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INVESTIGATION ON MSW FLY ASH TREATMENT BY REACTIVE CALCIUM ALUMINATES AND PHASES FORMED

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ABSTRACT

In this study hydration reactions of MSW fly ash with an experimental $C_{12}A_7$ / C_3A - cement are investigated. The fly ash has high contents of soluble calcium sulphates, alkali chlorides and heavy metals. During the first hours the calcium aluminates react with the calcium sulphate to form ettringite. On condition that the amount of added cement is sufficient, after complete consumption of calcium sulphates further hydration leads to additional crystallization of Friedel's salt. The same course of hydration is found for synthetic model mixtures of calcium aluminate + gypsum + alkali chlorides. TEM/EDX-analysis indicates that ettringite is able to incorporate the heavy metals Pb and Zn by substitution, but no contents of Cl^- are detected. Treatment by reactive calcium aluminates could be a suitable method for the immobilization process of a wide range of toxic wastes.

Introduction

Municipal solid wastes (MSW) are increasingly incinerated. The generated fly ashes often contain high amounts of soluble sulphates, chlorides and heavy metal salts and need to be disposed of safely. To protect the environment these salts must be immobilized and deposited in suitable disposal sites. The use of cement based systems and the fixation capabilities of cementitious minerals have been discussed, [1, 2]. In many cases the leaching susceptibilities of these solidified wastes can be decreased drastically. With cements like OPC very often delayed setting and weak hardening occur. For example, setting can be seriously delayed by the influence of zinc on the hydration of calcium silicates, [3]. Therefore, many existing solutions are not adequate and the problem of stabilization remains. The use of calcium aluminate cements can be a suitable approach to eliminate such negative effects.

The stabilization and immobilization process of MSW fly ashes with high contents in SO_3 by addition of calcium aluminates is characterized by rapid formation of mineral reservoirs with ettringite-type structure. The extraordinary capability of ettringite for the crystallo-chemical fixation of toxic elements has been discussed, [4, 5, 6, 7]. In the published literature there is little information about the characterization of MSW fly ash [8, 9].

The objectives of this study were to contribute to the present knowledge about the chemical and mineralogical characteristics of MSW fly ashes and to focus on the hydration reactions taking place when these waste materials are stabilized and immobilized by reactive calcium aluminates. The new phases formed and fixation mechanisms of SO_4^{2-}, Cl^- and heavy metals were investigated.

Materials and Experimental

Calcium aluminate used in this study was a highly reactive $C_{12}A_7$ / C_3A - cement (CAC), a laboratory product kindly provided by Lafarge Fondu International, with a molar ratio of CaO : Al_2O_3 of 2.0. Therefore, to simplify matters, the calcium aluminate cement can be formulated as "C_2A". The ratio of $C_{12}A_7$: C_3A is approximately 3:1. By XRD traces of α-Al_2O_3 were detected. The specific surface area (Blaine) is 4000 cm^2/g.

The sample of MSW fly ash (electrofilter ash) was from a French municipal solid waste incinerator power plant. The chemical analysis is given in TABLE 1. The mineralogical characterization of the fly ash was carried out mainly by XRD, SEM and SEM-EDX.

TABLE 1
Chemical Analysis of the MSW Fly Ash [% by Weight]:

SiO_2	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**SO_3**	**CO_2**	**Cl**	**P_2O_5**
20.2	12.3	1.2	1.4	19.3	2.5	6.2	6.4	8.3	1.3	10.5	1.3
ZnO	**PbO**	**CuO**	**CdO**	**As_2O_3**	**Hg**		H_2O + carbon				
3.0	1.2	1250*	514*	65*	21*		~5				

*ppm

Mixtures of fly ash, calcium aluminate and water were processed in the following way: fly ash and CAC were mixed by shaking in a plastic container. After addition of deionized water the paste was stirred by hand for 5 minutes, cast in cylindrical moulds of 30mm x 50mm and then cured at 25°C and 100% relative humidity. Fly ash / calcium aluminate ratios and water/solid ratios were varied. Samples were drilled out after chosen periods and investigated by XRD. The course of hydration of the mixtures was additionally followed by heat flow calorimetry. Further information about the characteristics of hydration products and microstructure of the hardened pastes was obtained by SEM and TEM/EDX investigations.

When mixed with fly ash the calcium aluminates mainly react with calcium sulphates and Cl^-. To investigate the hydration reactions of $C_{12}A_7/C_3A$ - cement with calcium sulphate in the presence of alkali chlorides, but without the influence of other ions, model mixtures of calcium aluminate + gypsum + alkali chlorides were shaken continuously in polyethylen bottles at w/s=10 and T=25°C. The ratio of calcium aluminate : gypsum was varied and for a certain ratio a set of identical samples was prepared respectively. To get information about the course of hydration the suspensions were filtered off after various periods of time. The solids were investigated by XRD directly after filtration as wet pastes at 100 % relative humidity under exclusion of CO_2 using a 'wet cell'. The procedure of preparation is described, more in detail, elsewhere, [7].

For the designation of XRD reflections in figures of this paper the following abbreviations are used: e=ettringite, mcl=monochloroaluminate, a=anhydrite, h=hemihydrate, g=gypsum, n=sodium chloride, k=potassium chloride, q=quartz, cc=calcite, ge=gehlenite, an=anorthite, r=rutile, p=perovskite.

