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Waste Materials in Construction: Putting Theory into Practice

INFLUENCE OF THE TYPE OF CEMENT USED ON THE LEACHING OF CONTAMINANTS FROM SOLIDIFIED WASTE CONTAINING ARSENIC

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Introduction

The waste material studied originates from a metallurgical process and contains large amounts of arsenic (32 wt%), as As_2O_3. Besides arsenic, the waste also contains Sb (17%) and Pb (14%). The waste was solidified with cement and pozzolanic materials to reduce the leachability of the contaminants from the waste. The solidification procedure was optimised and the concentration of arsenic in the leachate of the extraction test DIN 38 414 was lowered from ca. 5 g/l to ca. 5 mg/l. Addition of lime played a major factor in this reduction [1]. The low concentration of arsenic (5 mg/l) was reached due to the formation of both $CaHAsO_3$ and $Ca(OH)_2$ in the leachate of the S/S waste. Formation of $CaHAsO_3$ alone cannot lower the arsenic concentration beneath ca. 55 mg/l.

It can be said that the concentration of arsenic in the leachate of the solidified waste material is highly dependent on the concentration of calcium in the leachate, and on the formation of $Ca(OH)_2$. The concentration of calcium in the leachate is, of course, dependent on the amount of calcium added to the waste during the solidification process.

In this paper, the effect of cement alone, without lime addition is discussed. Increasing the percentage of CaO in the amount of cement added is also likely to reduce the leachate arsenic concentration. To investigate this, different types of cement were used in the solidification recipe. Cement types can differ in their composition, water demand, setting time, price, etc... In Table 1, the composition of the cement types used is given.

Experimental

The waste material was solidified according to the recipes in Table 2. The amount of cement for each S/S sample is given as the ratio of binder mass to waste mass, together with the water to cement ratio (W/C).

Sample 'eco' has a higher water-to-cement ratio than the other samples, because Ecobind 50 has a higher water demand. The solid waste specimens have a diameter of ca. 4.5 cm and a height of ca. 1.35 cm. The volume to surface area ratio (V/S) ranges from 0.41 to 0.44. Before the solidification product was subjected to any leach test, it was allowed to harden for 2 weeks.

The DIN 38414 extraction test [2], and the N^2 semi-dynamic leach test [3] were applied to the samples. In the semi-dynamic leach test, a leaching volume of 600 ml was used. Over the 3 week duration of the experiment, 21 renewals were performed.

Extraction test

The results of the extraction test are presented in Table 3, where the concentration (mg/l) of Ca, As, Sb and Pb is given, together with the leachate pH.

From these tests it can clearly be seen that the concentration of arsenic in the leachate of the S/S samples decreases as the pH value of the leachate and the calcium concentration increase. The concentration of antimony hardly changes between the different recipes. The low lead

concentrations are a consequence of the rather low pH values of the leachates. Lead leaching increases only very rapidly above pH 12 [4].
The relationship between As and Ca leaching, the pH value and the type of cement used can better be understood from Figure 1. The amount of Ca leached from the S/S sample, and the leachate pH can be related to the amount of CaO present in the cement used for solidification. As more Ca is present in the leachate, the pH of the leachate rises, and accordingly the concentration of As decreases. Thus, the cement type used is more effective in the order: Cem III, Cem II, Cem I, Ecobind 50. Nevertheless, the concentration of arsenic in the leachate, in this series of experiments, does not reach the minimum value of ca. 5 mg/l, which is obtained when lime is added to the S/S sample. The still high values for the As concentration are a consequence of the low Ca concentrations. Calculating the saturation indices (SI) for the compounds $CaHAsO_3$ and $Ca(OH)_2$ shows that the first compound is formed, whereas the second is in a state of undersaturation.

