



## Chemical activation in view of MSWI bottom ash recycling in cement-based systems

A. Poletti<sup>\*</sup>, R. Pomi, E. Fortuna

Department of Hydraulics, Transportation and Roads, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Rome, Italy

### ARTICLE INFO

#### Article history:

Received 14 November 2007

Received in revised form 3 June 2008

Accepted 6 June 2008

Available online 13 June 2008

#### Keywords:

Incinerator bottom ash

Chemical activation

Pozzolanic activity

Mechanical strength

Heavy metal leaching

### ABSTRACT

In the present study, the feasibility of recycling incinerator bottom ash in cementitious systems by means of chemical activation was investigated. Different Na-, K- and Ca-based hydroxides and salts were selected for the experiments on the basis of their recognized effects on activation of typical pozzolanic materials. The evolution of mechanical properties of bottom ash/Portland cement mixtures and the leaching of trace metals from the materials were a matter of major concern. The experiments were arranged according to a full factorial design, which also allowed to derive a predictive model for unconfined compressive strength as affected by bottom ash content as well as activator type and dosage. Among the activators tested, calcium chloride was found to affect mechanical strength far more positively than the other species used, at the same time ensuring low metal release from the material. On the other hand, the use of potassium sulfate was observed to cause a significant increase in metal leaching at pH < 12, which was probably associated to the release of contaminants initially immobilized within the structure of ettringite as soon as it converted into monosulfate over time.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

The intrinsic reactivity of fresh incinerator bottom ash (BA) is well established (see, e.g., [1–3]). It originates from the fact that the bottom ash minerals formed under high-temperature combustion conditions are typically subjected to rapid cooling down to ambient temperatures during quenching downstream of the combustion unit. This leads to chemical instability of such minerals under normal atmospheric conditions, which accounts for a pronounced chemical reactivity of the material, particularly in alkaline environments.

The work presented here is part of a broader research in which different methods are being investigated to improve the leaching behavior and enhance the promote applications of municipal solid waste incinerator (MSWI) bottom ash by exploiting the chemical reactivity of the material. The treatment methods studied so far include accelerated ageing using different processes (carbonation, use of sorbing compounds or soluble phosphates [4–6]) as well as chemical and thermal activation to promote the pozzolanic behavior of bottom ash [7–9]. As for the effect of bottom ash addition to cement-based systems, the findings from previous studies indicated a weak pozzolanic behavior, so that the mechanical strength

of bottom ash–Portland cement products was always lower than that of pure Portland cement systems [7,8]. More recently, the use of appropriate activators combined with thermal activation of bottom ash was found to promote the development of mechanical strength for bottom ash–Portland cement mixtures. In particular, while the Na-based activators  $\text{Na}_2\text{SiO}_3$ , NaOH and  $\text{Na}_2\text{SO}_4$  were not effective in activating the pozzolanic properties of bottom ash,  $\text{CaCl}_2$  was capable of improving mechanical strength, with an increase in unconfined compressive strength (UCS) from 33 MPa for Portland cement pastes to 40 MPa and 46 MPa for pastes cured for 10 days at 40 °C and containing 10 wt.% and 20 wt.% of bottom ash, respectively [9].

In the present work, further investigation on the role of chemical activators in the development of physical, mechanical and leaching characteristics of MSWI bottom ash/Portland cement mixtures has been conducted.

### 2. Materials and methods

The bottom ash used in the present study comes from a grate-type MSW incinerator located in northern Italy. Bottom ash was naturally aged in non-airtight vessels for a period of about 8 years. At the time of testing, the material was homogenized by quartering and characterized for phase oxide and elemental composition as well as anion content. The oxide composition was determined from total X-ray fluorescence (TXRF). The elemental composition was

<sup>\*</sup> Corresponding author. Tel.: +39 06 44 585 037; fax: +39 06 44 585 037.  
E-mail address: [alessandra.poletti@uniroma1.it](mailto:alessandra.poletti@uniroma1.it) (A. Poletti).

determined by atomic absorption spectrometry (AAS) after sample digestion according to the APHA 3030H procedure. Anions were analyzed by ion chromatography after solubilization according to the Italian UNI 8520 method. According to the method, chlorides were solubilized using hot deionized water, while acid-soluble sulfates were extracted using 3% HCl.

Different Ca-, Na- and K-based compounds, including NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub>, CaCl<sub>2</sub>·2H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>SO<sub>4</sub> and KOH, were used in preliminary tests with the purpose of activating the pozzolanic properties of bottom ash. Reagent-grade chemicals were used throughout the experiments. The chemical activators were selected, on the basis of a literature survey, among those recognized to be capable of promoting development of pozzolanic reactions from typical pozzolanic materials [10–18]. A preliminary activation step was applied to bottom ash by heating at 90 °C for 3 h of slurries (L/S = 2 ml/g) containing ball-milled (<150 μm) bottom ash and the chemical activator. After the pre-treatment step, bottom ash was oven-dried at 105 °C.

The pozzolanic activity of bottom ash was evaluated through the standard Italian procedure (UNI-EN 196, parte 5a), the so-called Fratini test. Mixtures of bottom ash + class 42.5 R ordinary Portland cement (OPC) were preliminarily activated as described above, and the material was then suspended in deionized water (L/S = 5 ml/g) for 8 days at 40 °C. At the end of the curing period, the suspension was filtered and analyzed for Ca and total alkalinity. The measured values were compared with the solubility curve of Ca(OH)<sub>2</sub>; data points below the curve imply undersaturation of the solution with respect to Ca(OH)<sub>2</sub>, indicating that the Portlandite produced by cement hydration is consumed as a result of pozzolanic reactions.

Cementitious mixtures were prepared (see Table 1) by blending different proportions of ball-milled bottom ash and OPC at a water/total solids weight ratio of 0.4. The investigated BA/(BA + OPC) ratios were 20 wt.%, 40 wt.% and 60 wt.%. The acti-

vator additions adopted were 1.5, 3.0 and for some blends, 4.0%, expressed as activator/(BA + OPC) ratios. Control samples containing OPC only as well as 20 wt.%, 40 wt.% and 60 wt.% of natural pozzolan were also prepared for reference purposes. The experiments were arranged according to a full factorial design of two factors (bottom ash content and activator dosage) at three levels in three blocks (activator type) [19,20].

