The effect of gyrolite substituted with cadmium ions on the hydration kinetics of OPC at early stages

Kestutis Baltakys

Professor, Department of Silicate Technology, Kaunas University of Technology, Kaunas, Lithuania

Anatolijus Eisinas

Researcher, Department of Silicate Technology, Kaunas University of Technology, Kaunas, Lithuania

Raimundas Siauciunas

Professor, Department of Silicate Technology, Kaunas University of Technology, Kaunas, Lithuania

This study examined the effect of gyrolite substituted with cadmium ions on the kinetics of the hydration of ordinary Portland cement (OPC) at early stages of hydration. Gyrolite was synthesised after 48 h at 200°C from a stoichiometric composition (calcium oxide/silica dioxide = 0.66) of calcium oxide and a hydrated silica mixture. Calcium silicate hydrate substituted with cadmium ions (97 mg cadmium ions/g) was added as a partial replacement of the OPC at levels of 0%, 2.5%, 5% and 7.5% by weight of the total cementitious material. Therefore, the water-to-cement ratio of all OPC samples was 0.5. It was found that the additive of a synthetic contaminated with cadmium ions (~97 mg cadmium ions/g) retained very good adsorption properties for the alkaline and alkaline earth ions that penetrated into the gyrolite structure. It was estimated that this additive accelerates the early stage (5–7 h) of hydration of OPC and its individual compounds. It was found that during the main reaction of calcium silicate, the additive of gyrolite contaminated with cadmium ions had no influence on the apparent reaction rate (W_{app}) of the hydration process (7–12 h): in all samples, the increase in the degree of hydration ($\Delta\alpha$) was almost the same: $\Delta\alpha = 15\%$.

Notation

c	concentration
k_{app}	reaction rate
n_{app}	evaluated reaction order
S_a	specific surface area
T	time
W_{app}	apparent reaction rate
X_τ	amount of tricalcium silicate that reacted
$\Delta\alpha$	degree of hydration

Introduction

The removal of toxic heavy metals from industrial wastewater is one of the most important issues of environmental remediation (Buamah *et al.*, 2008; Havelcova *et al.*, 2009; Panuccio *et al.*, 2008). Immobilisation of heavy metals can be carried out by using chemical agents or materials that combine metal ions to form stable, non-mobile, poorly soluble compounds. For this purpose, phosphates, zeolites, calcium silicate hydrates, carbonates, hydroxides, or even industrial byproducts can be used (Chen *et al.*, 2008; Demir *et al.*, 2008; Erdem *et al.*, 2004; Giergiczny and Krol, 2008; Kosobucki *et al.*, 2008; Murari *et al.*, 2008).

However, from an ecological point of view, one task still remains: the utilisation or disposal of these materials after the immobilisa-

tion of heavy metals. One of the main methods for the disposal of such materials is to use them as additives in various binders (Chen *et al.*, 2007; Cvetkovic *et al.*, 2009; Hashem *et al.*, 2011).

The calcium silicate hydrates are an important group of silicate minerals with compositions varying over a large range of molar ratios of calcium oxide/silica dioxide (C/S) (0.44–3.0) and with crystallographic structures ranging from amorphous to highly crystalline. Among the different silicate minerals, calcium silicate hydrates are the prime candidates for heavy metal binding because of their abundance and appropriate structure (Coleman *et al.*, 2006; El-Korashy, 2004; Kasperaviciute *et al.*, 2008; Siauciunas *et al.*, 2004).

Ordinary Portland cement (OPC) is the most adaptable binder currently available for the utilisation of heavy metals. Hydration products of Portland cement are portlandite and calcium silicate hydrates. It should be noted that calcium silicate hydrate adsorbents have chemical compositions and structural peculiarities similar to those of OPC hydration products. Silicate adsorbent substituted with heavy metal ions can be utilised as the additive in Portland cement composites. Presumably, the heavy metal ions remain stable in cement stone and do not transfer into the solution.

