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Pb elution characteristics of cement bypass dust sludge

Kyoung Seok Kim, Yong Sik Chu* and Sung Kwan Seo
Energy & Environmental Division, Korea Institute of Ceramic Eng. & Tech., Jinju 660-031, Korea

Cement manufacturing plants use a chlorine bypass system to reduce the contents of chlorine. As bypass system is used, bypass dust is generated which has mainly KCl and small amount of heavy metals. During the KCl elution process, sludge winds up being generated and it contains a large amount of Pb which is required high costs for it to be buried. Through this study, we tried to fix the heavy metals by mixing the sludge that came from the bypass dust with the ordinary Portland cement. In order to fix the Pb, the sludge and OPC were mixed together to manufacture sphere-shaped products that have a diameter of 1cm. The product was put in a thermo-hygrostat for 3 and 7 days at 23 °C with a relative humidity of 80%. After the curing process, all products of Pb contents were analyzed. The amount of Pb elution was different according to the composition of dust which came out of the cement factory. The amount of Pb elution went down as the amount of sludge that was less used and with longer curation periods. In particular, it was confirmed that the Pb content with 7 days of curation satisfies standard value of 3 mg/L.

Key words: Cement Bypass Dust, Sludge Heavy Metal Immobilization, KCl, Ettringite.

Introduction

Recently, cement factories are using various industrial wastes and household wastes as auxiliary raw materials and fuel to cut manufacturing costs and resource recycle resources [1]. These industrial wastes and household wastes contain chlorine, alkaline components and small amounts of heavy metals [2]. Chlorine and alkaline compounds are volatile in the kiln at high temperature making a coating form inside the kiln body to interfere with the transport of raw materials and clinker. Also the chloride produced by the chlorine causes the physical properties of cement to get weaker.[3-4] Therefore, a chlorine bypass system is attached and used in the kiln preheater area to remove the alkalis and chlorine [5]. Most of the bypass dust (hereinafter referred to as "dust") are generated through the system is composed of potassium chloride, limestone, quicklime, etc., but also heavy metals such as Pb are contained as well [6-8].

In order to obtain KCl from the dust, first, dust is mixed with distilled water to get the slurry. And then it is stirred, and gets filtered. After filtration of the manufactured slurry, the filtrated slurry is dried to obtain the KCl [9]. During this process, the unfiltered sludge is separated as designated waste because of its high heavy metal content [10]. It not only adversely affects the human body and environment, but the waste has to be treated or put in a landfill with a higher cost compared to ordinary waste.

Therefore, in this study, Pb was fixed by the mixing of residual sludge and ordinary Portland cement, and then Pb elution amount was analyzed and examined.

Experimental Method

In this study, we used the bypass dust from the domestic "S" cement manufacturing plant. In order to analyze the characteristics of raw dust and the products, chemical analysis and crystallinity analysis were carried out. For the analysis, the inductively coupled plasma spectrometer (ICP-OES 8300, Perkin Elmer, USA) was used for the chemical compositions and the X-ray diffractometer (D/MAX-2500V, Rigaku, Japan) was used for the crystallinity. In addition, the scanning electron microscope (SM-300, Topcon, Japan) was used to analyze the products to observe the ettringite microstructure. To analyze the Pb elution characteristics of the products, first, the dust and distilled water was set at a ratio of 1 : 3.

Then the slurry (dust + water) was stirred for 30 minutes at 20 °C. When the stirring was completed, it was then filtered by using a filter paper. After filtration, the residual sludge was dried at a constant temperature in a controlled dryer at 100 °C. The dried sludge was then mixed with 2 : 1, 3 : 1, 4 : 1 and 5 : 1 by the weight ratio of OPC. The manufactured samples were made by adding distilled water which is 20% of its own weight to make a 1cm sphere-shape. The samples were cured in the thermo-hygrostat for 3 days and 7 days at 23 °C with 80% relative humidity. After curation, the characteristics of the Pb elution were analyzed according to the waste process test.