The blends were cast in 30-mm cubic moulds and maintained at ambient temperature and RH > 90% for 24 h, then demoulded and allowed to cure at 40 °C and RH > 90% for 10 days and 21 days.

Measurements of UCS were made on triplicate specimens according to the ASTM C109 method.

The ANC test [21] was applied after mechanical strength testing on ball-milled (< 150 μm) and oven-dried (60 °C) specimens; grinding was performed in N<sub>2</sub> atmosphere in order to prevent carbonation. The ANC test was conducted in a tumbling machine on eleven 5 g sub-samples contacted by 30 ml HNO<sub>3</sub> solutions with increasing acid concentrations. After 48 h, the pH of the suspensions was measured and the solid material was then separated from the liquid by centrifugation followed by 0.45 μm filtration. The liquid samples were acidified with concentrated HNO<sub>3</sub> and analyzed for heavy metals by means of AAS analyses.

The evolution of the hydration process was followed by the analysis of Portlandite content of the hardened materials, which was determined using the titration method proposed by Franke and Sisomphon [22], and occasionally by means of thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses for reference purposes.

The factorial design approach used allowed for a statistical analysis of the experimental results with an evaluation of the main effects as well as the linear and quadratic interactions between the factors as affecting the properties of the bottom ash/OPC mixtures. Main and interaction effects were calculated by means of orthogonal contrast coefficients [19,20]. The analysis of variance ((ANOVA) [19,20]) was also applied to derive an estimation of the statistical significance of the effects as well as the error of the experiments. The significant effects were then used to derive a polynomial relationship, referred to as the response surface, having the general analytical expression:

$$y = a_0 + a_1x_1 + a_2x_2 + a_{11}x_1^2 + a_{22}x_2^2 + a_{12}x_1x_2 + a_{112}x_1^2x_2 + a_{1122}x_1x_2^2 + a_{1122}x_1^2x_2^2 \quad (1)$$

where  $y$  is the response variable (e.g., UCS),  $x_1$  and  $x_2$  the levels of the two factors “bottom ash content” and “activator dosage” and  $a_{(ij)(j)}$  the coefficients of the polynomial function, which were estimated by means of linear regression of the experimental data.

### 3. Results and discussion

The chemical characteristics of bottom ash are reported in Table 2. Silicon, calcium and aluminum oxides were the main constituents of bottom ash, accounting for about 80% of total solids and yielding a ternary composition in the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–CaO system similar to that of pozzolanic materials such as coal fly ash. The chloride and sulfate content was 0.12% and 0.76% dry weight, respectively.

The results from pozzolanic activity testing of bottom ash in the presence of activators are depicted in Fig. 1. Oblique lines are drawn at constant total alkalinity values, while the bold curve gives the theoretical solubility of Portlandite. At the lower bottom ash dosage (20%), the only positive response of the pozzolanic activity test was given by 3% CaCl<sub>2</sub>; none of the other combinations, irrespective of the amount of activator added, was capable of promoting the pozzolanic properties of the material to an appreciable degree. For a bottom ash level of 40%, the pozzolanic behavior was

**Table 1**  
Mixture formulations

Miscela	BA/(BA + OPC) (%)	Activator/(BA + OPC) (%)				Pozzolan (%)
		KOH	K <sub>2</sub> SO <sub>4</sub>	CaCl <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	
OPC	0					
C1	20					
C2	40					
C3	60					
P1						20
P2						40
P3						60
M1	20	1.5				
M2	20	3				
M3	40	1.5				
M4	40	3				
M5	60	1.5				
M6	60	3				
M7	20		1.5			
M8	20		3			
M9	40		1.5			
M10	40		3			
M11	60		1.5			
M12	60		3			
M13	20			1.5		
M14	20			3		
M15	40			1.5		
M16	40			3		
M17	60			1.5		
M18	60			3		
M19	20			4		
M20	40			4		
M21	60			4		
M22	40				1.5	
M23	40				3	

**Table 2**  
Elemental and phase-oxide composition of bottom ash

Element	Concentration (mg/kg dry wt.)	Oxide	Concentration (% dry wt.)
Al	55,320	SiO <sub>2</sub>	56.99
Ca	133,300	TiO <sub>2</sub>	0.49
Cd	<8	Al <sub>2</sub> O <sub>3</sub>	9.20
Cr	79	Fe <sub>2</sub> O <sub>3</sub>	3.97
Cu	2,660	MnO	0.08
Fe	11,240	MgO	3.46
K	3,073	CaO	13.22
Mg	12,540	Na <sub>2</sub> O	5.87
Mn	475	K <sub>2</sub> O	1.35
Ni	61	P <sub>2</sub> O <sub>5</sub>	0.70
Pb	1,287		
Zn	1,443		

