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## Hydration Study of Ordinary Portland Cement in the Presence of Lead(II) Oxide

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The aim of this work was to investigate the effect of the addition of lead(II) oxide on hydration heat and specific conductivity of a CEM I Portland cement. The heat released during hydration was determined by differential microcalorimetry up to 48 hours of hydration and the specific conductivity by a digital conductometer. Thermogravimetric analysis was employed in the characterization of the cement structure. The hydration heat results show that the addition of lead(II) oxide affects the cement hydration kinetics. Kinetic curves show that higher content of lead(II) oxide slows down the hydration processes and the heat values are lower. Addition of lead(II) oxide significantly delays the time to the appearance of maximum conductivity. Setting time is prescribed by standard for a particular type of cement and can be determined based on the appearance of specific conductivity maximum, which occurs at the setting time. It was found that the acceptable amount of lead (II) oxide in cement system was  $w = 0.25$  wt. %.

*Key words:*

Stabilization/solidification (S/S), hydration heat, specific conductivity, differential microcalorimetry, thermogravimetric analysis

### Introduction

Solidification/stabilization (S/S) is a technique for immobilizing hazardous wastes in binding materials, mostly cement-based, to delay the release of toxic components into the environment. Waste materials are often S/S treated and are then landfilled or recycled into new building materials.<sup>1–4</sup> Among metal wastes, those containing Pb represent a serious issue. Pb derivatives are employed in mining and metallurgic industries, manufacture of coating pigments, imprint and typographer and plastic incineration. In humans, Pb exposure can lead to a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system.<sup>5,6</sup>

Ordinary Portland cement (OPC) is often used as a binding agent on its own, or in combination

with cement replacement materials, which may be hydraulic (cement kiln dust) or pozzolanic (pulverized fuel ash, slag etc.) in nature.<sup>7</sup> The popularity of cement for waste S/S systems not only from an economic or convenience perspective, but predominantly from the way in which the fixation of the waste is effected: stabilization and solidification in essentially the one step. The alkalinity of the cement-waste matrix is advantageous because most metal ions have poor solubility at high pHs, while the physical integrity of the waste compensates for any amphoteric species which are not as easily stabilized at pH values greater than 7.<sup>8–10</sup>

Many studies have investigated the effect of lead on the hydration of cement phases. Lead retards the setting of cement due to the formation of compounds that cover the silicate phases. Glasser<sup>11</sup> reported that calcium silicate hydrates (C–S–H) and calcium sulfoaluminate hydrates are largely responsible for the retention of Pb. Using X-ray diffraction, Hamilton et al.<sup>12</sup> identify no lead compounds in cement/lead oxide system after a 28-day curing time, and they concluded that lead compounds in cement matrices are amorphous. Tashiro et al.<sup>13</sup> re-

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ported that common hydration products are formed during the hydration of  $C_3A$  in the presence of  $PbO$ . However, it decreases the compressive strength of  $C_3A$ .<sup>13</sup>

In the present study, a  $PbO$  was solidified and stabilized by different proportion of OPC. This work has examined the effect of  $PbO$  on hydration processes using differential microcalorimetry, conductometry and thermogravimetric analysis. The main task of this study was to determine an acceptable amount of  $PbO$  in the cement system for its successful stabilization and solidification.

## Materials and methods

### Materials and sample preparation

All the measurements were carried out using OPC and different content of lead(II) oxide. OPC (according to EN-197 CEM I) was obtained from CEMEX Croatia cement plant (Kaštel Sućurac, Croatia). Its chemical composition and physical properties are shown in Tables 1 and 2. Lead(II) oxide,  $PbO$ , p.a., was obtained from P.P.H. Polskie Odezywniki Chem-Gliwice, Poland.

Table 1 – Chemical composition of OPC

Composition	%
$SiO_2$	22.85
$Al_2O_3$	4.81
$Fe_2O_3$	2.79
CaO	65.23
MgO	1.61
$K_2O$	1.89
$Na_2O$	0.18
Loss of ignition	0.04

Table 2 – Physical and mechanical properties of OPC

Physical property	Value
Specific surface according to Blaine ( $cm^2 g^{-1}$ )	3300
Standard consistency (%)	26
Setting time – start (min)	85
Setting time – end (min)	150
Average flexural strength (MPa)	
after 3 days	6.26
after 28 days	8.44
Average compressive strength (MPa)	
after 3 days	33.50
after 28 days	50.70

Samples for microcalorimetric measurements were prepared by mixing cement and 0 – 1 wt. % of  $PbO$ . The total mass of the solid sample was constant at 4 g. Water to solid ratio of 0.5 was used for all mixes, and the measurements were carried out at a temperature of 20 °C.