Cement hydration is a complex process involving a large number of simultaneous chemical reactions (Bullard *et al.*, 2011; Thomas *et al.*, 2011). When a saturated adsorbent is introduced as a substitute addition to cement in the cement–water reaction system, the system becomes even more complex (Taylor, 1997). The new hydration products thus formed affect the dynamics and kinetics of the cement hydration and solidification processes, changing both the composition and the properties of the cement gel. When the adsorbent addition contains cadmium, this element, which is harmful to the environment, is introduced into the newly formed cement composite (Eisinas *et al.*, 2013). Presumably, this additive can affect the early hydration of OPC samples. As these reactions are exothermic, isothermal calorimetry is among the most accurate methods to monitor the global reaction process through the rate of heat production (Eisinas *et al.*, 2012; Jansen *et al.*, 2012; Juilland *et al.*, 2010; Kumar *et al.*, 2012).

The main objective of this study was to determine the effect of gyrolite substituted with cadmium ions on the hydration kinetics of OPC at early stages of hydration.

Materials and methods

Materials

In this study the following reagents for gyrolite synthesis were used as starting materials: fine-grained hydrated silica (Reaktiv, Russia; ignition losses 21.28%; specific surface area (S_a) = 1155 m²/kg) and calcium oxide was burned at 950°C for 0.5 h (S_a = 548 m²/kg; purity 96%).

Samples of OPC (EN 197-1, type CEM I, 52.5R) were prepared in a laboratory grinding mill by grinding cement clinker (JSC Akmenes Cementas, Lithuania) with a 4.5% additive of gypsum (Sigma-Aldrich, Germany) up to S_a = 450 m²/kg. The chemical analysis and phase composition of the clinker are shown in Table 1.

Manufacture of gyrolite

Pure gyrolite was synthesised in hydrothermal conditions after 48 h at 200°C from a stoichiometric composition (C/S = 0.66) of a calcium oxide and hydrated silica mixture (Figure 1(a)). These synthesis conditions were chosen according to previously pub-

lished data (Siauciunas *et al.*, 2004). The product was filtered off, dried at 50 ± 5°C, and put through a sieve with an 80 µm mesh.

Adsorption experiments

Adsorption experiments were carried out at 25°C in a Grant SUB14 thermostatic absorber by stirring 1 g of gyrolite (S_a = 71.02 m²/g) in an aqueous solution containing 1 g of cadmium ions/dm³ for 120 min (Figure 1(b)). In this case, 5.5 ml ammonium hydroxide (c = 10%) was used to maintain the alkaline reaction medium (pH 8.70). The percentage of exchange was determined on the basis of the variations in the concentration of the cations in the solution and in gyrolite. The saturated adsorbent was rinsed with distilled water, dried at 50 ± 5°C, and dissolved in hydrogen chloride (1:1). The concentration of calcium and cadmium ions was determined using an atomic absorption spectrometer (Perkin-Elmer Analyst 4000).

Effect on the hydration kinetic of OPC and immobilisation in cement stone

An eight-channel TAM Air III isothermal calorimeter was used to investigate the heat evolution rate of OPC and OPC blended with 2.5%, 5% or 7.5% by weight of gyrolite contaminated with cadmium ions (Figure 1(c) and (e)). Glass ampoules (20 ml) each containing 3 g of dry cementitious material were placed in the calorimeter, and the injection unit for each ampoule was filled with water to reach a water-to-(OPC + additive) ratio of 0.5. After a steady temperature of 25°C had been reached, the water was injected into the ampoules and mixed inside the calorimeter with the dry material for 20 s (frequency 2–3/s). The heat evolution rate was then measured over a period of 92 h. Repetition of the measurements showed deviations in total heat of less than 3% for samples of similar types. Apart from the first minutes of water addition and mixing, the heat evolution rates were essentially identical.

Analytical techniques

The products of sorption were characterised by X-ray diffraction analysis. The X-ray powder diffraction data were collected with a DRON-6 X-ray diffractometer with Bragg–Brentano geometry using copper K α radiation and a graphite monochromator operating at a voltage of 30 kV and an emission current of 20 mA.