Special leaching tests on the fly ash and on hydrated CAC / fly ash mixtures were carried out to support identification of mineralogical composition and to investigate chemical fixation of heavy metals, SO_4^{2-} and Cl^-. Fly ash and hydrated mixtures were carefully powdered to particle size < 0.35 mm (fly ash particles are nearly all below this limit). 2g of powder were shaken with 50 ml of solvent in a polyethylen bottle for 10 minutes. The leaching period was kept short to avoid re-precipitation. After filtration the residues were dried in normal air and investigated by XRD and SEM/EDX. The filtrates were chemically analyzed. Solvents: NaOH-solution with pH=11.5, deionized H_2O, acetic acid with various concentrations from 0.01-N to 2-N, 2-N HCl.

Results

Mineralogical characterization of MSW fly ash

By XRD (supported by leaching tests) the following mineralogical phases were detected:

main phases:	**in minor quantities:**	**in traces:**
- alkali chlorides: KCl, NaCl - anhydrite, $CaSO_4$ (orthorhombic)	- gypsum, $CaSO_4 \cdot 2H_2O$ - calcite, $CaCO_3$ - quartz, α-SiO_2 - rutile, TiO_2 - gehlenite, C_2AS - anorthite, $(Ca,Na)(Al,Si)_2Si_2O_8$	- ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ - monochloroaluminate, $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ - hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$ - perovskite, $CaTiO_3$ - laurionite, PbOHCl

SEM and light-microscopic studies additionally reveal presence of platy carbon particles and high contents of spheroidal glass particles (FIG. 1).

By optical light microscopy the glass spheres are observed to be very inhomogeneous ranging from colorless and transparent, yellowish or brownish colored and transparent up to black and

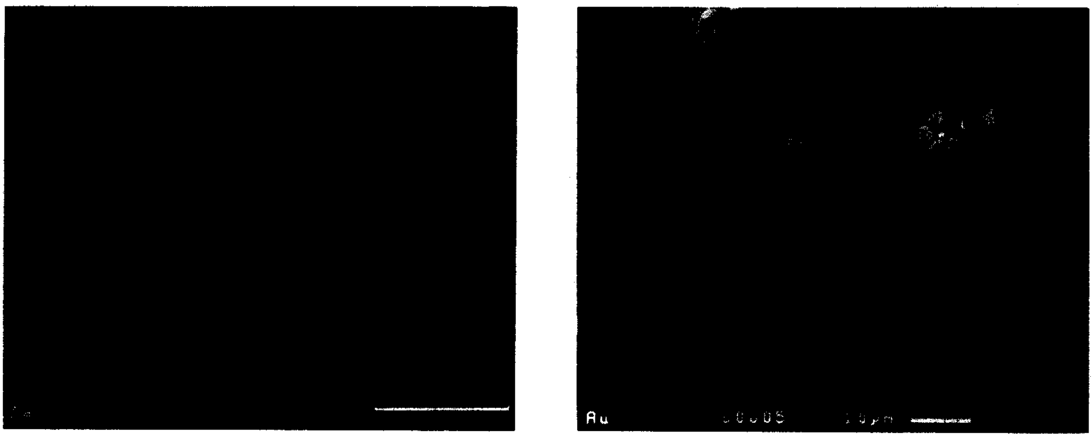

FIG. 1
SEM Micrographs of MSW Fly Ash. Left: Agglomeration of Cubes of Alkali Chlorides, small Needles of Ettringite, Calcium Sulphates and spheroidal Glass Particles.
Right: Example of a Glass Sphere.

TABLE 2
SEM/EDX Analysis of Glass Spheres isolated from MSW Fly Ash, ∅ 30-150 µm.

N°	1	2	3	4	5	6	7	8
Ca	19.0	35.2	31.4	24.8	38.4	12.7	4.4	30.4
Al	12.1	9.8	11.9	23.9	24.2	26.0	18.4	9.3
Si	26.5	36.5	35.0	36.9	32.3	39.2	25.3	36.4
Na	3.4	3.8	3.8	-	0.5	9.2	17.7	5.4
K	0.5	0.4	1.8	7.0	-	4.4	6.7	0.3
Mg	4.6	2.6	-	-	-	3.7	-	-
P	-	-	-	-	-	-	20.5	-
Fe	31.3	5.6	11.8	2.1	1.4	0.8	0.8	5.0
Ti	0.8	0.8	0.6	2.5	0.6	1.2	0.2	7.3
Zn	1.1	4.0	2.6	2.0	-	2.0	3.4	4.3
Cu	-	0.5	0.5	0.9	0.5	-	0.3	0.4
Pb	0.3	0.4	-	-	2.0	-	1.0	1.2
color	black	yellow	brown	white	white	colorless	white	yellow

opaque. In TABLE 2 the results of SEM/EDX analysis of some spheres are listed. The spheres were isolated from the fly ash and carefully washed with water to remove adhesive salts and particles. The chemical composition varies in a wide range indicating high local differences in chemical composition and temperature within the waste material during the incineration process. Besides Si, Ca and Al the spheres can contain Na and K in various amounts. Black or brown spheres have high contents of iron. For nearly all investigated spheres the EDX analysis has shown contents in Ti, Zn, Cu and Pb. Sphere N° 7 is remarkably rich in phosphorus.

Gypsum, hemihydrate, ettringite and monochloroaluminate are formed subsequently by self hydration of previously dry fly ash. At the incinerator plant some water was added to the fly ash to improve storage conditions.