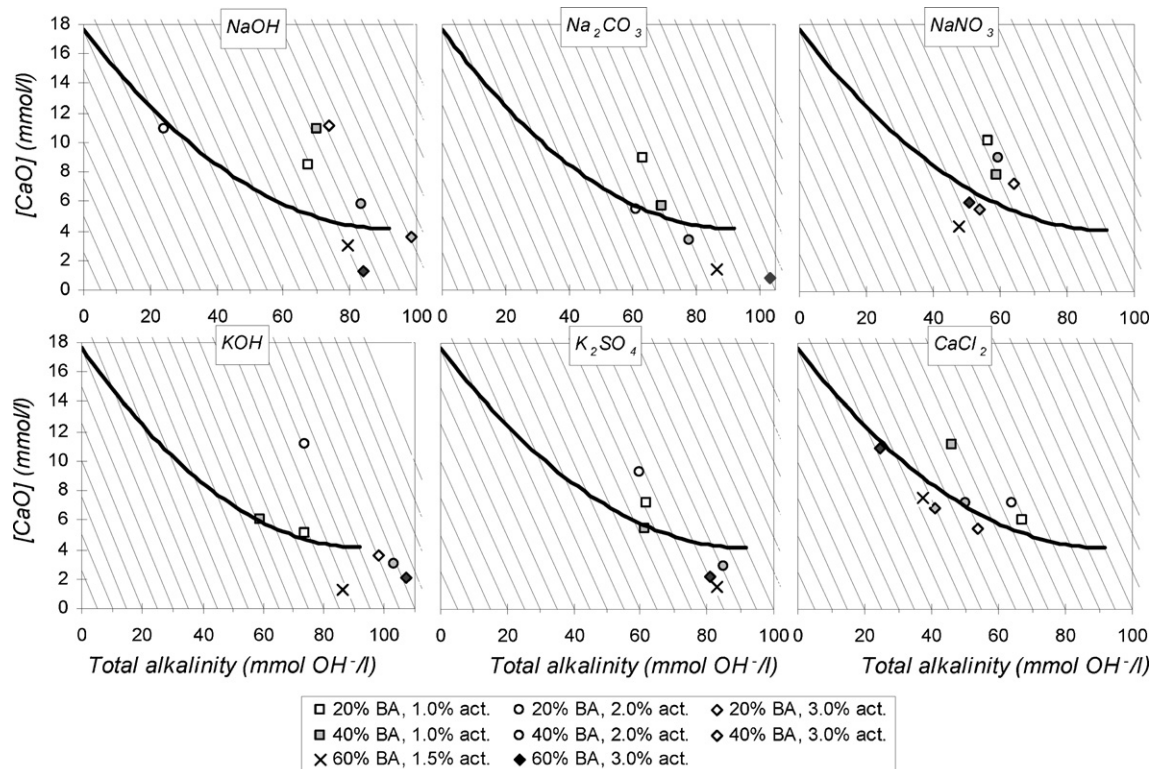
exhibited at either 2% or 3% activator addition depending on the activator type. For the highest bottom ash content, both the activator dosages adopted (1.5% and 3%) resulted in data points below the saturation curve of Portlandite. Overall, the results from pozzolanic activity testing suggest that the aluminosilicate minerals in bottom ash exhibiting pozzolanic properties are likely only a portion of the total, so that for significant Portlandite consumption to occur either elevated activator additions or high bottom ash dosages are required.

The mechanical properties of bottom ash/OPC mixtures are depicted in Fig. 2 for the three activators KOH, K<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> as a function of bottom ash content and activator dosage. Error bars were also included to indicate the standard deviation of experimental data. After 21 days of curing, UCS was appreciably improved by the use of activators. Increasing the activator dosage variously affected mechanical strength: while doubling the activator dosage from 1.5% to 3% did not produce any appreciable gain in UCS in the case of KOH and K<sub>2</sub>SO<sub>4</sub>, the effect of activator addition was appreciable for CaCl<sub>2</sub>. This was found to promote mechanical strength

development much better than the other activators tested, especially at higher additions; the use of 4% CaCl<sub>2</sub> at 20% bottom ash content yielded as a high 21-day UCS as OPC.

As observed in a previous study [9], an increase in bottom ash content resulted in a UCS decrease, indicating that the amount of hydrates formed as a result of pozzolanic reactions is presumably inadequate to counterbalance the decrease in mechanical strength caused by dilution of cement.

The contribution of bottom ash to mechanical strength was investigated by means of the so-called specific UCS (SUCS) as proposed by Pu [23] and defined as the UCS value of the specimen divided by its cement content. The approach is based on the assumption that mechanical strength in the presence of admixtures is given by two contributions, one from the hydration phases of cement and the other from the additional solid phases formed by the admixtures. According to its definition, the SUCS of the control mixture (OPC) can be regarded as the contribution of 1% cement to mechanical strength. Any SUCS higher than that of the control mixture thus indicates further contribution (i.e., in addition to that produced by cement) of the material to mechanical resistance. Compressive strength data reported in Fig. 2 are plotted in specific terms in Fig. 3. When looking at the SUCS of the mixtures without any activator addition, the effect of bottom ash on mechanical strength appears to be mainly associated to dilution of Portland cement; as curing time progressed, the negative contribution of bottom ash to strength was more pronounced, with significantly lower UCS and SUCS values if compared to Portland cement. In the presence of activators, at the earlier age (10 days) a positive contribution of bottom ash to strength, as evidenced by the data points above the SUCS of OPC, was observed at 60% bottom ash content for all the compounds tested; in the case of CaCl<sub>2</sub> all the investigated mixtures, irrespective of their bottom ash content, displayed SUCS values higher than Portland cement.