Oxides										
	Silicon dioxide	Aluminium oxide	Iron oxide	Calcium oxide	Magnesium oxide	Sodium oxide	Potassium oxide	Sulfur trioxide	Ignition of losses	Insoluble particles
Amount: %	19.72	5.41	4.21	62.76	3.41	0.16	1.08	2.08	0.93	0.24
Minerals	Tricalcium silicate		Calcium orthosilicate		Tricalcium aluminium oxide		Tetracalcium oxide-aluminium oxide iron oxide			
Amount: %	63.19		8.89		7.21		12.81			

Table 1. Chemical and mineralogical composition of clinker

Figure 1. Principal scheme of experiment. OPC, ordinary Portland cement

Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (EDS) was performed using an Evo 50 instrument at an accelerating voltage of 20 kV, a working distance of 10 mm for scanning electron microscopy observation and a 200 s accumulation time for EDS analysis.

Results and discussion

It was determined that the cation exchange reaction proceeded intensively in the first minute of the adsorption process because 87.54 mg cadmium ions/g entered into the structure of gyrolite when the initial concentration was 1 g cadmium ions/dm³ (Table 2). By prolonging the duration of the adsorption process, the concentration of cadmium ions in the solution decreased slightly, and after 120 min almost all cadmium ions were

incorporated into the crystal structure of the gyrolite (96.96 mg cadmium ions/g) (Table 2).

Furthermore, calcium ions were released from the crystal lattice of gyrolite into the solution. The amount of released calcium ions was more than 6.5 mg calcium ions/g after 3 min (Table 2). When the duration of the adsorption process was prolonged, the concentration of calcium ions in the solution increased slightly. The desorption process of calcium ions ended after 60 min (13 mg calcium ions/g), because the concentration of ions was almost the same when the duration of sorption was prolonged (Table 2). It should be noted that gyrolite acts as a chemisorbent but not like the usual adsorbent, because during cation exchange, reactions proceed with only partial exchange (calcium ions ↔ cadmium ions); that is, in these reactions, the exchange

	Duration of adsorption: min				
	1	3	5	60	120
Adsorption capacity of gyrolite: mg/g	87.54	89.27	91.18	95.67	96.96
pH value of solution	8.65	8.66	8.75	8.64	8.69
Calcium ion concentrations in solutions	5.64	6.57	8.59	13.01	13.10

Table 2. The amount of adsorbed cadmium and released calcium ions by gyrolite

of calcium ions $\leftrightarrow$ cadmium ions was found to be non-stoichiometric. The chemical formula of gyrolite substituted with cadmium ions can be written as follows: $\text{Ca}_{15-1}\text{Cd}_{2-4}\text{Si}_{24}\text{O}_{60}(\text{OH})_8 \cdot 14+x\text{H}_2\text{O}$.

According to the chemical composition of the adsorbent, it was calculated that in the cadmium nitrate solution, substitution isomorphism is typical of gyrolite because approximately 38% of cadmium ions participate in the substitution/chemical reaction ($\text{gyrolite}-\text{Ca}^0 + \text{Cd}^{2+} \leftrightarrow \text{gyrolite}-\text{Cd}^0 + \text{Ca}^{2+}$), whereas the rest of these ions are present in gyrolite according to an addition interaction.

Analysis of the pH values of the solutions confirmed that ion exchange reactions proceeded or finished at the beginning of the sorption process (5–15 min). It should be emphasised that the pH value of the solution rapidly increased when gyrolite was mixed with the solution. This change is attributed to the degree of release of calcium ions from the structure of the gyrolite solid in solution during the reaction.

The results of EDS analysis indicate that cadmium ions incorporate into the structure of gyrolite, because after 120 min adsorption, EDS data show approximately 0.98 wt% of cadmium ions in the structure of crystal compounds (Figure 2(a)). The X-ray powder diffraction analysis showed that the structure of gyrolite did not change during sorption (Figure 2(b)).