Semi-dynamic leaching

The 4 different S/S samples (Table 2) were subjected to the semi-dynamic leach test, whereby after each interval of static leaching, the leachate pH was measured. The pH increased during the first leaching intervals, but rapidly a constant value of ca. 11.5 was reached, for all the samples. No significant difference in leachate pH between the different S/S samples, as occured for the leachate pH values of the extraction test, was observed. The leachates collected over the entire leach test were analysed for Ca, As, Sb and Pb. The fractions released over the different leach periods were summed to calculate the CFR value and plotted versus the square root of the leach time. In Figure 2, the CFR plots for As are presented.
From these plots it can be seen that the fraction of arsenic leached, at the end of the test, from the S/S samples increases in the following order: Cem I (3.3%) < Eco (7.0%) < Cem III (8.2%) < Cem II (10.7%). Also the CFR values for calcium increase in the same order: Cem I (5.5%) < Eco (6.6%) < Cem III (7.6%) < Cem II (8.4%).
Also the CFR plots for Sb and Pb follow the same trend. The cumulative fractions of Sb released for the 4 S/S samples vary between 3.7% and 5.0%; those for Pb vary between 0.05% and 0.07%.
For the leachate of each static leach period, the saturation index SI for the compound $CaHAsO_3$ is calculated using the measured concentrations of Ca, As and the leachate pH. During the total duration of the semi-dynamic leach test (21 periods of static leaching) the SI values for all of the 4 S/S samples remained negative, indicating that the leachate is in a state of undersaturation in regard to the compound $CaHAsO_3$ and that no precipitate is formed. Thus, the elements Ca and As coming out of the S/S sample and into the solution do not affect one another. Their concentration in the leachate is the result of the ease with which they are released from the S/S sample, and thus of the integrity of the monolithic S/S sample. This explains the order of the CFR plots for the 4 samples: it is the same for all the elements (Ca, As, Sb and Pb). The sample that releases the highest fraction of the element As (sample Cem II), also releases the highest fraction of Ca, Sb and Pb. The same is true for the sample that releases the second, third and fourth highest fraction of the respective elements.
The CFR plots for the elements Ca, Sb and Pb can all be fitted by a straight regression line. The plots for arsenic initially show a different behaviour, but after 6 intervals of static leaching, the plots can also be fitted with a straight regression. From the slope of these straight lines, the effective diffusion coefficients can be calculated. These are given for Ca and As in Figure 3.

Conclusions

Samples were prepared with different types of cement. At the end of the extraction test performed on the samples, chemical equilibrium was reached in the leachate, with formation of the compound $CaHAsO_3$. $Ca(OH)_2$ however was not formed. With only the formation of $CaHAsO_3$ in the leachate, the arsenic concentration cannot be lowered to the value of 5 mg/l that is reached with samples prepared with lime addition (where the Ca concentration reaches values of ca. 900 mg/l). The concentration of Ca in the leachate and the leachate pH can be related to the amount of CaO present in the cement type.

During the semi-dynamic leach test, performed on the same set of samples, the compound $CaHAsO_3$ is not formed in the leachate. The release of the contaminants is a consequence of the physical structure of the monolithic S/S sample. No clear relation could be found between the composition of the cement and the concentration of the contaminants in the leachate. Leachability indices can be calculated and can be compared with those from S/S samples prepared with lime. This indicates that As has a smaller leachability index (is more released) from the S/S samples prepared with only cement compared to the S/S samples prepared with lime addition, whereas Ca has a higher leachability index (is more retained).

References

[1] Dutré V. and Vandecasteele C., An evaluation of the solidification/stabilisation of industrial arsenic containing waste using extraction and semi-dynamoic leach tests, Waste Manag., in press.

[2] DIN Deutsches Institut für Normung, DIN 38 414 S4, Oktober 1984.

[3] Côté P.L., Constable T.W. and Moreira A., An evaluation of cement-based waste forms using the results of approximately two years of dynamic leaching, Nucl. Chem. Waste Manag. 7 (1987) 129-139.

[4] Conner J.R., Chemical fixation and solidification of hazardous wastes, Van Nostrand Reinhold, New York, 1990.