Samples for conductometric measurements were prepared in the same way as the samples for microcalorimetric measurements, except total mass of the solid sample was 100 g.

Cement pastes for thermogravimetric analysis were hydrated 28 days in a thermostat at a 20 °C. After this curing time, they were ground and sieved through a standard 4900 mesh  $cm^{-2}$  sieve.

## Methods

### Differential microcalorimetry

The microcalorimetric measurements used to examine the interferences with the waste stabilization process were conducted by means of a differential microcalorimeter of the conduction-isoperibolic type.<sup>14</sup> An ALMEMO 2290-8 data logger was used to register heat effects of the hydration processes in the microcalorimeter, monitoring the change of voltage  $dU = f(t)$ . The recorded values were processed by software “HYDRATION” on a computer, obtaining the values of the heat of hydration, the relative reaction degree, and the heat release rate for the given hydration conditions.

### Conductivity

The conductometric measurements used to provide the conductivity in the cement pastes were conducted by means of an ISKRA MA 5964 microprocessor conductometer connected to a computer via an RS 232 C. The conductometric cell electrode was made of stainless steel with a constant  $C = 0.285 cm^{-1}$ .

### Thermogravimetric analysis

Thermal analysis was performed on a Pyris 1 TGA at 20 °C  $min^{-1}$  from 50 to 850 °C in 10 ml  $min^{-1}$   $N_2$  flow.

## Results and discussion

To determine the effect of  $PbO$  on OPC hydration, the method of continuous observation of early hydration, microcalorimetry, was applied, which monitors heat released during hydration. The heat released heats the operating cell of a differential microcalorimeter,<sup>15</sup> causing a difference in temperatures between the operating and the reference

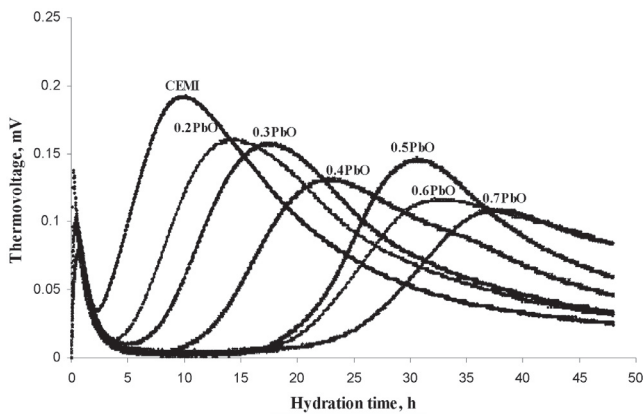


Fig. 1 – Thermovoltage curves ( $dU = f(t)$ ) for the samples with different additions of PbO (wt. %)

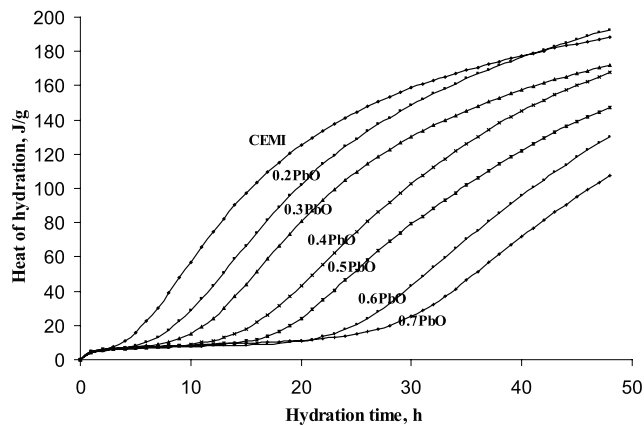


Fig. 2 – Heat of hydration dependence of time for different additions of PbO (wt. %)

cell, measured as tension difference,  $dU$ , by thermocouples. Figs. 1, 2, 3 and 4 show that during the hydration occur effects manifested in the form of maximums and minimums at different times of hydration. The first peaks are short and occur immediately after contact of water and cement composites. Formation of hydration products developed an adequate amount of heat. The shape, position and size of the main peak, which releases the majority of the heat of hydration, depends on the amount of PbO added. In the sample CEM I (Fig. 1), the second or main maximum is noticeable and becomes less pronounced with the increase of PbO, and the maximum occurrence is registered in the later times of hydration. The main peak is followed by a period of slower hydration, characterized by a small amount of developed heat, and a reduced overall rate of hydration.