In order to confirm that gyrolite acts as a chemisorbent, the adsorbents were dried and immersed at different pH: solution 1 (pH 6.11); solution 2 (pH 8.70); solution 3 (pH 11.57). In this case, different amounts of ammonium hydroxide ($c = 10\%$) were used to maintain the alkaline reaction medium. It was determined that cadmium ions did not appear (≥ 0.01 wt%) in the aqueous media under all experimental conditions (Figure 3).

In previous work (Eisinas *et al.*, 2012) it was proved that the synthetic gyrolite as an additive accelerates tricalcium silicate hydration and also changes the hydration mechanism of cement samples, because in the samples with 7.5% of additive the evaluated reaction order n_{app} grew about 2.5 times, meanwhile the reaction rate k_{app} increased about two times in comparison with pure samples. The experimental data and theoretical hypothesis were confirmed by thermodynamic calculations and were also described by Jander and Johnson–Mehl–Avrami–Kolmogorow hydration macromodels.

In order to estimate the effect of gyrolite with contaminated cadmium ions on the early hydration of OPC samples, heat evolution rate experiments were performed. Data on the rates of heat evolution (W/g_{OPC}) of the binary blended pastes are presented in Figures 4 and 5. The rate of heat evolution was calculated on the basis of a unit weight of OPC. Thus, the rates can be compared with each other, and the contribution of the gyrolite contaminated with cadmium ions can be separated out.

Figure 2. X-ray spectrometry analysis (a) and X-ray diffraction curves (b, curve 2) of gyrolite after adsorption of cadmium ions for 120 min at 25°C. For comparison: X-ray diffraction curves of pure gyrolite (b, curve 1)). Ca, calcium; Cd, cadmium; G, gyrolite; O, oxygen; Si, silicon

Figure 3. Quantity of cadmium ions in gyrolite structure after desorption process at different pH

In fact, this is the first time it has been determined that gyrolite contaminated with cadmium ions (~ 97 mg cadmium ions/g) retains very good adsorption properties for the alkaline and alkaline earth ions, which penetrate into the structure of gyrolite,

Figure 4. Heat evolution rate of ordinary Portland cement samples during the early stage of hydration. Amounts of additive, wt%: sample 1, 0; sample 2, 2.5; sample 3, 5; sample 4, 7.5

Figure 5. The influence of the amount of gyrolite contaminated with cadmium ions on the rate of heat evolution of ordinary Portland cement samples for the following amounts of additive, wt%: sample 1, 0; sample 2, 2.5; sample 3, 5; sample 4, 7.5

causing the dissolution of individual phases of cement to proceed more quickly. For this reason, the addition of gyrolite contaminated with cadmium ions accelerates the early stage of the hydration of OPC and its individual compounds. In addition, the first peak of all samples with this additive produces an increase in the maximum heat evolution rate relative to OPC, and this effect grows as the amount of additive increases (Figure 4).

It was determined that in the samples with gyrolite, the induction period is effectively shortened: in pure OPC paste, hydration takes about 2.5 h, compared with only 20–30 min for a sample with 7.5% gyrolite (Figure 5).

For the first time, it has been proved that in the OPC samples with 2.5% additive, the maximum adsorption capacity of gyrolite substituted with cadmium ions for the alkaline and alkaline earth ions was reached after 8–9 h of hydration, because the amount of

cumulative heat started to decrease (until it reached ~ 60 J/g) and achieved the same level as pure OPC samples (Figure 6(a)). Meanwhile, in previous work (Eisinas *et al.*, 2012) it was determined that pure synthetic gyrolite additive, due to its adsorption properties, has a positive influence on the cumulative heat of OPC samples under all experimental conditions. Meanwhile, in the OPC samples with 5% or 7.5% additive, gyrolite substituted with cadmium ions had effects similar to those of the usual pozzolanic additives because the amount of cumulative heat grows with the increasing amount of gyrolite in the samples (Figure 6).