As shown by the following experiment, with the addition of more water the fly ash is able to hydrate further with time: the fly ash was mixed with water, w/s=0.5, and cured at 100 % relative humidity at 25°C. XRD investigation after 30 days curing indicates that about half of the anhydrite has converted into gypsum (FIG. 2). Additionally, the amount of ettringite has increased remarkably. The necessary aluminium for the formation of ettringite, obviously, has been supplied by hydration of the glass. After 70 days nearly all anhydrite has reacted and the amount of gypsum has increased considerably.

In addition, dry fly ash directly collected out of the electrofilter was investigated. This ash shows a chemical composition very close to that in TABLE 1, but contains much less water. The following phase composition was detected: alkali chlorides, anhydrite, quartz, gehlenite, rutile, calcite, perovskite, anorthite, the compound K_2ZnCl_4, glass-phase, carbon particles. The SO_3 - content of this ash is totally bound to anhydrite, no other SO_4^{2-} -bearing compound was distinguished. When mixed with water this fly ash slowly develops hydraulic reactivity (FIG. 3). In a stirred fly ash/water suspension (w/s=20) up to about 40 minutes the pH remains neutral and then relatively quickly increases to about 11. For mixtures of dry fly ash with water (w/s=0.5, curing at 100 % relative humidity) by XRD the same course of hydration as shown in FIG. 2 is detected: formation of gypsum at the expense of anhydrite and additional formation of ettringite. The hydration reaction of the fly ash must be caused by the hydraulic property of the glass phase.

Hydration of CAC / fly ash mixtures

Various mixtures with CAC contents from 5 -20 weight-% were investigated. In addition, for a

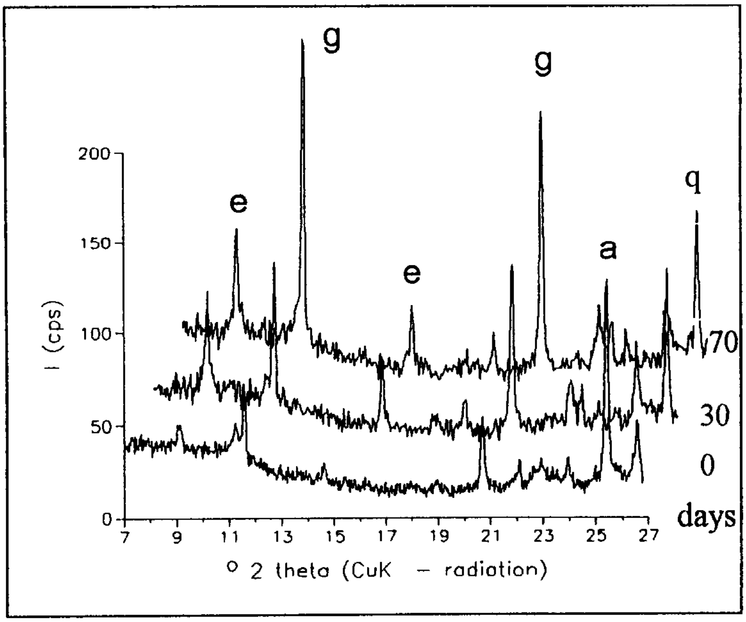

FIG. 2
XRD Diagrams of a hydrating
MSW Fly Ash / Water Mixture (w/s=0.5, T=25°C).

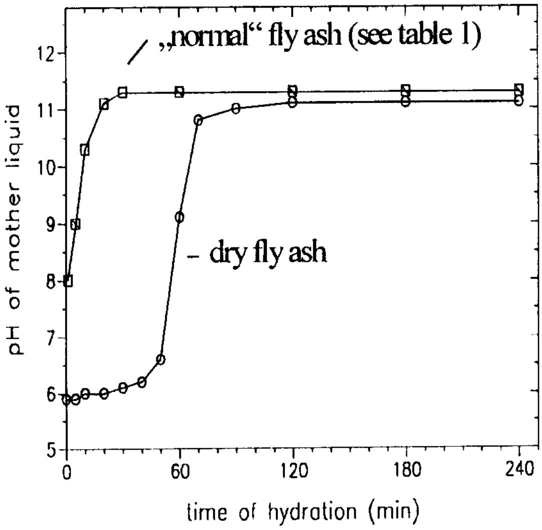

FIG. 3
MSW Fly Ash / Water Suspensions
(w/s=20), Course of pH with Time.

certain content of CAC the water/cement ratio was varied.

The XRD diagrams given in FIG. 4 show the sequence of hydration reactions in a mixture of 84.5 % fly ash + 15.5% CAC at w/c=2.7 (w/s=0.42) as a function of hydration time. During the first hours ettringite is formed significantly at the expense of CAC and calcium sulphates. At first, the more soluble sulphate phase, gypsum, is consumed by this reaction. Subsequently, the amount of less soluble anhydrite decreases. After 4 hours only traces of anhydrite are detected by XRD and amount of ettringite formed has nearly reached its maximum. After complete consumption of calcium sulphates monochloroaluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) starts to