**Fig. 1.** Pozzolanic activity testing of BA/OPC mixtures.

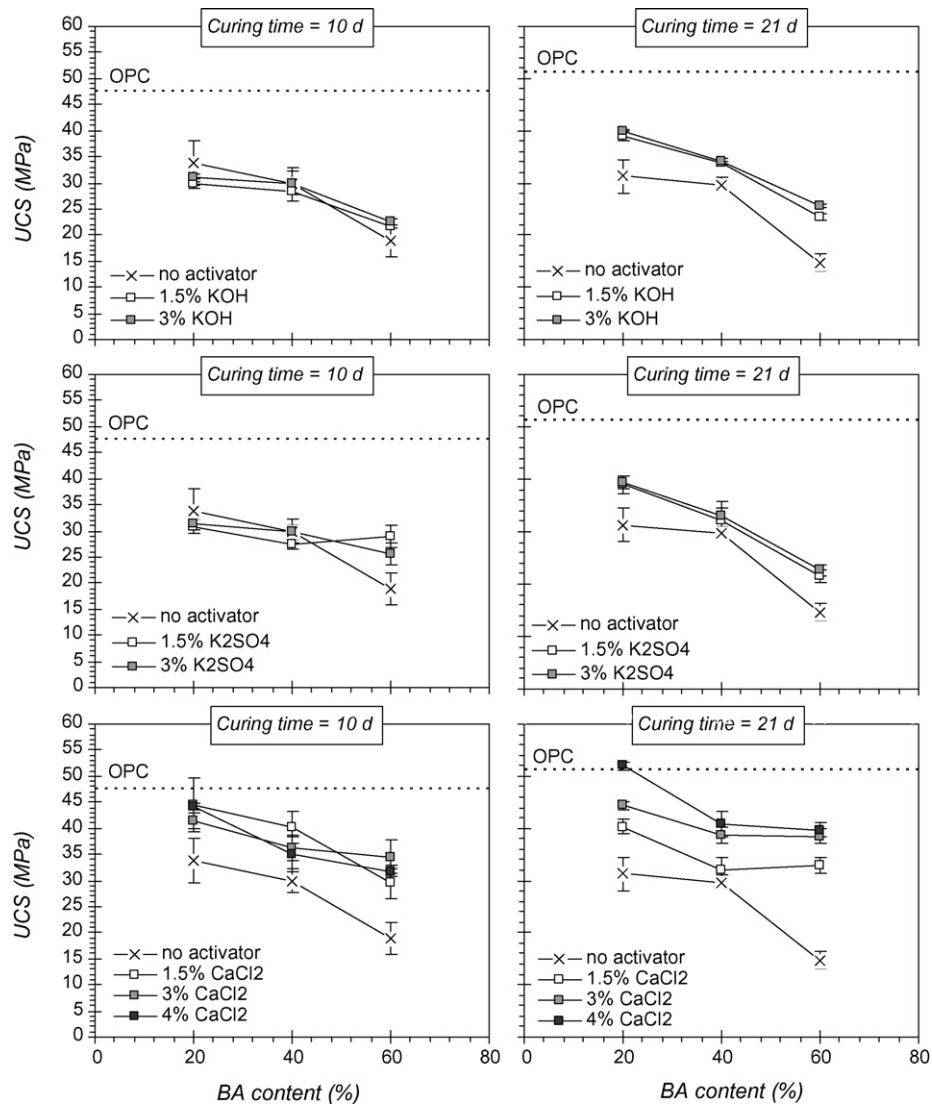


Fig. 2. UCS as a function of bottom ash content and activator dosage.

For longer curing (21 days) the role of chemical activators in promoting mechanical strength development was also evident for a bottom ash content of 40%. Again, the mixtures containing CaCl<sub>2</sub> showed better mechanical properties if compared to the other mixtures.

The interpretation of specific mechanical strength data suggests that, under the experimental conditions tested, bottom ash was not able *per se* to promote mechanical strength development, so that the effect of bottom ash addition to cement was basically related to dilution of the hydrate system. When the activators were added to the mixtures, a gain in UCS was observed which was as more pronounced as both activator dosage and curing time increased.

In order to get deeper insight into the hydration process of bottom ash/OPC systems in the presence of chemical activators, the linear and quadratic effects of the two factors “activator dosage” (A) and “bottom ash content” (B) on mechanical strength were estimated and the ANOVA was conducted to derive information on their statistical significance. Table 3 shows a summary of the results obtained from the statistical analysis of UCS data.

Comparing the effects of the three activators on UCS, the positive contribution of CaCl<sub>2</sub> to strength as compared to KOH and K<sub>2</sub>SO<sub>4</sub> was found to be mainly associated to the main effect A<sub>L</sub> (which increased UCS by 9.9 MPa and 15.3 MPa from average values

of 34.3 MPa and 33.6 MPa at 10 days and 21 days, respectively) as well as to the linear × linear interaction between the two factors (which yielded a strength gain of 8.0 MPa and 8.7 MPa at 10 days and 21 days, respectively); at 21-day curing, the linear × quadratic

Table 3  
Main and interaction effects on UCS (values in MPa)

	KOH		K <sub>2</sub> SO <sub>4</sub>		CaCl <sub>2</sub>	
	10 days	21 days	10 days	21 days	10 days	21 days
Average	27.3	30.2	28.5	29.3	34.3	33.6
Main effects						
A <sub>L</sub>	0.2	<b>8.0</b>	1.4	<b>6.5</b>	<b>9.9</b>	<b>15.3</b>
B <sub>L</sub>	<b>-10.5</b>	<b>-15.6</b>	-7.5	<b>-16.9</b>	<b>-12.3</b>	<b>-10.0</b>
A <sub>Q</sub>	2.0	<b>-5.6</b>	-1.7	<b>-4.7</b>	<b>-11.2</b>	<b>-4.5</b>
B <sub>Q</sub>	<b>-6.3</b>	<b>-7.0</b>	-1.5	<b>-7.0</b>	-3.5	0.4
Interactions						
A × B <sub>L×L</sub>	<b>6.4</b>	2.1	<b>9.2</b>	-0.1	<b>8.0</b>	<b>10.7</b>
A × B <sub>L×Q</sub>	1.2	<b>10.5</b>	5.0	<b>9.2</b>	10.9	<b>18.8</b>
A × B <sub>Q×L</sub>	-7.0	0.4	<b>-16.8</b>	1.7	8.2	<b>-7.6</b>
A × B <sub>Q×Q</sub>	-2.6	-6.4	<b>-20.0</b>	-10.4	9.7	<b>-25.9</b>

A=factor “activator dosage”; B=factor “bottom ash content”. L=linear; Q=quadratic. Bold values denote statistically significant (95% confidence level) effects.

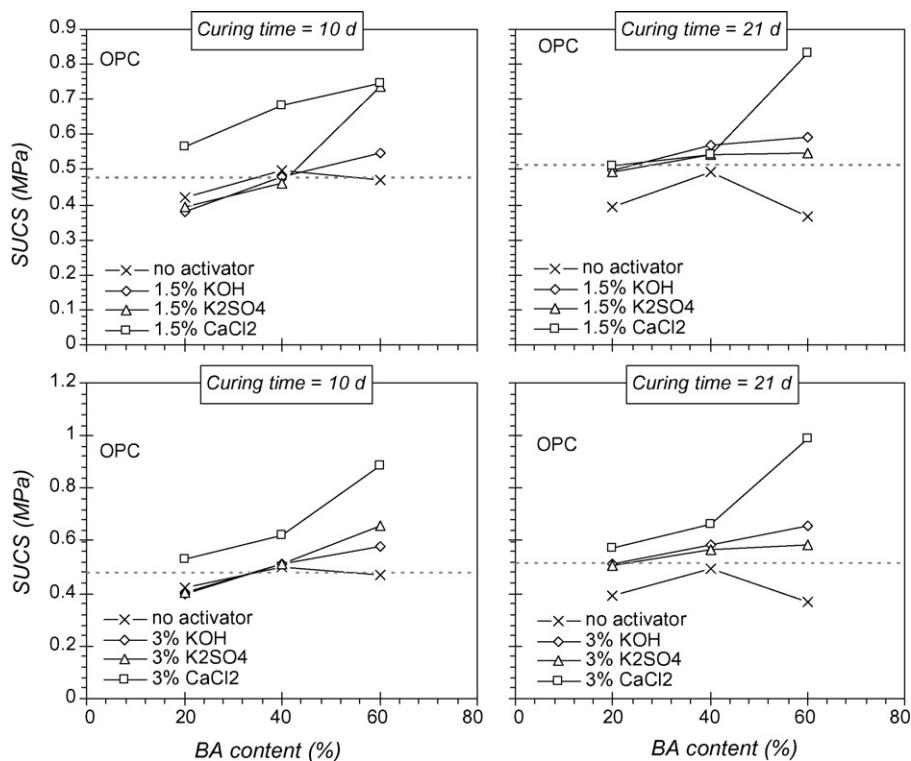


Fig. 3. SUCS as a function of bottom ash content and activator dosage.