In order to explain the effect/influence of gyrolite contaminated with cadmium ions on hydration of the OPC samples, a new experiment was performed: the test of gyrolite contaminated with cadmium ions stability in the mixtures with calcium hydroxide

Figure 6. The influence of the amount of gyrolite on the cumulative heat of OPC samples when the amount of additive was as follows, wt%: sample 1, 0; sample 2, 2.5; sample 3, 5; sample 4, 7.5. OPC, ordinary Portland cement

when the C/S ratio is 1.75. It was determined that at the beginning of the experiments, the crystalline part of gyrolite remains stable, and only after 8–9 h of hydration does this compound recrystallise into calcium silicate hydrate with higher basicity. These data were confirmed by X-ray diffraction results (Figure 7). It should be noted that after 10 h of hydration, the main diffraction peak with d -spacing of 2.231, characteristic of gyrolite, was not identified. In the dominant products were semicrystalline calcium silicate hydrates with a C/S ratio of 0.8–2.0. This phenomenon was also confirmed by a decrease in the rate of heat evolution (Figure 5).

It is known that cement is a mixture of phases that react at different rates, and there are problems in determining, and even in defining, the degree of hydration α for the whole cement.

In this report, α was determined by summing the amounts of tricalcium silicate that had reacted after heat evolution experiments at different time periods. The maximum heat evolution rate during hydration of OPC is associated with the main reaction of tricalcium silicate ($\Delta H = -561 \text{ J/g}_{(\text{C}_3\text{S})}$).

Figure 7. X-ray diffraction pattern of gyrolite contaminated with cadmium ions and calcium hydroxide mixture at an initial molar ratio of C/S = 1.75, W/S = 10.0, temperature 25°C, and the following durations of hydration, h: 1, 0 (after mixing); 2, 7; 3, 9. C, calcium silicate hydrates (C/S ratio in this phase varies from 0.8 to about 1.3); D, calcium silicate hydrates (C/S: 1.3–2.0); G, gyrolite; Gg, gyrolite gel; P, portlandite

For this reason, the amount of tricalcium silicate (X_τ) that reacted was calculated from heat flow data by using following equation

$$2. \quad X_\tau = \frac{\Delta H_H}{\frac{\Delta H_{\text{C}_3\text{S}} \cdot c_{\text{C}_3\text{S}}}{100\%}} \cdot m$$

where X_τ is the amount of tricalcium silicate that reacted, g; ΔH_H is enthalpy of hydration, calculated using heat flow data, J/g_{OPC}; $\Delta H_{\text{C}_3\text{S}}$ is enthalpy of tricalcium silicate, J/g_{C₃S}; $c_{\text{C}_3\text{S}}$ is the amount of tricalcium silicate in pure OPC, %; and m is the mass of OPC sample, g.

The amounts of tricalcium silicate that reacted during OPC hydration with different amounts of additive are presented in Figure 8. These results provide evidence that the main reaction of this silicate (Equation 1) occurs during the hydration process from 7 to 12 h in all samples.

According to the kinetic equation of chemical process (Levenspiel, 1999), the apparent reaction rate (W_{app}) of the hydration process (7–12 h) can be expressed as follows

$$3. \quad W_{\text{app}} = \frac{dx}{d\tau} = k_{\text{app}}(f(c))^n$$

where k_{app} is the constant of the apparent reaction rate, and $f(c)^n$ is the influence of the reagent concentration on the reaction rate.

Figure 8. Differential kinetic curves of reacted tricalcium silicate during ordinary Portland cement hydration with the following amounts of additive, wt%: sample 1, 0; sample 2, 2.5; sample 3, 5; sample 4, 7.5

By plotting Σx_τ as a function of τ , a linear apparent hydration rate of the tricalcium silicate plots is obtained (Figure 8), and their R^2 fluctuates in the range of 0.9973 to 0.9998 (Table 3). In this case, the apparent order of reaction (n) becomes close to zero, and Equation 3 can be written as follows

$$4. \quad W_{app} = \frac{dx}{d\tau} = k_{app}, \text{ g/h}$$

The slope of these linear plots (Figure 9) determines the values $tga = k_{app}$. The values of reaction order and rate constant are given in Table 3.