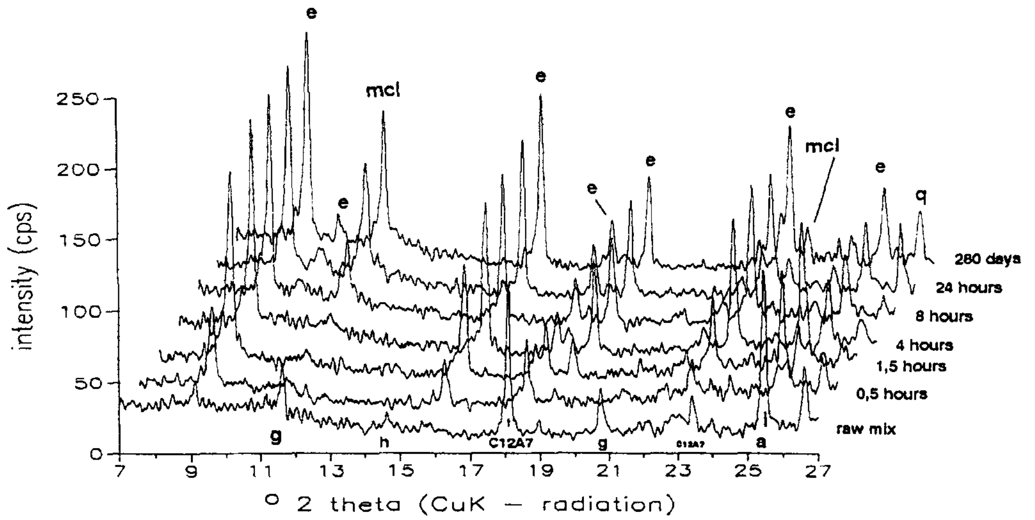

FIG. 4
XRD Powder Diagrams of a hydrating Mixture of 84.5 % MSW Fly Ash / 15.5 % CAC at w/c=2.7 (w/s=0.42).

form by reaction of the remaining calcium aluminates with Cl^- until CAC is totally consumed at about 2 days. During formation of monochloroaluminate the intensities of XRD-reflexions of ettringite remain about constant. Up to 9 months curing no further changes of the phase composition of the mixture is detected by XRD. Only a small part of total Cl^--content of the fly ash is incorporated in monochloroaluminate, the major part remains as free alkali chloride.

In order to transform all the SO_4^{2-}-content of the fly ash , which is bound to $CaSO_4.nH_2O$ (traces of ettringite in the fly ash neglected) , into ettringite the theoretical demand for CAC corresponds to a mixture of 10,7 w.-% CAC / 89,3 w.-% fly ash. This calculation refers to CaO of ettringite-stoichiometry. For this mixture the theoretical minimal water demand corresponding to the necessary crystal water of ettringite can be calculated to a water/cement ratio of 1,7.

In FIG. 5 the XRD diagrams of various CAC / fly ash mixtures, hydrated for $\geq$ 5 days, are summarized.

It can be seen clearly that for all mixtures with $\geq$ 10.7 % CAC the peak intensities of ettringite are nearly constant. Furthermore, variations of the w/c ratio have no significant influence on the amount of ettringite formed. The more the content of CAC of the mixtures exceeds 10,7 % the more lamellar monochloroaluminate is additionally formed after crystallization of ettringite.

In mixtures containing less than 10,7 w.-% CAC (= less than the amount that would be necessary to bind all sulphate of the fly ash as ettringite) the extent of ettringite formed is directly proportional to the amount of CAC. The less CAC is present the less ettringite is formed and the more the calcium sulphate of the fly ash remains unreacted. For example, in a mixture of 7.5 % CAC / 92.5 % fly ash even after 14 days of hydration unreacted anhydrite is still detected by XRD.

Generally, in all mixtures investigated the CAC has completely reacted within 2 days. During hydration, apart from ettringite and monochloroaluminate, no other complex calcium aluminium hydroxi salts were detected by XRD.

Monochloroaluminate was always observed to crystallize in the hexagonal form. Compared to

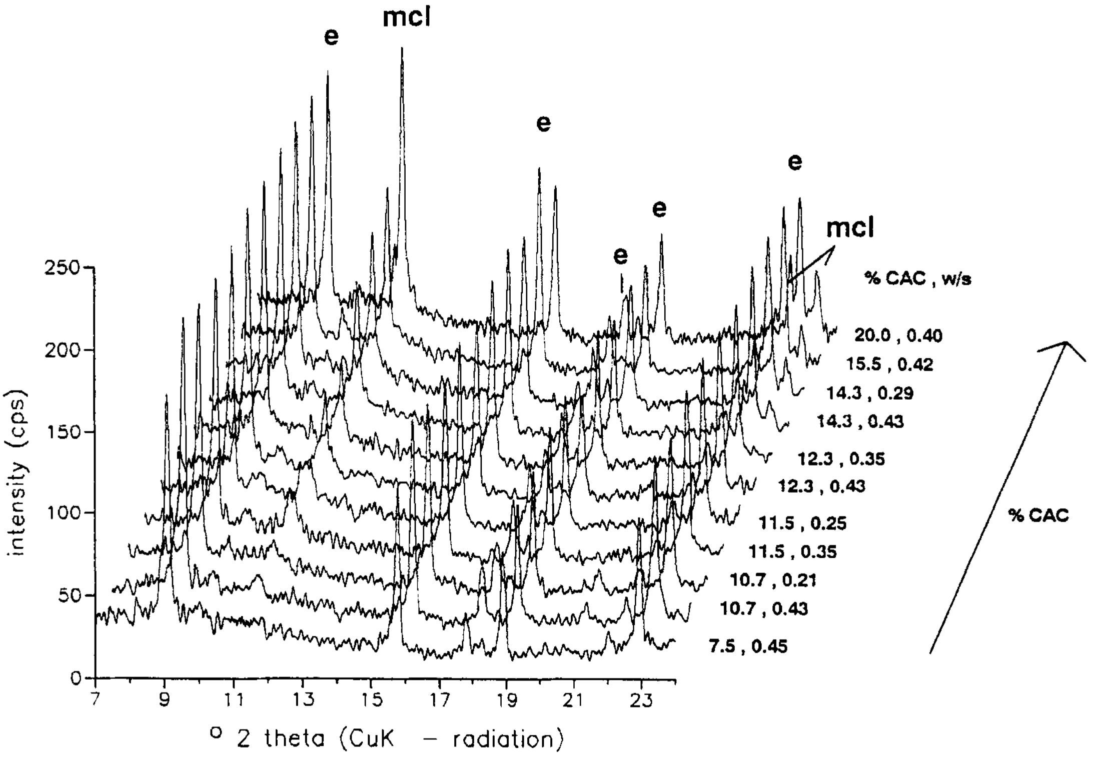

FIG. 5
XRD Powder Diagrams of Fly Ash / CAC Mixtures, Hydration Time ≥ 5 days.