A  $\times$  B interaction was also found to significantly increase UCS by 18.8 MPa. As far as the behavior of KOH and  $K_2SO_4$  was concerned, at the lower curing time the main effects (both linear and quadratic) of the factors on UCS were all negative or slightly positive, while the only significant positive joint effect was in both cases the linear  $\times$  linear interaction. As curing time increased, the main effect  $A_L$  became positive for both the activators, which explains the gain observed in mechanical strength for KOH and  $K_2SO_4$  with time (see Fig. 2); however, at 21-day curing the other main effects  $B_L$ ,  $A_Q$  and  $B_Q$ , that became statistically significant, were all negative, which provides the reason for the lower UCS values observed at 21-day curing for KOH and  $K_2SO_4$  as opposed to  $CaCl_2$ .

On the basis of data in Table 3, the polynomial model represented by Eq. (1) was applied taking only the significant effects into account, in order to derive the response surfaces for UCS for the activator types tested. These are depicted in Fig. 4 as contour plots, which provide a graphical representation of the predictive model for UCS as a function of bottom ash dosage and activator type and addition. The increased curvature of the response surfaces with curing time in the case of KOH and  $K_2SO_4$  is due to the fact that at 21-day curing quadratic effects became significant. The downward curvature of the response surfaces for  $CaCl_2$  at 21-day curing provides an indication of the more benign effect exerted by the activator on mechanical strength for longer curing times, especially at lower bottom ash contents.

The hydration behavior of the mixtures in the presence of activators was further investigated by means of indirect measurements of the  $Ca(OH)_2$  content. Fig. 5(a) reports the TGA/DSC patterns for the mixtures OPC, M19 and P3 (see Table 1) cured for 10 days. The DSC curves show the presence of two endothermic peaks in the low temperature region, with maxima at  $\sim 90^\circ C$  and  $\sim 160^\circ C$ , which are related to the loss of physically bound water and dehydration of different Ca silicate hydrates. In particular, the loss of hydration water from such phases was indicated by a region of linear weight decrease in the temperature range  $130\text{--}450^\circ C$ ; the total mass loss

in this range was comparable ( $\sim 7\%$ ) for the two mixtures OPC and M19, while much lower ( $\sim 4\%$ ) for P3.

Two additional endothermic peaks were identified on the DSC curves, with maxima at  $\sim 460^\circ C$  and  $\sim 750^\circ C$ , which were associated to the decomposition of  $Ca(OH)_2$  with loss of water and  $CaCO_3$  with loss of  $CO_2$ , respectively. The amount of Portlandite in the sample was calculated according to Eq. (2), where  $\Delta M_{450\text{--}500}$  and  $\Delta M_{720\text{--}780}$  are the mass losses associated to the  $Ca(OH)_2$  peak (temperature range  $450\text{--}500^\circ C$ ) and the  $CaCO_3$  peak (temperature range  $720\text{--}780^\circ C$ ), and  $M$  is the initial sample mass.

$$Ca(OH)_2(\text{wt.}\%) = \frac{4.11\Delta M_{450\text{--}500} + 1.68\Delta M_{720\text{--}780}}{M} \times 100 \quad (2)$$

For the three mixtures in Fig. 5(a) the Portlandite content was found to be 13.4% for OPC, 8.7% for M19 and 3.0% for P3. Data derived from TG analyses for these and three additional samples cured for 21 days were correlated with 0.1N  $HNO_3$  titration volumes derived from the titration method reported in Ref. [22]. For the remaining samples only titration measurements were done, and the relationship determined as indicated in Fig. 5(b) was used to calculate the  $Ca(OH)_2$  content in the material. This was plotted in Fig. 6 as a function of bottom ash content and activator dosage at 21-day curing. The dashed lines in Fig. 6 represent the theoretical decrease in Portlandite content that would be observed if the effect of bottom ash addition involved dilution of the OPC hydrate system only. The corresponding plots at 10-day curing were similar in shape, although  $Ca(OH)_2$  contents were generally higher and the variations between the different activators tested were less appreciable.

The observed decrease in Portlandite content with curing time is an indication of the progressive consumption of this phase by pozzolanic reactions. The pozzolanic behavior of bottom ash was also found to be promoted by increased activator dosages, which enhanced Portlandite consumption. However, comparing graphs in Fig. 6 with UCS data in Fig. 2, one can infer that the effect of the activators on mechanical strength is not exclusively related to the