It was determined that during hydration from 7 to 12 h, the value of k_{app} did not depend on the amount of gyrolite in OPC samples (Table 3).

Thus, after 7 h of process, the additive of gyrolite contaminated with cadmium ions did not influence the reaction rate (stage II). Meanwhile, gyrolite stimulated the earliest tricalcium silicate hydration in all samples (stage I), and as the amount of this

Figure 9. Quantity of reacted tricalcium silicate during ordinary Portland cement hydration with following amounts of additive, wt%: sample 1, 0; sample 2, 2.5; sample 3, 5; sample 4, 7.5

additive increased in the samples, the first stage shortened: from 7 h in pure OPC samples to 4–5 h in samples with 7.5% additive (Figure 10). One of the main reasons is that gyrolite serves as a nucleation site (growing calcium silicate hydrate and calcium hydroxide on the surface of the particles of gyrolite) for the formation of hydration products. It is possible that the addition of gyrolite contaminated with cadmium ions stimulates the formation of hydration products on its surface. In this case, the crystal structures of tricalcium silicate were more smoother and covered by other compounds; the crystal agglomerates were smaller and had different forms and sizes compared with pure samples (Figure 11(a) and (b)). In this case, the diffusion of reagents through the continuous layer of hydrates is not a limited stage.

The results of EDS analysis confirmed that gyrolite contaminated with cadmium ions adsorbs alkaline ions during the hardening of OPC samples (Figure 11(d)) because these crystal agglomerates also contain 1.30 wt% magnesium, 1.26 wt% aluminium, 0.60 wt% potassium and 1.89 wt% iron. It should be noted that the chemical composition of the hydration products is very close to that of the compounds formed on the crystal structures of tricalcium silicate in pure OPC samples (Figure 11(a) and (c)). These data agree with results of the heat evolution experiments.

Figure 10. Dependence of reaction rate (W_τ) on hydration time (τ) of different samples: 1, OPC; 2, OPC + additive. I, II, III, hypothetical macro stages of the hydration process. OPC, ordinary Portland cement

Amount of additive: %	X_τ : g	X_0 : g	T : h	T_0 : h	W_{app} : g/h	R^2
0	0.131	0.034	12	7	0.019	0.9973
2.5	0.125	0.039			0.017	0.9989
5.0	0.154	0.056			0.020	0.9992
7.5	0.162	0.066			0.019	0.9998

Table 3. Kinetic parameters of reacted tricalcium silicate during ordinary Portland cement hydration

Figure 11. Scanning electron micrographs (a, b) and X-ray spectrometry analysis curve (c, d) of products. The duration of hydration at 25°C was 5 h. (a, c) Pure OPC samples; (b, d) OPC samples with 7.5% additive. Chemical composition of spectrum 1, wt%: O, oxygen, 53.46; Si, silicon, 5.28; Mg, magnesium, 1.25; Al, aluminium, 2.00; S, sulfur, 1.04; K, potassium, 0.79; Fe, iron, 2.10; Ca, calcium, 34.08; and spectrum 2, wt%: O, oxygen, 49.15; Si, silicon, 6.82; Mg, magnesium, 1.30; Al, aluminium, 1.29; S, sulfur, 1.19; K, potassium, 0.60; Fe, iron, 1.89; Ca, calcium, 37.80; C, carbon; OPC, ordinary Portland cement

In order to estimate the possibility of the immobilisation of cadmium ions in cement stone, the heat evolution experiments were repeated at different time periods (1, 3, 5, 7 and 10 min) under normal conditions. A liquid phase during OPC hydration was collected by vacuum filtration. The results of liquid phase

analysis showed that cadmium ions were bound in the cement stone under all experimental conditions (Table 4).

