Cementitious binders for immobilization of hazardous elements

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Abstract
The paper deals with development of cementitious binders for immobilization of certain toxic elements or groups of elements (oxyanions-forming elements, heavy metals, amphoteric elements). The base of the binders for stabilization of cationic and certain anionic contaminants are clinkers with phosphorus incorporated into the structure of clinker silicates. Hydration of such binders results in formation of phases with the apatite structure, which is known to be able to immobilize hazardous elements, and belite and alite structures for formation of binding hydrosilicates, ensuring the physical compactness of the hydrated matter and also the fixation of some toxic elements. Further binders tested for immobilization properties were clinkers with other types of anionic substitutions in belite and alite (SO_3) or other cement types (e.g., calciumaluminate - CAC), their mixtures with supplementary additives (sorbents, additives changing the Ca/Si ratio of C-S-H gel, or substance providing phosphorus for formation of insoluble compounds with apatite structure). The prepared binders were mixed with water doped with various toxic elements; after a defined period of cement stone hydration the specimens were subjected to long-term testing of leachability of individual toxic elements. The research methods involved besides leaching tests were also optical and electron microscopy.

Keywords
cementitious binders, toxic elements, leachability test, immobilization, WDX analysis

1. Introduction

The main goal of stabilization or solidification (s/s) is steady reduction of the mobility of toxic substances contained in processed wastes [1]. Stabilization lies in a change of physical and/or chemical properties of wastes by mixing them with proper additives [2]. Currently, s/s technique is recognized as one of the solutions to fix contaminants and has been identified by the US EPA (Environmental Protection Agency) as the Best Demonstrated Available Techniques for 57 regulated hazardous wastes [3]. Depending on the nature of the waste and the type of utilized admixtures, various physico-chemical reactions occur in the treated waste materials – sorption, substitution, hydration, precipitation, encapsulation. The stabilized waste can be disposed in a landfill or utilized in a suitable way – e.g. as building material – without introducing a risk of ensuing contamination of the environment.

The aim of this research project is development of special binders for immobilization of certain toxic elements or groups of elements (oxyanions-forming elements, heavy metals, amphoteric elements). The base of the binders for stabilization of cationic and certain anionic contaminants will be clinkers with phosphorus incorporated into the structure of clinker minerals. Hydration of such binders results in formation of phases with the apatite structure, which is known to be able to immobilize hazardous elements [4, 5] and belite and alite structures for formation of binding hydrosilicates, ensuring the physical compactness of the hydrated matter and also the fixation of some toxic elements.

The main object of research is dicalciumsilicate and tricalciusilicate with isomorphous admixture of Al/Ca phosphates („phosphobelite“ or „phosphoalite“); to a lesser extent, other types of anionic substitutions in C_2S and C_3S or other solid-solution mineral phases („sulfobelite“) or other cement types (e.g., calciumaluminate) or other supplementary additives (sorbents, additives changing redox state of hazardous elements) can be utilized to bind toxic elements.

2. Materials and methods

In order to assess the immobilization efficiency of different simple and blended binders, test bodies were prepared with mixing water enriched with soluble salts of toxic elements. Their concentrations had two constraints: one is the fact that high contents of heavy metal cations (for example Cu, Zn, Sn, Cd) with highly insoluble hydroxy compounds in alkaline solutions retard setting [6]. The other constraint is in detection limits of the method of leachate analysis. This does not make much problems with leachates obtained by the so called batch („shaken“) method, but can be difficult in case of the long-term, monolithic („tank“) test, where the target concentrations are in ppb range. The resulting compromise was 1000 – 2500 mg/kg dry binder paste. Expectedly, there was certain delay in the start of early hydration, but final strengths were comparable with controls without toxic elements addition.