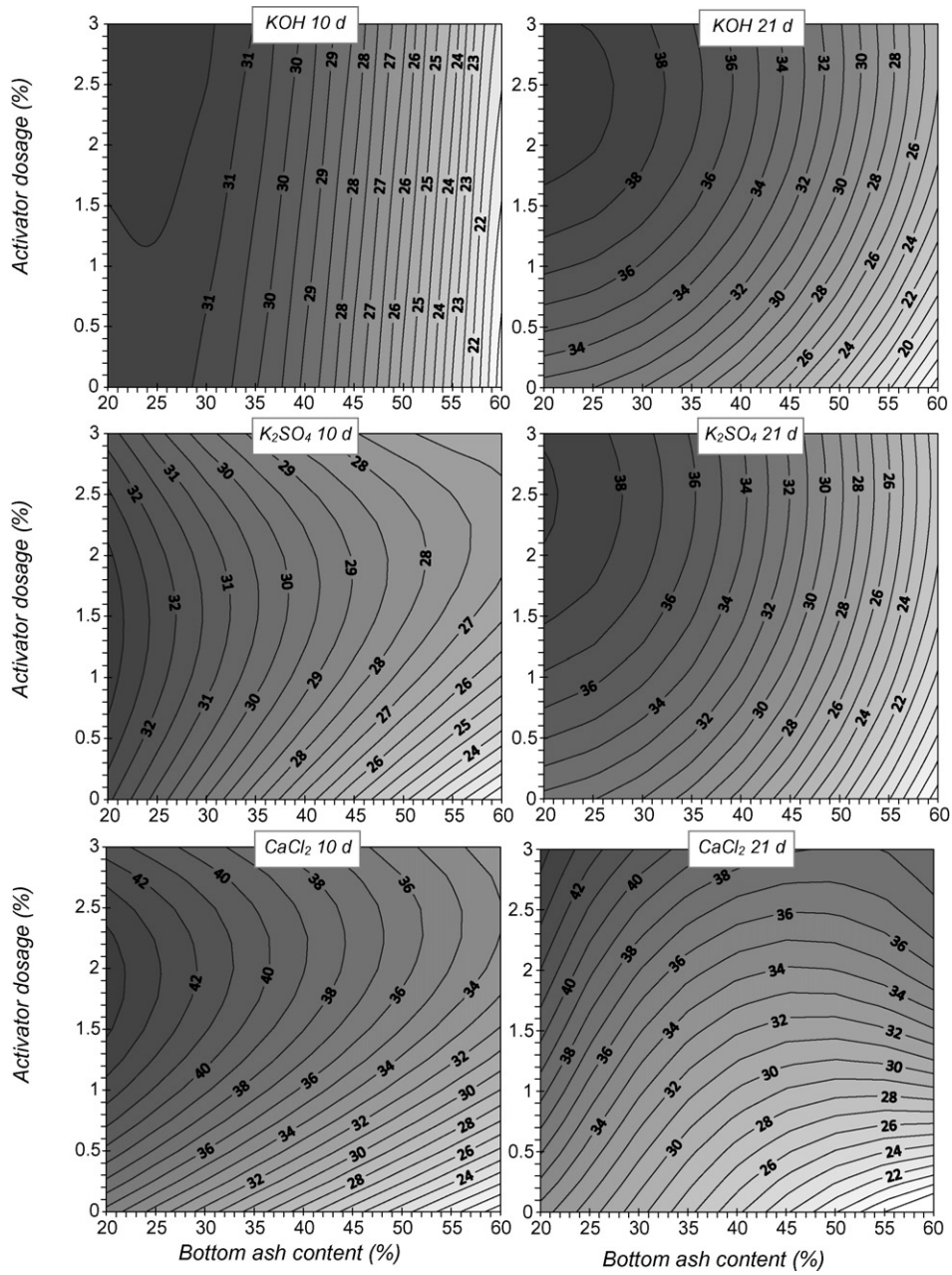


Fig. 4. Response surfaces for UCS as derived by Eq. (1) (values in MPa).

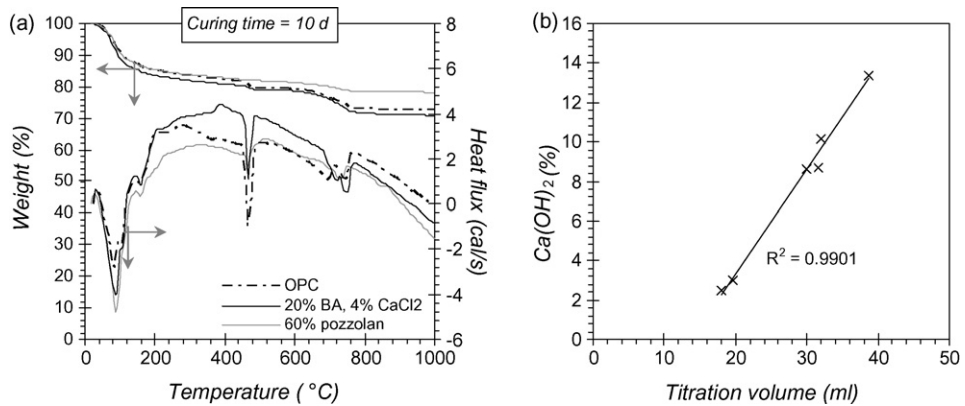


Fig. 5. (a) TGA (left y-axis) and DSC (right y-axis) patterns for mixtures OPC, M19 and P3, and (b) correlation between TG and titration results.

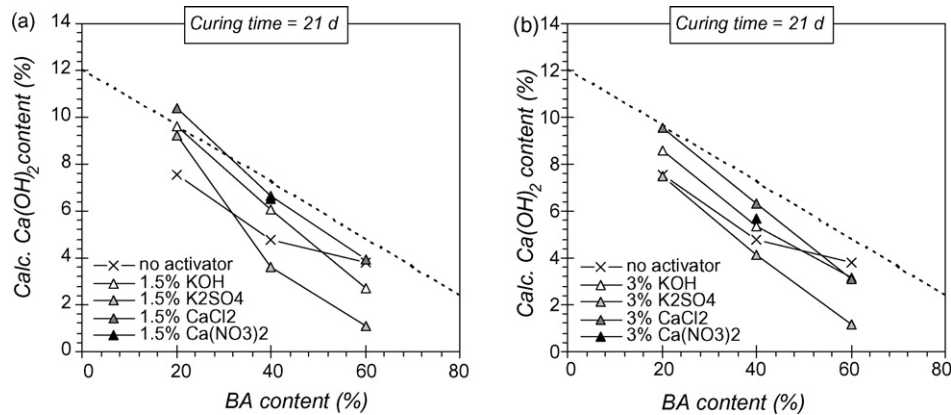


Fig. 6. Calculated  $\text{Ca(OH)}_2$  content as a function of bottom ash content and activator dosage.

enhanced pozzolanic behavior of bottom ash. Such a conclusion can be drawn considering that, while the mixtures containing  $\text{CaCl}_2$  displayed the highest UCS values, they also had the highest Portlandite contents; on the other hand, the calculated Portlandite content decreased with  $\text{CaCl}_2$  addition, and this also resulted in improved mechanical strength. This feature can only be explained considering the ability of  $\text{CaCl}_2$  to induce the formation of other hydrates in addition to those produced by pozzolanic reactions. Hydrated calcium chloroaluminate ( $\text{C}_3\text{A}(\text{CaCl}_2)\text{H}_{10}$ ), commonly referred to as Friedel's salt, is known to form in cement-based systems in the presence of chloride forms (see, e.g., [11,24–29]); however, from the DSC curves of  $\text{CaCl}_2$ -containing mixtures at both 10 days and 21 days of curing no evidence could be gained of Friedel's salt formation, which would be indicated by an endothermic effect in the temperature range 310–380 °C [11,26–28]. Further mineralogical investigation is required to clarify the hydration mechanisms of incinerator bottom ash in cementitious systems in the presence of  $\text{CaCl}_2$ .