It was determined that after 7 h of hydration, only 0.034 g (i.e. 5.3% of the tricalcium silicate) had reacted in pure OPC samples

Duration of hydration: min	Pure OPC samples	OPC with 5% gyrolite substituted with cadmium ion additive samples	
	Calcium ions: mg/dm ³	Cadmium ions: mg/dm ³	Calcium ions: mg/dm ³
1	660.2	<0.0008	576.9
3	580.9		563.2
5	495.7		572.8
7	485.1		578.4
10	535.6		571.1

Table 4. Dependence of calcium and cadmium ion concentrations on duration of hydration. OPC, ordinary Portland cement

(Figure 9). Meanwhile, in samples with 7.5% gyrolite contaminated with cadmium ions, 10.5% of this compound had reacted after the same amount of time (Figure 9). Further reduction of its quantity depends on the duration of hydration. It was determined that during hydration from 7 to 12 h, in all samples, the increase in $\Delta\alpha$ was almost the same, $\Delta\alpha = 15\%$. It was observed that after 12 h, when the degree of tricalcium silicate hydration became higher, the reaction rate of the samples slowed down. It should be noted that this phenomenon corresponds to the law of mass action, according to which the rate of reaction depends on the molar concentration of the reactants involved in any chemical reaction. Thus, the addition of gyrolite contaminated with cadmium ions has no influence on further hydration processes (stages II and III) (Figure 10).

The data obtained at the laboratory scale showed that OPC samples with gyrolite contaminated with cadmium ion additive are not detrimental to the environment. In order to apply the encapsulation of heavy metals in gyrolite, followed by cement immobilisation to industrial production, more research must be conducted. These studies should include: the effects of heavy metal mixture on gyrolite adsorption capacity and cement hydration process; long-term leaching behaviour and immobilisation mechanism; and the short- and long-term mechanical and durability properties of the samples produced.

Conclusions

It was determined that during OPC hydration, gyrolite contaminated with cadmium ions (~ 97 mg cadmium ions/g) retained very good adsorption properties for the alkaline and alkaline earth ions that penetrated into the gyrolite structure. It was estimated that this additive accelerated the early stage (5–7 h) of hydration of OPC and its individual compounds. It was also determined that in the samples with gyrolite, the induction period was effectively shortened: in pure OPC paste, hydration takes about 2.5 h, compared with only 20–30 min for a sample with 7.5% gyrolite.

It was found that during the main reaction of calcium silicate, the addition of gyrolite contaminated with cadmium ions had no influence on the apparent reaction rate (W_{app}) of the hydration process (7–12 h): in all samples, the increase in the degree of hydration ($\Delta\alpha$) was almost the same, $\Delta\alpha = 15\%$. In this case, the crystal surfaces of tricalcium silicate were smoother, not covered by other compounds, and the crystal agglomerates were smaller and had different forms compared with pure samples. Also, the diffusion of reagents through the continuous layer of hydrates is not a limited stage.

Acknowledgement

This research was funded by a grant (no. MIP-077/2012) from the Research Council of Lithuania.

REFERENCES

- Buamah R, Petrusevski B and Schippers JC (2008) Adsorptive removal of manganese (II) from the aqueous phase using iron

oxide coated sand. *Journal of Water Supply Research and Technology* **57**(1): 1–11.