The results show that the amount of PbO affects the final value of heat of hydration (Fig. 2). Increasing PbO decreases the heat of hydration after the first 48 hours of hydration. The cement sample with 0.2 wt. % PbO develops heat of hydration

of  $192.5572 \text{ J g}^{-1}$  and with 0.7 wt. % of PbO  $107, 2194 \text{ J g}^{-1}$ . The value of heat of hydration of the sample CEM I is  $188.2810 \text{ J g}^{-1}$ . These results were expected since the proportion of active components (Portland cement), which releases heat decreases.

The heat release rate and degree of hydration behave equally (Fig. 3 and 4).

Fig. 5 shows the functional dependence of the maximum heat released and the time to maximum of the addition of PbO.

For the addition of PbO, the function of heat of hydration has the form:

$$z = -195.65x^2 + 17.362x + 190.07,$$

where  $z$  is the maximum heat released ( $\text{J g}^{-1}$ ) and  $x$  represents addition of PbO in wt. %.

Time to heat maximum can be calculated by the equation:

$$y = 30.915x^2 + 17.038x + 9.2138,$$

where  $y$  is the hydration time in hours, and  $x$  is the addition content.

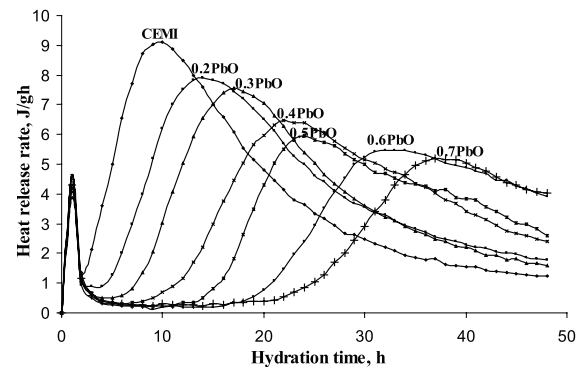


Fig. 3 – Heat release rate for samples with different additions of PbO (wt. %)

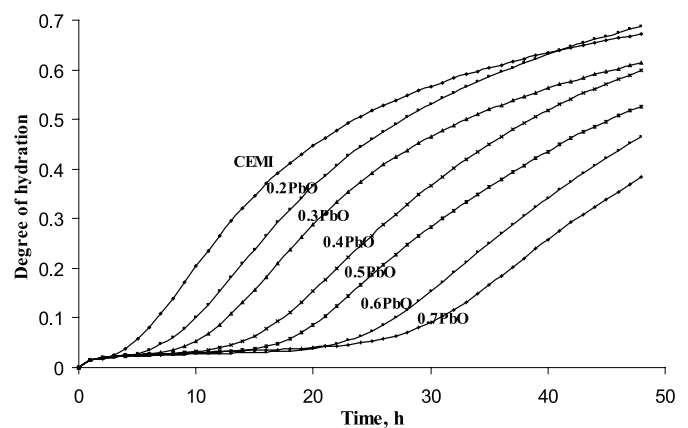


Fig. 4 – Degree of hydration for Portland cement pastes with different additions of PbO (wt. %)

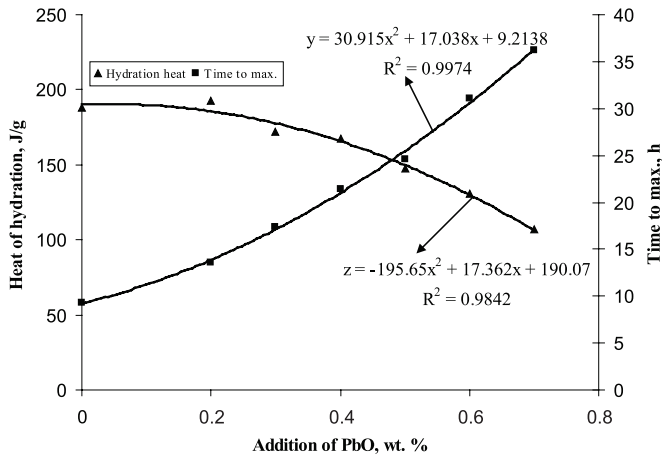


Fig. 5 – Functional dependence of the maximum heat released and time to maximum for the different additions of PbO (wt. %)