In order to assess the environmental behavior of the investigated mixtures, the release of a number of heavy metals as a function of

pH at 21-day curing was also evaluated. The results are reported in Fig. 7 for 1.5% activator addition. The corresponding curves obtained for 3% activator dosage were very similar to those depicted in Fig. 7, thereby indicating that the amount of activator added did not significantly affect the release of metals, at least at later stages of hydration.

For all the mixtures with the exception of those containing  $\text{K}_2\text{SO}_4$ , the leaching of Cu, Pb, Zn and also Cr (not reported graphically here) was in all cases well below 0.5 mg/l for pH values >6. Only at lower pH values did metal leaching increase significantly. This is a result of dissolution of the hydrates incorporating trace metals that occurs under acidic conditions. The higher metal leaching observed when using  $\text{K}_2\text{SO}_4$  as the activator is probably a result of the increased amounts of sulfates leading to the formation of higher amounts of ettringite that is formed at the early stages of hydration. It is well known (see, e.g., [30,31]) that ettringite displays an immobilization capacity towards a number of both heavy metals cations and oxyanions. It is tempting to hypothesize that trace contaminants are immobilized within the cementitious matrix as long as they can be retained within the structure of

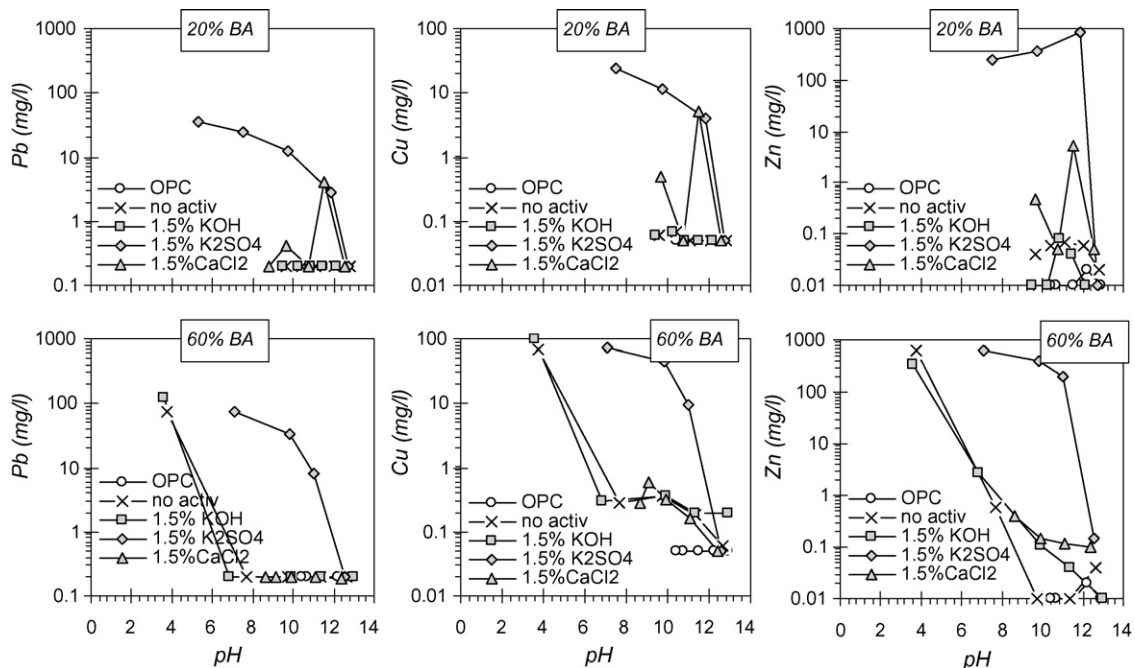


Fig. 7. Leaching of Cu, Pb and Zn from mixtures as a function of pH (activator dosage = 1.5%; curing time = 21 days).

ettringite; when this converts to monosulfate as hydration proceeds, the contaminants become available for leaching at pH values below 12, which is the stability threshold for this phase [31,32]. This may explain why in the present study metal concentrations in the leachate from 21-day-old mixtures containing  $K_2SO_4$  were systematically higher if compared to the other mixtures. The negative effect of sulfate-based activators on metal leaching is an aspect that must be seriously evaluated when assessing the feasibility of utilization of incinerator bottom ash in cement-based systems.

#### 4. Conclusions

The present work was aimed at studying the mechanical and leaching properties of cementitious mixtures containing incinerator bottom ash in the presence of different K-, Na- and Ca-based activators. On the basis of preliminary pozzolanic activity testing and results from previous studies on the same material, three activators including KOH,  $K_2SO_4$  and  $CaCl_2$  were selected as potentially exerting a beneficial effect on the mechanical characteristics of the material.

It was found that KOH and  $K_2SO_4$  produced similar effects on mechanical strength, and the improvement attained on UCS was only visible for longer curing times. On the other hand,  $CaCl_2$  had a positive influence on mechanical strength at earlier stages of hydration already. In this case, the gain in UCS also increased with curing time and was more pronounced at higher activator additions, so that at 21-day curing the addition of 4%  $CaCl_2$  at a 20% bottom ash content yielded as a high UCS as OPC.

On the basis of the Portlandite content of the mixtures, it was inferred that the effect of the activators tested on the evolution of the hydration process is partly related to the enhanced pozzolanic properties of bottom ash. However, the experimental results indicated that additional mechanisms still to be clarified are likely to play a role in determining the mechanical behavior of the bottom ash/OPC mixtures.

When using either KOH or  $CaCl_2$ , the leaching of heavy metals from the material was maintained at low levels under pH conditions corresponding to the stability range of the main hydration phases. The use of  $K_2SO_4$ , although yielding similar mechanical properties if compared to KOH, was found to be very critical in terms of heavy metal release, which strongly increased for  $pH < 12$ . This indicates that the use of sulfate-based activators in cementitious mixtures containing incinerator bottom ash is not recommended when environmental impact issues including trace metal leaching are concerned.