The large number of binders to be tested led to choosing toxic elements representative of the main groups of toxic elements: cations-forming Cd, Ni (true "heavy metals"), Pb and Zn (amphoteric heavy metals) and anions-forming metals and metalloids (Cr, V, As). The soluble salts used were combined in the following way: $Pb(NO_3)_2$ + $CdNO_3.4H_2O$, $ZnSO_4.7H_2O$ + $NiCl_2.6H_2O$, K_2CrO_4+NH_4VO_3 and $NaAsO_2$ was used alone. Each salt was added in amount corresponding approximately to 2 grams of each toxic element per 1 kg of binder. The chemicals were first dissolved in a constant volume of demineralized mixing water assigned for processing of the given binder. Pastes prepared from individual cement binders were cast in forms with dimensions 2 x 7 x 10 cm and stored in humid environment, where they matured for 28 days. More than 100 hydrated test bodies were prepared for long-term monolithic testing. Collaterally, the same number of test bodies was prepared for determination of the contents of studied elements in dry matter by ICP-OES and for determination of toxic elements leachability by the batch method.

The properties of mortars were confronted with the control – ordinary Portland cement CEM I 52.5N. The commercial cements were used alone or blended together with cement included OPC, Portland blast furnace cement, calcium aluminate cement (CAC) and white Portland cement. The specially prepared phosphorus-doped clinkers were developed within another project, aimed at safe disposal of meat-and-bone meal by utilizing both as alternative fuel and as calcium-rich raw material [7]. Other specially prepared cements were made from low-saturated clinkers doped with sulfur [8] and reference alite-rich and belite-rich clinkers not doped with P or S. Ten kilograms of each raw meal was mixed in the calculated proportions and grinded in order to obtain amount of clinker sufficient for performing planned testing of cements made of them. Sulfur-doped low saturated clinkers with prevalent belite were burned at 1350°C, the other clinkers at 1450°C in superkanthal furnace with holding time individually chosen to keep the content of residual free lime low enough not to cause unwanted volume changes during hydration. The phase composition was quantified using microscopic point counting.

The burned clinkers with gypsum added as setting regulator were grinded to cements with the same specific surface of 400 m^2/kg. The following parameters were determined for them: specific gravity, specific surface, particle size distribution, setting and volume stability according to EN, setting according to Tussenbrock, heat of hydration, measured by adiabatic calorimeter, dissolution heat according to EN and compressive and tensile strengths after 2, 7, 28 and 90 days of hydration according to EN.

In the ensuing phase, test bodies were prepared from various binders with added pure chemical compounds of the toxic elements for the purpose of study of their leachability. The binders that were used in this step can be divided into five groups (see Table 1).

Table 1. Overview of cement binders for testing of PHE immobilization

<table>
<tr><th>Group</th><th>Binder</th></tr>
<tr><td>Reference binders</td><td>CEM I 52.5N, CEM II/B-S 32.5R, White CEM I
CAC - Gorkal 40, Gorkal 50
A97S0 - high alite clinker, not doped with foreign elements
B80S0 - high belite clinker, not doped with foreign elements</td></tr>
<tr><td>Cements from clinkers doped with P_2O_5</td><td>AP1 (cement from alite clinker with 1% P_2O_5)
AP2 (cement from alite clinker with 2% P_2O_5)
CAC 70% + AP1.5 30% (alite clinker with 1.5% P_2O_5)
AP7/MKM (alite clinker with 7% P_2O_5 as granules of MBM ash)</td></tr>
<tr><td>Cements with addition MBM ash</td><td>CEM I 52.5N (90%) + MBM ash (10%)
White CEM I (90%) + MBM ash (10%)
CAC (95%) + MBM ash (5%)
CAC (90%) + MBM ash (10%)
CEM I 52,5N (50%) + CAC (40%) + MBM ash (10%)</td></tr>
<tr><td>Cements with addition of diatomite</td><td>CAC (80%) + calcined diatomite (20%)
CEM I 52.5N (75%) + raw diatomite (20%) + MBM ash (5%)
CEM I 52.5N (80%) + raw diatomite (20%)
CAC (75%) + calcined diatomite (20%) + MBM ash (5%)
CAC (80%) + raw diatomite (20%)
CAC (75%) + raw diatomite (20%) + MBM ash (5%)
CEM I 52.5N (70%) + CAC (10%) + raw diatomite (20%)</td></tr>
<tr><td>Clinkers doped with SO_3</td><td>B89S5, B83S8, A92S8, B90S6MA2.5 – cements made from clinkers doped with SO_3, those do not contain yeelemite (numbers after S correspond to SO_3 concentration in %)</td></tr>
</table>

Technological parameters of all specially prepared cements were satisfactory. The strength parameters of all cements are excellent and also the lowest ones in sulfobelite cement B83S8 are suitable for solidification purposes. It is nevertheless necessary to count with distinct decrease in technological parameters after the addition of real waste.

