintegrated during the shaking period, and therefore, As could more easily be released.

Barium was added as an aqueous solution of bariumchloride: the amount of Ba added ranged from 0 to 17 g per 10 g of waste. After one week, the samples are solid
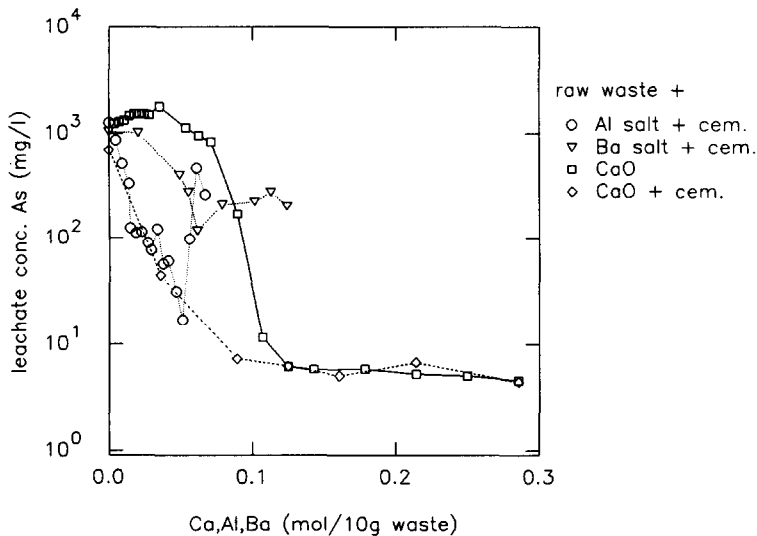

Fig. 7. Comparison between S/S procedures with lime, aluminium salt and barium salt.

but not very hard. The results are presented in Fig. 6. Barium lowers the concentration of arsenic in the leachate but the values do not decrease below 200 mg/l. It appears that the lower arsenic concentration cannot be attributed to the formation of barium arsenate, because the concentration of Ba rises as the concentration of As reaches a constant value. A possible explanation is that As is adsorbed on a bariumcarbonate precipitate.

Addition of Al and Ba thus does not allow to make unambiguous conclusions as to the oxidation state of As in the leachate from the solidified waste, because other factors also play a role. This subject is presently being studied further.

A comparison can be made between the solidification procedures using different additives. This is graphically presented in Fig. 7. All three elements, Ca, Al and Ba, reduce the leachability of As from the solidified waste. The addition of lime or of lime and cement gives the best results.

4. Conclusions

The arsenic concentration in the leachate of the solidified waste is significantly lower than in the raw waste material. The main factor in reducing the concentration of this species in the leachate is the addition of lime to the waste. This result reflects the formation of a hardly soluble calcium–arsenic compound, since the concentration of arsenic leached reaches a constant value as soon as enough binder material is added. Other additives, replacing lime, were investigated to further reduce the leachability of As from the waste. One has to keep in mind however that the leaching procedure used gives a far worse indication of leaching than the one that will really occur in the environment. Here, the use of cement or other pozzolanic materials plays indeed an important role in the long-term leachability from the monolithic solid structure formed. Therefore, also static and semi-dynamic leaching tests are being performed in order to better understand the mechanism of immobilisation and the mechanism of leaching so that the release of contaminants over a longer period of time can be better estimated [11].

Acknowledgement

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