pure synthetic of monochloroaluminate [10] the cell constant c_0 was somewhat increased from 46.9 Å to 47.1 - 47.2 Å. This could be caused by the partial replacement of Cl^-- ions by OH^- and CO_3^{2-} within the interlayer [11].
The microstructure of hardened CAC / fly ash mixtures is relatively porous. By SEM it can be seen that ettringite has crystallized in bunched elongated prisms with lengths up to 20 µm. Platey crystals of monochloroaluminate have diameters less than 1µm and can hardly be analysed by TEM method because of their rapid decomposition under the electron beam.

Model mixtures: hydration of CAC + gypsum in presence of alkali chlorides, w/s=10

1. "C_2A" : $CaSO_4 \cdot 2H_2O$ = 1,5 : 3 , (NaCl, KCl = 3) :

After reaction time of 7 days the XRD pattern of a hydrated mixture of 9 mmol "C_2A", 18 mmol $CaSO_4 \cdot 2H_2O$, 18 mmol KCl and 18 mmol NaCl shows exclusively reflections of pure ettringite. (Concerning the proportions of CAC : calcium sulphate : alkali chlorides, this model mixture corresponds to a mixture of 10,7 w.-% CAC / 89,3 w.-% fly ash).The XRD powder diagram of an analogous mixture, but without addition of alkali chlorides, after the same time of hydration is nearly identical. Thus, the presence of high concentrations of alkali chlorides seems not to influence formation of ettringite. Alkali chlorides remain quantitatively in solution.

In presence or absence of 3 NaCl and 3 KCl:

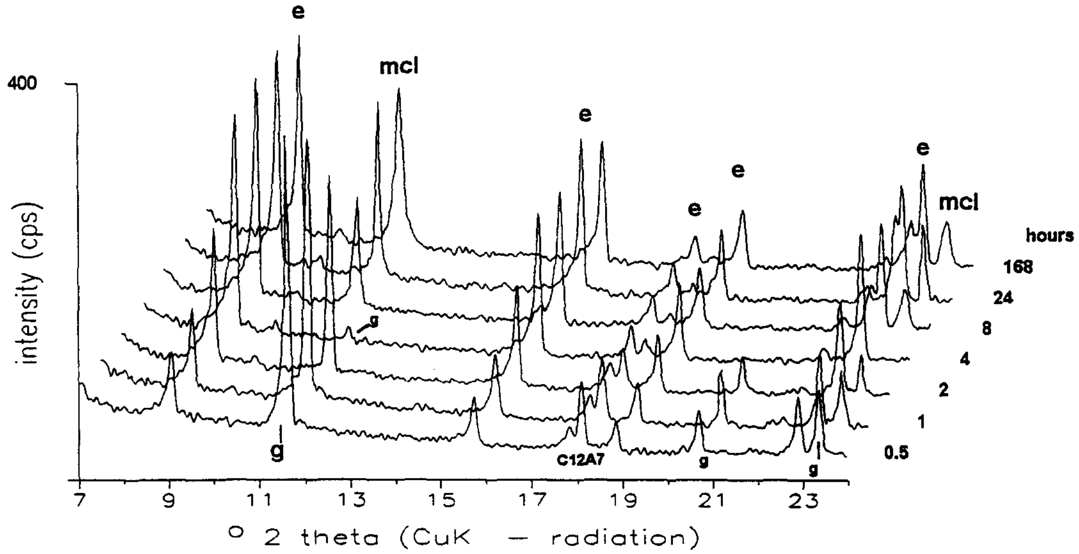

FIG. 6
XRD Powder Diagrams of hydrating Mixtures of 2.25 "C_2A" + 3 $CaSO_4 \cdot 2H_2O$ + 3 NaCl + 3 KCl; Diagrams taken directly from wet Pastes at 100% relative Humidity.

$$1{,}5\ \text{"}C_2A\text{"} + 3\ CaSO_4 \cdot 2H_2O + aq. \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + \tfrac{1}{2}\ AH_3$$

2. "C_2A" : $CaSO_4 \cdot 2H_2O$ = 2,25 : 3 , (NaCl, KCl = 3):

The XRD diagrams given in FIG. 6 show the sequence of reactions occurring in a mixture of 13.5 mmol "C_2A", 18 mmol $CaSO_4 \cdot 2H_2O$, 18 mmol NaCl and 18 mmol KCl (theoretically, concerning the proportions of CAC : calcium sulphate : alkali chlorides, this model mixture corresponds to a mixture of 16.0 w.-% CAC / 86.0 w.-% fly ash). Within the first hours gypsum and calcium aluminates react to form ettringite. At about 4 hours gypsum is consumed and only traces of $C_{12}A_7$ are present, whereas relatively high proportions of C_3A are detectable by XRD. This indicates, that in this mixture $C_{12}A_7$ reacts faster than C_3A. With progress of time monochloroaluminate is formed by reaction of the remaining CAC (mainly C_3A) with Cl^- - ions . At 24 hours this reaction is finished. Up to the maximum time of observation of 7 days no further changes are detected.