In the batch leaching test, the hydrated (min. 28 days) test bodies were crushed <10 mm, the material was mixed with distilled water at S/L = 1:10 and shaken "over head" for 24 hours. The decanted leachates were filtered through a 0.45 µm pore filter. The leachates were analyzed by ICP-MS (Agilent).

In the long-term semi-dynamic test, performed according to NEN7345, a monolithic specimen is subjected to leaching in a closed tank to evaluate surface area related release. The leachant demineralized water is renewed after 8 hours and 1, 2, 4, 9, 16, 36, 64 days using a leachant to product volume ratio (L/V) of 5. The leachate was also filtered and analyzed by ICP-MS.

For the purpose of assessing the (re)distribution of the used toxic elements upon hydration, fragments of cement paste after 28 days of hardening were embedded in epoxy resin (Araldite®), polished and studied by optical microscopy methods. Furthermore, the polished sections were coated with carbon and analyzed with electron microscopy and WDX analysis, using microprobes CAMECA SX 100 and Jeol JXA8600. The study involved acquisition of X-ray maps of the main binder constituting elements (Ca, Mg, Si, Al, Fe, S, P) and respective trace elements given above.

3. Results and discussion

3.1 Results from the batch test

There are aspects in the batch test that do not allow to acquire through it a knowledge of the toxic element´s behavior under conditions fully corresponding to real situations e.g. in landfills. These aspects involve in case of cementitious s/s materials the facts that

- soon after the start of the test, the pH of the leachate settles at levels much higher (> 11) than precipitations or surface water in the landfill
- the prescribed form (granular material < 10 mm size) does not correspond to the monolithic nature of the stabilizates/solidificates
- the length of the leachate–stabilizate contact is not comparable with the length of their contact in real storage site.

This test nevertheless provides a quick orientation, especially in optimization of binder designs. In case of our research, the leachabilities are compared with leachability found in reference OPC mortar, which behaves in the test in a similar way, although the leachant pH in experiments with calcium aluminate cements is about 1 to 1.5 units lower than the leachant from OPC reference.

In all experiments, the concentration in the leachate was compared with the concentration in leachate from reference OPC; both normalized with the contents in the dry mortar (as these are only roughly equal). The results from chosen mortars are given in Table 2.

From the data in Table 2 several possible conclusions can be drawn:

- Calculations of Pearson´s correlation coefficient from 2x2 correspondence tables have shown that the presence of calcium aluminate cement in the s/s binder has a strong positive effect on the immobilization of all abovementioned toxic elements; the strength of the correlation decreases from Pb (r=0.905) through Cr (r=0.73), V (r=0.66), Zn (r=0.65) to As (r=0.61). The positive effect of CAC on the immobilization (as compared with OPC) can be explained by the substitution of the toxic elements in the products of hydration of the main CAC clinker phases [9] or simply by the fact that most of these elements show the solubility minimum in pH ranges slightly below the range in OPC, but equal to that found in pore solutions in CAC (cf. Fig. 1).
- White cement compared with common Portland cement (PC) shows lower leachability of Pb, Cd, Zn, Cr, Ni and V, but increases leachability of As.
- From the phosporus-doped cements (AP1, AP2, AP7/MBM), the lowest leachability shows in the case of Pb and As the one with the lowest P_2O_5 content (AP1). Chromium and zinc, on the contrary, are least leachable from the cement with the highest P_2O_5 content (AP7/MBM). Anyway, all tested P-enriched binders show leachability of all studied hazardous element lower than those in the reference binder CEM I 52.5N.
- Sulfobelite cements very strongly increase the leachability of all anions-forming elements (Cr, V and in two cases As) and in one case also that of Pb and in another case of Zn. The toxic elements have probably been substitutionally incorporated into ettringite and subsequently released upon its transformation to monosulfate. Increased leachability of some elements from clinkers doped with sulfur can also be caused by a slow hydration and hardening of belite which is present in predominant amount.