Table 1

Composition of cement types, major compounds (wt%)

Cement type	Al_2O_3	CaO	Fe_2O_3	SiO_2
Cem III/B 42.5 HSR L	8.5	46.5	2	28.5
Cem II/A-M 32.5 R	8.6	53.3	3.6	24.5
Cem I 52.5	5	63.3	3.1	19.8
Ecobind 50	4	68	3	20

Table 2
Solidification recipes for the 4 S/S samples

Sample	Cem III/B 42.5 HSR L	Cem II/A-M 32.5 R	Cem I 52.5	Ecobind 50	W/C
cem III	2.2	0	0	0	0.55
cem II	0	2.2	0	0	0.55
cem I	0	0	2.2	0	0.55
eco	0	0	0	2.2	0.64

Table 3
Leachate pH and leachate concentration (mg/l)

Sample	pH	Ca	As	Sb	Pb
cem III	11.41	222	295	24.6	nd
cem II	11.63	255	134	15.4	0.01
cem I	11.81	204	94.6	14.7	0.02
eco	12.03	485	18.3	14.8	0.31

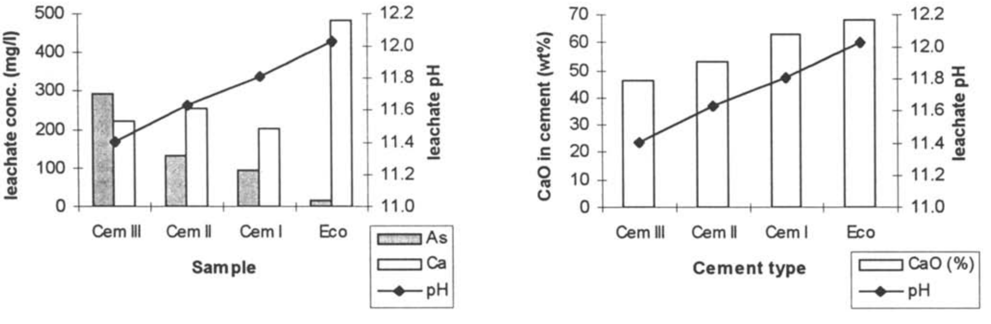

Figure 1 Leachate concentration of As, Ca and leachate pH of the 4 samples (left); amount of CaO (wt%) in the cement types (right)

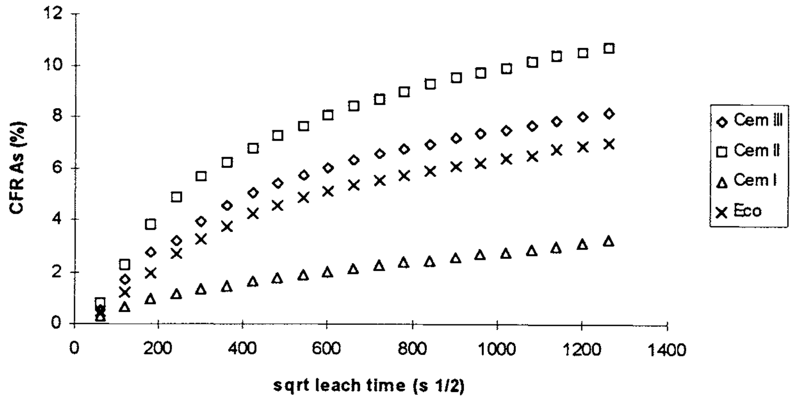

Figure 2 CFR plot for arsenic for the 4 S/S samples

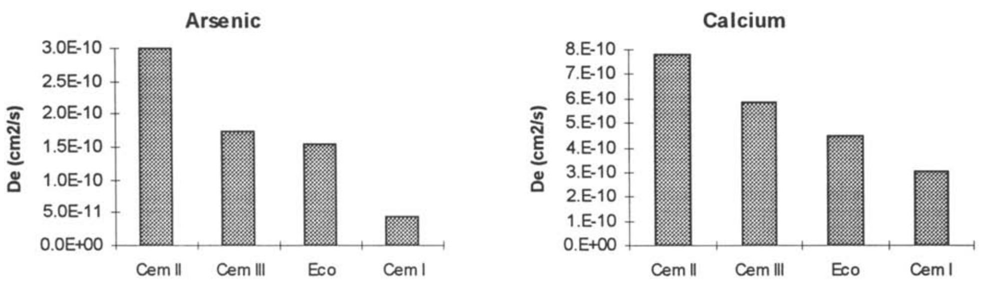

Figure 3 Effective diffusion coefficients D_e (cm^2/s) for As and Ca