Table 3 – Time to maximum appearance of conductivity for various addition of PbO

Addition of PbO, wt. %	Time to maximum appearance, min
0.00	105
0.05	115
0.10	135
0.25	205
0.50	560
0.75	1060
1.00	1780

Thus, for each addition of PbO the maximum value of the heat released during hydration and time to achieve the maximum of heat can be calculated.

Specific conductivity of cement pastes was continuously observed in order to use these curves to determine the conductivity maximums, which indicate the setting time of the cement pastes. The time to appearance of the maximum can be used as a parameter for estimating the addition of PbO, which does not delay the setting of cement paste more than the standard allowed. The introduction of PbO into the reaction system leads to slower hydration, but hydration curves have a typical shape with reduced specific conductivity (Fig. 6).

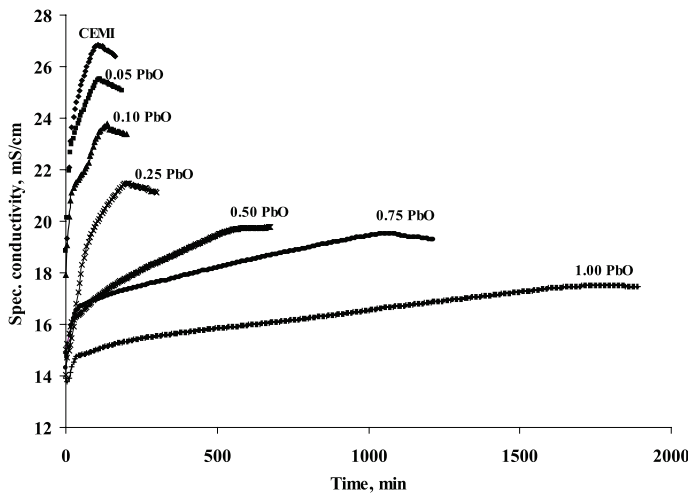


Fig. 6 – Specific conductivity of cement pastes with different additions of PbO (wt. %)

According to the technical specification<sup>16</sup> and standard<sup>17</sup> for OPC, the start of setting should occur after 60 minutes. For practical application, the end of setting time should occur in below 200 minutes. It was found that PbO addition to the cement-water system is acceptable up to 0.25 wt. % (Table 3). Increased shares of PbO above 0.25 wt. % signifi-

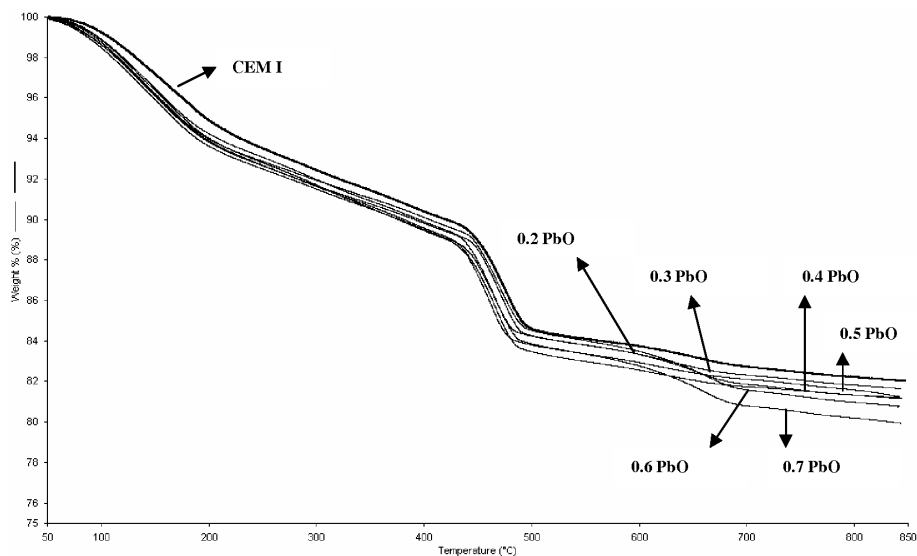


Fig. 7 – Thermal analysis of a hydrated cement sample with addition of PbO (wt. %), cured for 28 days

cantly delay the setting time and is not acceptable for the system.