- The addition of diatomite has certain positive effect on the immobilization of toxic elements – an effect that can probably be explained by the release of reactive silica into the hydrating mortar, which changes the C/S ratio of the C-S-H product towards the composition better fixing the toxic elements. Richardson [10] confirms that in the case of cement – puzzolana blends, C/S ratio in C-S-H is changed and also morphology of C-S-H is modified compared to hydrated OPC.
- The results obtained with blended binders have shown that the addition of MBM ash decreases the leachability of Zn, Ni and As, but in one case increases that of Cr (binder # 27 in Table 2) and in another (binder # 17 in Table 2) of V.
- The most promising combinations occurred to be the combination of 90 wt. % of calcium aluminate cement with 10% of MBM ash, which releases distinctly lesser amounts of all PHEs, in case of Pb, Cd, Zn, Ni, Cr and As to less than 28% of that observed in the reference PC. Another promising is a blend of 70% CAC with 30% of P-doped clinker AP1.5. The fixation of these elements can probably be attributed to formation of discrete microaccumulations of insoluble metal hydroxides, in case of phosphorus-enriched clinkers of precipitates of analogues of apatite, where the toxic elements substitute both Ca (Zn, Ni, Pb, Cd) and PO_4^{3-}groups (VO_4^{3-}, CrO_4^{3-}, AsO_4^{3-}).

Table 2. Leachability of individual toxic elements in % of leachability of reference binder (CEM I 52.5N)

Binder #	Binder description	Pb	Ni	Zn	Cr	V	As
1	CEM I 52.5N	100	100	100	100	100	100
33	CEM II/B-S 32.5R	183	92	81	46	51	33
2	White CEM I	65	<3	50	45	43	153
44	CAC - Gorkal 50	0.6	35	23	13	0.1	44
6	AP1 (alite clinker with 1% P_2O_5)	49	<3	34	54	62	55
7	AP2 (alite clinker with 2% P_2O_5)	89	<3	23	53	81	94
8	AP7/MKM (alite clinker with 7% P_2O_5 as granules of calcined MBM)	60	<3	26	46	43	88
13	B89S5 (belite clinker with 5% SO_3)	37	30	<3	342	233	40
15	B83S8 (belite clinker with 8% SO_3)	107	51	<3	188	188	36
9	CEM I 52.5N (90%) + MBM ash (10%)	58	<3	21	48	41	52
10	White CEM I (90%) + MBM ash (10%)	69	<3	35	70	68	112
17	CAC 95% + MBM ash 5%	2	58	21	7	136	20
11	CAC (90%) + MBM ash (10%)	1	4	17	27	0.1	3
12	CEM I 52.5N (50%) + CAC (40%) + MBM ash (10%)	18	79	25	46	22	10
18	CAC 80% + calcined diatomite 20%	0.1	<3	14	2	55	89
27	CEM I 52.5N 75% + raw diatomite 20% + MBM ash 5%	23	<3	<7	165	75	7
21	CEM I 52.5N 80% + raw diatomite 20%	13	27	7	117	123	59
24	CAC 75% + calcined diatomite 20% + MBM ash 5%	0	35	10	1	46	20
20	CAC 80% + raw diatomite 20%	1	29	7	4	0.2	70
40	CAC 75% + raw diatomite 20% + MBM ash 5%	0.3	30	12	0.4	0.3	10
26	CAC 70% + AP1.5 30%	0.1	<3	5	2	62	1
42	CEM I 52.5N 70% + CAC 10% + 20% raw diatomite	1	40	25	170	19	29