Theoretically, the hydration reaction can be formulated as follows:

$$\begin{aligned} 2.25\ \text{"}C_2A\text{"} + 3\ CaSO_4 \cdot 2H_2O + 3NaCl + 3KCl + aq. \longrightarrow\ & 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 0.88\ AH_3 \\ & + 0.38\ 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O \\ & + 3\ K^+ + 3\ Na^+ + 5.25\ Cl^- + 0.75\ OH^- \end{aligned}$$

Concerning the course of hydration no significant differences between the investigated model mixtures and mixtures of CAC / fly ash are detectable.

TEM / EDX investigations of the ettringite formed in the described model mixtures do not indicate any incorporation of Cl^-, sodium or potassium

Characterization of ettringite-phase formed during hydration of CAC / fly ash mixtures

To get direct information about the chemical composition of single crystals of ettringite analytical transmission electron microscopy was applied. Pulverized samples were leached with water to wash out the soluble alkali chlorides. In TABLE 3 5 out of 35 EDX analyses of crystals of ettringite are listed. In every case remarkable contents of Pb and Zn were detected. For the majority of investigated crystals a chemical composition close to N° 4 and 5 was found. More rarely, extremely high contents of Zn (N° 1) and Pb (N° 1, 2, 3) were found (FIG. 8). Additionally, traces of Si and Fe were found. Cl was always < 0.5 weight-%. Contents of alkalis (Na, K) were not detectable.

It should be mentioned that the analyses are semi-quantitative and therefore do not allow exact stoichiometric calculations. But nevertheless the results of the present study indicate the general capability of ettringite to incorporate lead and zinc. This is in good agreement other work, [5].

In spite of the detected contents of heavy metals, in XRD powder diagrams taken during both early and advanced hydration of all investigated CAC / fly ash mixtures the 2 theta values of the reflections of ettringite always very precisely fit with the data for pure $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$, [10]. This agrees with laboratory synthesis experiments and theoretical RIETVELD calculations, [13].

TABLE 3
TEM / EDX analysis* (% by weight) of Crystals of Ettringite formed in Mixtures of CAC / Fly Ash

N°:	1	2	3	4	5	pure ettr.**
Ca	45.4	49.6	35.2	45.1	50.4	61.6
Al	10.4	12.4	11.6	15.1	12.9	13.8
S	18.8	18.7	16.9	24.5	25.8	24.6
Si	<1	1.3	1.0	1.4	1.8	-
Fe	1.6	<1	<1	1.0	<1	-
Zn	9.5	3.0	1.3	4.3	1.7	-
Pb	14.3	14.1	33.1	8.1	6.4	

* Cu not analized (Cu specimen holder !), analysis referred to compositions without O and H.
** calculated

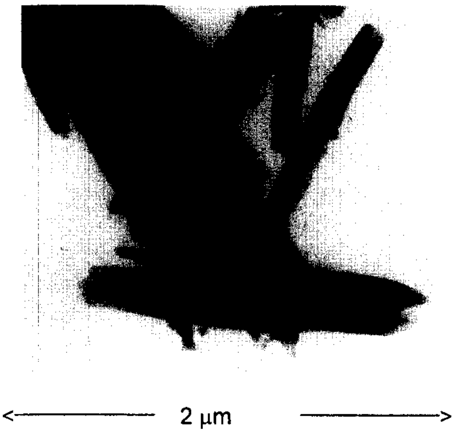

FIG. 7
Crystals of Ettringite containing Pb and Zn, TEM. Analysis: see EDX-spectrum FIG.7 and TABLE 3, N° 1

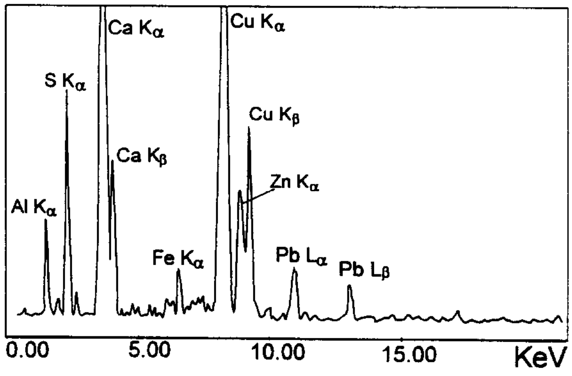

FIG. 8
EDX-Spectrum of Ettringite-Phase, see FIG. 7 and TABLE 3 (N°1)

Leaching of fly ash and hydrated calcium aluminate / fly ash mixtures

The leaching procedure on pure fly ash and hydrated mixtures of calcium aluminate / fly ash was carried out by increasing the degree of acidity of the solvents. The filtrates were analyzed for CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, Na_2O, Cl^-, SO_3, Pb, Zn, Cd and Cu. Only a few selected results of this investigation are given in this paper.