Fig. 7 shows the thermal curves obtained on heating hydrated cement samples cured for 28 days. Several losses appear on these curves.

The first loss between 100 – 200 °C corresponds to the decomposition of the nearly amorphous hydrates, mainly C–S–H as well as calcium sulphoaluminate hydrates. The decomposition continues gradually, as evidenced by the slow loss in mass between 200 and 450 °C. A great loss then occurs corresponding to the decomposition of Portlandite,  $\text{Ca}(\text{OH})_2$ . The loss of weight around 700 °C was assumed to represent decomposition of  $\text{CaCO}_3$ . The addition of PbO shifts the peaks to the lower temperatures and shows a higher mass loss.

## Conclusion

The hydration heat results show that the addition of lead(II) oxide affect the cement hydration kinetics. The kinetic curves show that higher content of lead(II) oxide slow down the hydration processes and the heat values are lower.

Addition of lead(II) oxide significantly delays the time to appearance of maximum conductivity, which indicates the setting time of the cement pastes. Time to appearance of the maximum can be used as a parameter for estimating the addition of PbO, which does not delay the setting time of cement paste more than the standard allowed.

It was found that the acceptable amount of lead (II) oxide in cement system was  $w = 0.25$  wt. %.

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## List of symbols

S/S	– solidification/stabilization
OPC	– ordinary Portland cement
C–S–H	– calcium sulfoaluminate hydrate
C <sub>3</sub> A	– calcium aluminate
PbO	– lead(II) oxide

## References

1. Spence, R. D., Shi, C., Introduction, in: Spence, R., Shi, C. (Ed.), Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, pp 1–48, CRC Press, Boca-Raton, 2005.
2. Martens, E., Jacques, D., Van Gerven, T., Wang, L., Mallants, D., *Cem. Concr. Res.* **40** (2010) 1298.
3. Chen, Q. Y., Tyrer, M., Hills, C. D., Yang, X. M., Carey, P., *Waste Manage.* **29** (2009) 390.
4. Gervais, C., Ouki, S. K., *J. Hazard. Mater.* **B93** (2002) 187.
5. Gollmann, M. A. C., da Silva, M. M., Masuero, A. B., dos Santos, J. H., *J. Hazard. Mater.* **179** (2010) 507.
6. Thevenin, G., Pera, J., *Cem. Concr. Res.* **29** (1999) 1605.
7. Giergiczny, Z., Krol, A., *J. Hazard. Mater.* **160** (2008) 247.
8. Bone, B. D., Barnard, L. H., Boardman, D. I., Carey, P. J., Hills, C. D., Jones, H. M., MacLeod, C. L., Tryer, M., Science Report, Environment Agency, Bristol, 2004.
9. Gougar, M. L. D., Scheetz, B. E., Roy, D. M., *Waste Manage.* **16** (1996) 295.
10. Olmo, I. F., Chacon, E., Irabien, A., *Cem. Concr. Res.* **31** (2001) 1213.
11. Glasser, F. P., Chemistry of cement solidified waste forms, in: R. D. Spencer, R. D. (Ed.), Chemistry and Microstructure of Solidified Waste Forms, pp 1–40, Lewis Publishers, Boca Raton, 1993.
12. Hamilton, I. W., Sammes, N. M., *Cem. Concr. Res.* **29** (1999) 55.
13. Tashiro, C., Oba, J., *Cem. Concr. Res.* **9** (1979) 253.
14. Krstulović, R., Krolo, P., Ferić, T., *Periodica Polytechnica* **33** (1989) 315.
15. Krstulović, R., Dabić, P., *Cem. Concr. Res.* **30** (2000) 693.
16. Technical specification for CEM I 42,5 R Sv. Juraj cement factory, Split, Croatia.
17. EN 196-3, Test Methods for Cement, CEN/TC 51.