3.2 Long term leachability experiments

The mode of leaching was studied with the use of long-term monolithic "tank" tests according to NEN EU 7375. The results in this area show that the leaching of toxic elements is diffusion controlled; the overall thickness of the surficial layer from which they are leached over 3 months does not exceed 0.2 mm. Cumulative long-term (64 days) release lower than in the reference CEM I 52.5N was observed in case of zinc in large majority of tested binders. On the contrary, long-term release of chromium was lower only in a few of them; the exceptions are binders from P-doped clinkers (AP1, AP1.5), binders containing MBM ash and binders from sulfobelite clinkers.

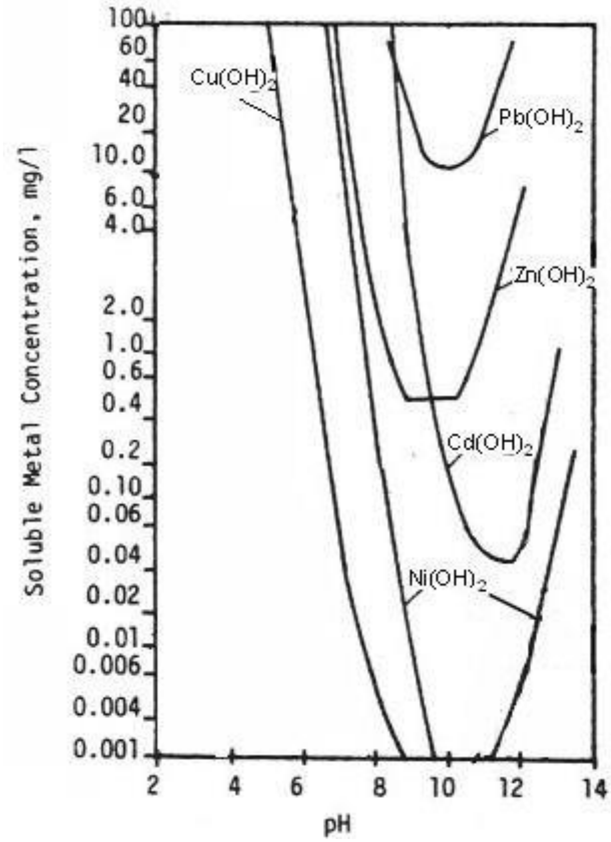

Fig. 1 Solubilities of selected toxic elements´ hydroxides and sulfides in relation to pH (after Bhattacharyya et al. 1981 [11])

3.3 X-ray mapping

The electron microprobe study through the acquisition of X-ray maps and BSE images of mapped areas has shown, that in most cases the hazardous elements, though applied dissolved in water, eventually form discrete microaccumulations. In binders based on P-doped clinkers, Cr and Ni precipitated as discrete microparticles (Fig. 3 and 6), while V and Zn occur finely distributed in the matrix (Fig. 4, 7).

Ni forms microaccumulations also in other types of binders, especially in CAC-based binders. Vanadium and nickel occur in most studied mortars homogenously distributed. Arsenic was dispersed in the hydrated binder matrix relatively homogenously, with moderately increased concentrations observable around grains of MBM ash as well as relict CA clinker grains (cf. Fig. 8, 9). In most binders studied by X-ray mapping, cadmium occurs to form microaccumulations or increased concentrations in porous MBM ash particles (Fig. 10).

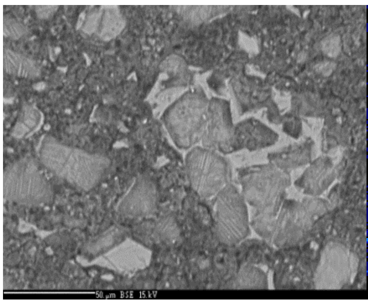

Fig. 2 Binder #6 (BSE image, clinker with 1% P_2O_5)