- Bullard JW, Jennings HM, Livingston RA et al. (2011) Mechanisms of cement hydration. *Cement and Concrete Research* **41**(12): 1208–1223.
- Chen QY, Hills CD, Tyrer M et al. (2007) Characterization of products of tricalcium silicate hydration in the presence of heavy metals. *Journal of Hazardous Materials* **147**(3): 817–825.
- Chen XC, Chen LT, Shi JY, Wu WX and Chen YX (2008) Immobilization of heavy metals by *Pseudomonas putida* CZ1/goethite composites from solution. *Colloids and Surfaces B-Biointerfaces* **61**(2): 170–175.
- Coleman NJ, Brassington DS, Raza A and Mendhamb AP (2006) Sorption of Co^{2+} and Sr^{2+} by waste-derived 11 A tobermorite. *Waste Management* **26**(3): 260–267.
- Cvetkovic VS, Purenovic JM, Purenovic MM and Jovicevic JN (2009) Interaction of Mg-enriched kaolinite–bentonite ceramics with arsenic aqueous solutions. *Desalination* **249**(2): 582–590.
- Demir G, Coruh S and Ergun ON (2008) Leaching behavior and immobilization of heavy metals in zinc leach residue before and after thermal treatment. *Environmental Progress* **27**(4): 479–486.
- Eisinas A, Baltakys K and Siauciunas R (2012) The effect of gyrolite additive on the hydration properties of Portland cement. *Cement and Concrete Research* **42**(1): 27–38.
- Eisinas A, Baltakys K and Siauciunas R (2013) Utilisation of gyrolite with impure Cd^{2+} ions in cement stone. *Advances in Cement Research* **25**(2): 69–79, <http://dx.doi.org/10.1680/jadcr.11.00043>.
- El-Korashy SA (2004) Cation exchange of alkali metal hydroxides with some hydrothermally synthesized calcium silicate compounds. *Journal of Ion Exchange* **15**(1): 2–9.
- Erdem E, Karapinar N and Donat R (2004) The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science* **280**(2): 309–314.
- Giergiczny Z and Krol A (2008) Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites. *Journal of Hazardous Materials* **160**(2–3): 247–255.
- Hashem FS, Amin MS and Hekal EE (2011) Stabilization of Cu (II) wastes by C3S hydrated matrix. *Construction and Building Materials* **25**(8): 3278–3282.
- Havelcova M, Mizera J, Sykora I and Pekar M (2009) Sorption of metal ions on lignite and the derived humic substances. *Journal of Hazardous Materials* **161**(1): 559–564.
- Jansen D, Goetz-Neunhoffer F, Lothenbach B and Neubauer J (2012) The early hydration of ordinary Portland cement (OPC): an approach comparing measured heat flow with calculated heat flow from QXRD. *Cement and Concrete Research* **42**(1): 134–138.
- Juilland P, Gallucci E, Flatt R and Scrivener KL (2010) Dissolution

- theory applied to the induction period in alite hydration. *Cement and Concrete Research* **40(5)**: 831–844.
- Kasperaviciute V, Baltakys K and Siauciunas R (2008) The sorption properties of gyrolite for copper ions. *Ceramics-Silikaty* **52(2)**: 95–101.
- Kosobucki P, Kruk M and Buszewski B (2008) Immobilization of selected heavy metals in sewage sludge by natural zeolites. *Bioresource Technology* **99(13)**: 5972–5976.
- Kumar A, Bishnoi S and Scrivener KL (2012) Modelling early age hydration kinetics of alite. *Cement and Concrete Research* **42(7)**: 903–918.
- Levenspiel O (1999) *Chemical Reaction Engineering*. Wiley, New York, NY, USA.
- Murari P, Huan-Yan X and Sona S (2008) Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent. *Journal of Hazardous Materials* **154(1–3)**: 221–229.
- Panuccio MR, Crea F, Sorgona A and Cacco G (2008) Adsorption of nutrients and cadmium by different minerals: experimental studies and modelling. *Journal of Environmental Management* **88(4)**: 890–898.
- Siauciunas R, Janickis V, Palubinskaite D and Ivanauskas R (2004) The sorption properties of tobermorite modified with Na⁺ and Al³⁺ ions. *Ceramics-Silikaty* **48(2)**: 76–82.
- Taylor HFW (1997) *Cement Chemistry*, 2nd edn. Academic Press, London, UK.
- Thomas JJ, Biernacki JJ, Bullard JW et al. (2011) Modeling and simulation of cement hydration kinetics and microstructure development. *Cement and Concrete Research* **41(12)**: 1257–1278.

WHAT DO YOU THINK?

To discuss this paper, please submit up to 500 words to the editor at journals@ice.org.uk. Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editorial panel, will be published as a discussion in a future issue of the journal.