#### References

- [1] J.A. Meima, R.N.J. Comans, Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash, *Environ. Sci. Technol.* 31 (1997) 1269–1276.
- [2] T. Sabbas, A. Polettini, R. Pomi, T. Astrup, O. Hjelmar, P. Mostbauer, G. Cappai, G. Magel, S. Salhofer, C. Speiser, S. Heuss-Assbichler, R. Klein, P. Lechner, Management of municipal solid waste incineration residues, *Waste Manage.* 23 (2003) 61–88.
- [3] C. Zevenbergen, L.P. Van Reeuwijk, J.P. Bradley, R.N.J. Comans, R.D. Schuiling, Weathering of MSWI bottom ash with emphasis on the glassy constituents, *J. Geochem. Explor.* 62 (1998) 293–298.
- [4] A. Polettini, R. Pomi, The leaching behavior of incinerator bottom ash as affected by accelerated ageing, *J. Hazard. Mater. B* 113 (2004) 209–215.
- [5] A. Polettini, R. Pomi, The influence of accelerated ageing on leaching behaviour of incinerator bottom ash, in: G. Ortiz de Urbina, J.J.M. Goumans (Eds.), Proceedings of the WASCON 2003, Progress on the Road to Sustainability, Fifth International Conference of the Environmental and Technical Implications of Construction with Alternative Materials, San Sebastián (E), June 4–6, 2003, pp. 615–624.
- [6] A. Polettini, R. Pomi, M. Ragaglia, Accelerated ageing as a tool for sustainable disposal of incinerator bottom ash, in: R. Cossu, R. Stegmann (Eds.), Proceedings of the Sardinia 2005, Tenth International Waste Management and Landfill Symposium, S. Margherita di Pula (IT), October 3–7, 2005 (on CD ROM).
- [7] P. Filippini, A. Polettini, R. Pomi, P. Sirini, Physical and mechanical properties of cement-based products containing incineration bottom ash, *Waste Manage.* 23 (2003) 145–156.
- [8] C. Giampaolo, S. Lo Mastro, A. Polettini, R. Pomi, P. Sirini, Acid neutralisation capacity and hydration behaviour of incineration bottom ash–Portland cement mixtures, *Cement Concrete Res.* 32 (2002) 769–775.
- [9] A. Polettini, R. Pomi, G. Carcani, The effect of Na and Ca salts on MSWI bottom ash activation for reuse as a pozzolanic admixture, *Resour. Conserv. Recycl.* 43 (2005) 403–418.
- [10] Y. Fan, S. Yin, Z. Wen, J. Zhong, Activation of fly ash and its effects on cement properties, *Cement Concrete Res.* 29 (1999) 467–472.
- [11] Z. Giergiczny, Effect of some additives on the reactions in fly ash– $Ca(OH)_2$  system, *J. Therm. Anal. Cal.* 76 (2004) 747–754.
- [12] J. Qian, C. Shi, Z. Wang, Activation of blended cements containing fly ash, *Cement Concrete Res.* 31 (2001) 1121–1127.
- [13] C. Shi, R.L. Day, Acceleration of the reactivity of fly ash by chemical activation, *Cement Concrete Res.* 25 (1995) 15–21.
- [14] C. Shi, R.L. Day, Pozzolanic reaction in the presence of chemical activators. Part I. Reaction kinetics, *Cement Concrete Res.* 30 (2000) 51–58.
- [15] C. Shi, R.L. Day, Pozzolanic reaction in the presence of chemical activators. Part II. Reaction products and mechanism, *Cement Concrete Res.* 30 (2000) 607–613.
- [16] C. Shi, R.L. Day, Comparison of different methods for enhancing reactivity of pozzolans, *Cement Concrete Res.* 31 (2001) 813–818.
- [17] S. Song, H.M. Jennings, Pore solution chemistry of alkali-activated ground granulated blast-furnace slag, *Cement Concrete Res.* 29 (1999) 159–170.
- [18] S.-D. Wang, K.L. Scrivener, Hydration products of alkali activated slag cement, *Cement Concrete Res.* 25 (1995) 561–571.
- [19] G.E. Box, S.J. Hunter, W.G. Hunter, *Statistics for Experimenters. Design, Innovation and Discovery*, second ed., John Wiley & Sons, Hoboken, NJ, 2005.
- [20] D.C. Montgomery, *Design and Analysis of the Experiments*, sixth ed., John Wiley & Sons, Hoboken, New Jersey, 2005.
- [21] J.A. Stegmann, P.L. Côté, Investigation of test methods for solidified waste characterization—a cooperative program, Appendix B: Test Methods for Solidified Waste Evaluation, Environment Canada, Unpublished Manuscript Series Document TS-15, 1991.
- [22] L. Franke, K. Sisomphon, A new chemical method for analyzing free calcium hydroxide content in cementing material, *Cement Concrete Res.* 32 (2004) 1161–1165.
- [23] X. Pu, Investigation on pozzolanic effect of mineral additives in cement and concrete by specific strength index, *Cement Concrete Res.* 29 (1999) 951–955.
- [24] P. Hewlett, *Lea's Chemistry of Cement and Concrete*, fourth ed., Elsevier Butterworth-Heinemann Publisher, 2004.
- [25] H.F.W. Taylor, *Cement Chemistry*, second ed., Thomas Telford Publisher, London, 1997.
- [26] J. Cszimadia, G. Balázs, F.D. Tamás, Chloride binding capacity of aluminoferrites, *Cement Concrete Res.* 31 (2001) 577–588.
- [27] N. Saikia, S. Kato, T. Kojima, Thermogravimetric investigation on the chloride binding behaviour of MK-lime paste, *Thermochim. Acta* 444 (2006) 16–25.
- [28] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, The binding of chloride ions by sulphate resistant Portland cement, *Cement Concrete Res.* 25 (1995) 581–592.
- [29] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, Mechanisms of Friedel's salt formation in cements rich in tri-calcium aluminate, *Cement Concrete Res.* 26 (1996) 717–727.
- [30] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Ettringite and C-S-H Portland cement phases for waste ion immobilization: a review, *Waste Manage.* 4 (1996) 293–303.
- [31] M. Chrysochoou, D. Dermatas, Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: literature review and experimental study, *J. Hazard. Mater.* 136 (2006) 20–33.
- [32] J.A. Stegmann, N.R. Buenfeld, Prediction of leachate pH for cement paste containing pure metal compounds, *J. Hazard. Mater. B* 90 (2002) 169–188.