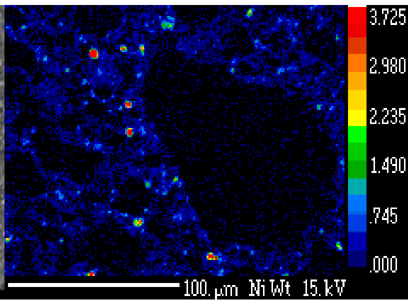

Fig. 3 Binder #6, X-ray map of Ni

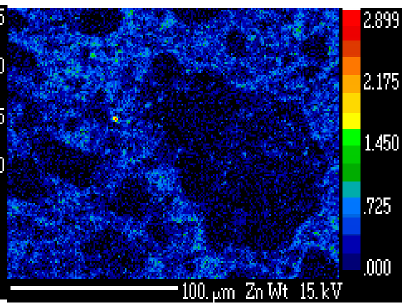

Fig. 4 Binder #6, X-ray map of Zn

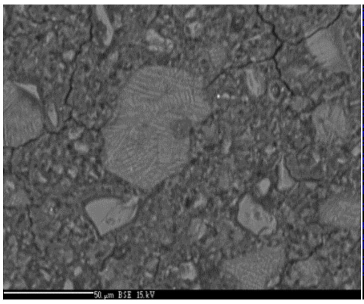

Fig. 5 Binder #6 (BSE image, clinker with 1% P_2O_5)

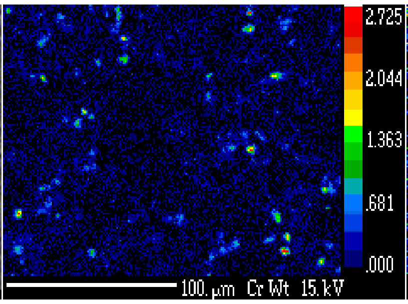

Fig. 6 Binder#6, X-ray map of Cr

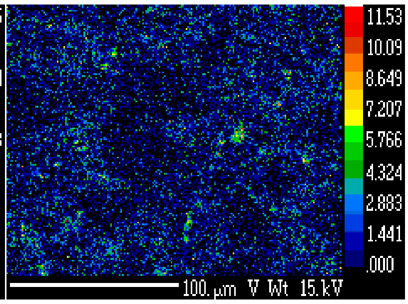

Fig. 7 Binder #6, X-ray map of V

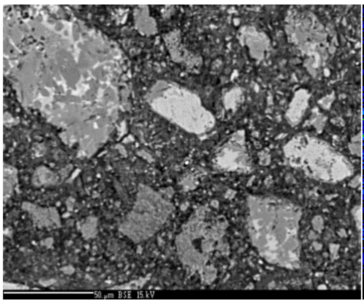

Fig. 8 Binder #11 (BSE 90%CAC + 10% MBM ash

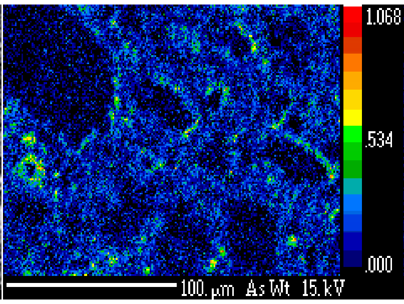

Fig. 9 Binder #11, X-ray map of As

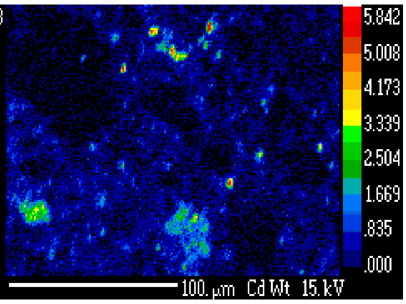

Fig. 10 Binder #11, X-ray map of Cd

Conclusions

All used test methods have shown that the immobilization properties of the ordinary Portland cement are weaker than those of binders containing calcium aluminate cements and/or cement enriched with phosphorus; among the latter, cements based on phosphorus-doped clinkers are more efficient than binders with MBM ash addition. In OPC-based cements, addition of diatomite can help to improve the immobilization of toxic elements by changing the Ca/Si ratio of C-S-H hydrates.

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