In FIG. 10 a sequence of XRD diagrams of leaching-residues of a 120 days hydrated mixture of 14.3 % calcium aluminate / 85.7 % fly ash (w/c=2, w/s=0.3) is shown. By leaching with diluted NaOH of pH=11.5 the highly soluble alkali salts NaCl and KCl are washed out. Therefore, the remaining phases are relatively enriched. In the range of pH 11.5 - 9 monochloroaluminate is more attacked by the solvents than ettringite. At pH-values <6 the ettringite-phase and lamellar monochloroaluminate are totally destroyed. With decreasing pH the insoluble phases such as quartz, rutile, perovskite, anorthite and gehlenite become dominant. At pH = 0.5 (solvent: 2-N HCl) gehlenite is partially destroyed. The XRD reflection at 33.4^0 2 theta (d=2.68 Å) presumably can be attributed to a hydrogrossular-phase with approximate composition $Ca_3Al_2(SiO_4)_2(OH)_4$ (in FIG. 10: "h"). In XRD diagrams of both unleached and leached fly ash this reflection does not occur. Obviously, this phase is formed during hydration of the CAC / fly ash mixture.

In residues of pure fly ash and hydrated CAC / fly ash mixtures as well, even after leaching with 2-N HCl, high contents of glass-spheres are visible by microscopic techniques.

FIG. 9 shows the leachability of the heavy metals Pb, Zn, Cu and Cd of pure fly ash and of the previously described hydrated mixture. Due to the chemical analysis (TABLE 1) of the fly ash the theoretical maximum concentrations are (2 g fly ash totally dissolved in 50 ml solvent): 430

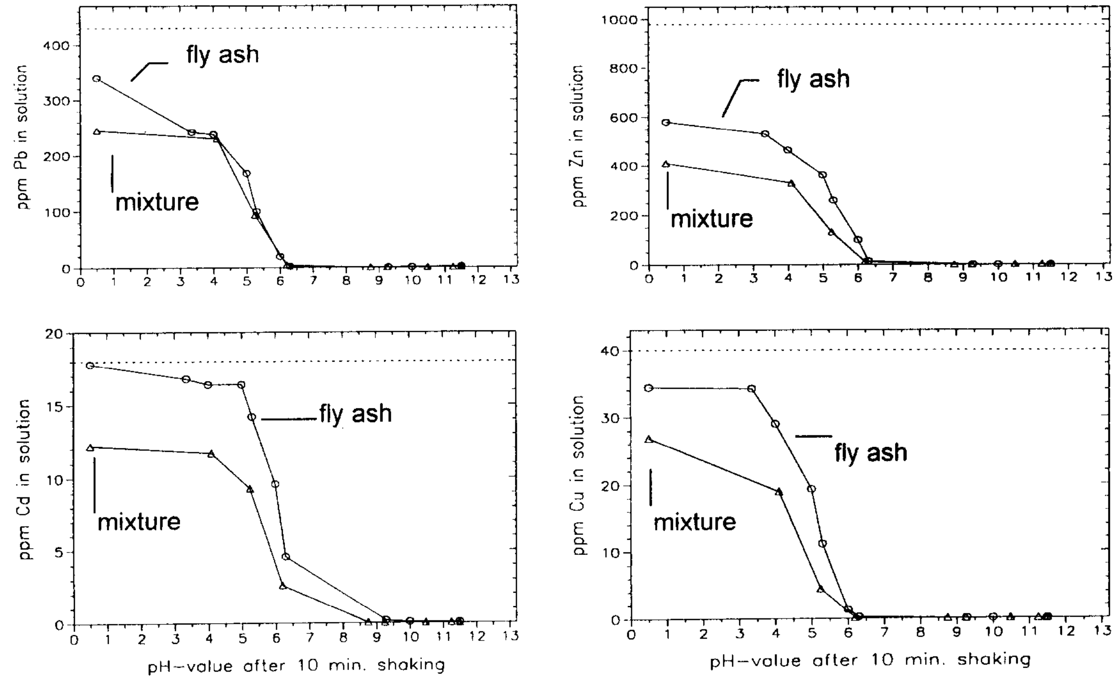

FIG. 9
Leaching Tests on Fly Ash and on hydrated Mixture of 14.3 % CAC / 85.7 % Fly Ash. Concentrations of leached Heavy Metals.

ppm Pb, 980 ppm Zn, 40 ppm Cu, 18 ppm Cd (FIG. 9: dashed lines). Because of addition of CAC and water in the hydrated mixture the fly ash is diluted about 1,5 times. Therefore, for the CAC / fly ash mixture the theoretical maximum concentrations of heavy metals are about one third lower.

In spite of partial destruction of ettringite and monochloroaluminate from alkaline to intermediate pH values the leachability of the heavy metals is extremely low. Most probably, within this pH-range, that part of the heavy metal ions which was primarily incorporated in ettringite (and monochloroaluminate) is immobilized subsequently by precipitation of metal hydroxides. Therefore, the observed leachability curves are very similar to precipitation curves of pure metal hydroxides. The leachability of Pb, Zn, Cd and Cu increases at pH values lower than 6.5. At pH=0.5 Pb and Zn are not washed out totally in contrast to Cd and Cu. Presumably Pb and Zn are still partially bound to an unleachable glass phase.

Discussion, Conclusion

By use of an experimental reactive $C_{12}A_7/C_3A$ cement in the solidification process of MSW fly ashes it is possible to fix heavy metals, SO_4^{2-} and Cl^- in hydration products. The formation of predominantly ettringite and Friedel's salt leads to fixation of toxic anions and cations. In the presence of both high concentrations of sulphates and chlorides, ettringite is the first hydrate to be formed and crystallizes immediately after addition of water. In contrast to results of [5] no Cl^- was detected in ettringite. After complete fixation of sulphates in ettringite within about 4 hours monochloroaluminate is subsequently crystallized. The observed sequence of formation of hydrates is supported by theoretical model calculations, [12].

In order to minimize the danger of later deterioration of stabilized material by secondary formation of ettringite a minimum dosage of CAC should be added such that all SO_3 of the fly ash will be bound as ettringite during early hydration. Therefore, in general, the amount of necessary CAC depends on the SO_3-content of the fly ash. The more CAC is added in addition to this minimum dosage, the more soluble Cl^- will be fixed as "insoluble" chloride in the crystal lattice of additionally formed monochloroaluminate. As discussed in [4, 5, 7] lamellar calcium aluminate hydroxi salts such as monochloroaluminate can incorporate toxic elements as well, and in this case can be regarded as a second generation of mineral reservoirs.

As shown recently by laboratory synthesis experiments Co, Ni, Cu, Zn [13] and Cd [7] can be partially incorporated in the crystal lattice of ettringite.

Contrary to the use of OPC in fixation processes the hydration mechanisms of reactive calcium aluminate cements are not delayed in the presence of Zn-salts.

Leaching experiments prove that it is necessary to lower the pH-value drastically for a complete destruction of the whole cementitious hardened waste material. The leachability of heavy metals only increases at pH-values lower than pH = 6.5.

Preliminary investigations have shown that the treatment of MSW fly ashes by reactive calcium aluminates can be the first step for solidification and fixation and can subsequently be followed by the addition of other binding materials such as OPC, slag cements, pozzolanic binders. The primary fixation of heavy metals, sulphates and chlorides by aluminates is followed by the formation of a dense microstructure, built up by crystallization of calcium silicate hydrates.

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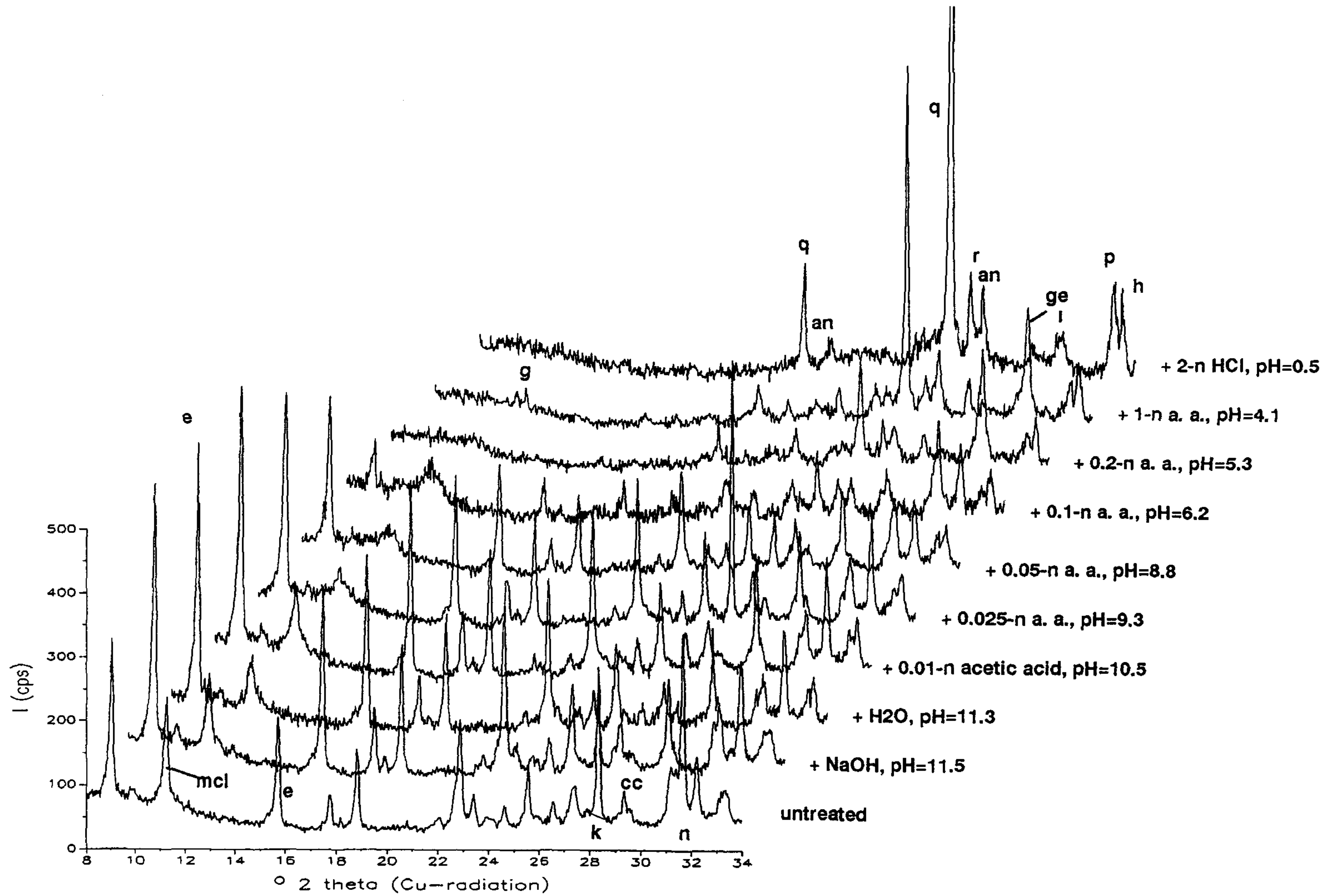

FIG. 10
XRD Powder Diagrams of Leaching Residues of a hydrated Mixture of 14.3% CAC / 85.7% Fly Ash (hydrated at w/c=2, w/s=3, 120 Days)

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