*Corresponding author:
Tel : +82-55-792-2463
Fax: +82-55-792-2458
E-mail: yschu@kicet.re.kr

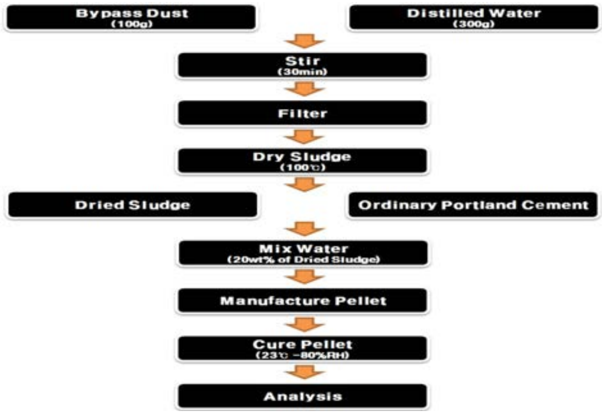


Fig. 1. Experimental flow chart.

Results and Discussion

Raw material analysis

Table 1 shows the results of the dust chemical analysis from the domestic cement manufacturing 1st plant and the 2nd plant of company "S". The contents of CaO in the dust were each 25.25% and 44.01, MgO were 1.50% and 2.50%, K_2O were 29.61% and 19.58%. SO_2 were 13.17% and 4.50%. Cl^- were 20.19% and 15.94%, and Pb were detected at 12,500ppm and 5,490 ppm. Fig. 2 shows the XRD pattern analysis results from each plants's dust. Various peaks were observed and the main peak was shown as the KCl. This meant that the KCl content in the dust was high. Fig. 3 shows the results of XRD pattern analysis from obtained sludge. The $Ca(OH)_2$ peak was strongly observed in the sludge, and the other KCl peak was also appeared. It was confirmed that most of the KCl compounds were passed and the CaO component in the residual sludge reacted with the residual water to form $Ca(OH)_2$.

Table 1. Amount of Elements and Heavy Metal in By-pass Dust.

Comp.	Chemical component (wt%)					Heavy metal (ppm)
	CaO	MgO	K_2O	SO_2	Cl^-	Pb
Plant. 1	25.25	1.50	29.61	13.17	20.19	12,500
Plant. 2	44.01	2.56	19.58	4.50	15.94	5,490

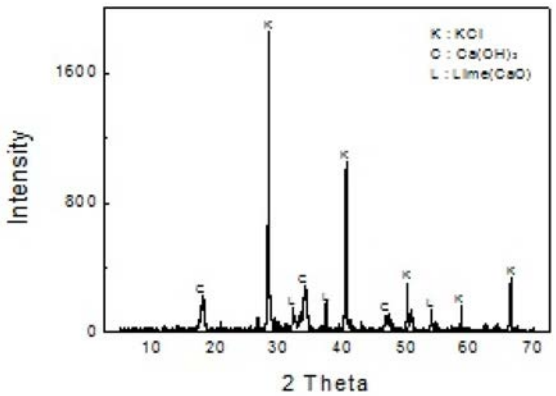


Fig. 2. XRD pattern of dust.

Comparison of Pb elution containment due to 3 days of curation.

Fig. 4 shows the Pb elution values of the manufactured products that were cured 3 days in the

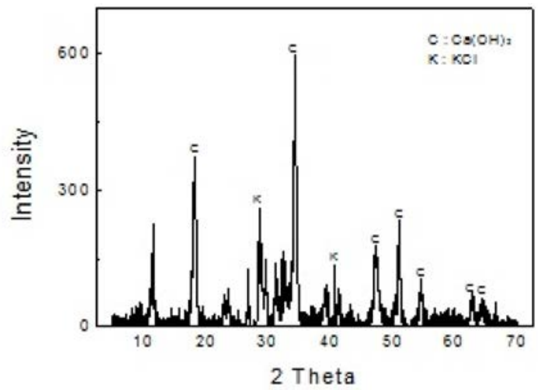


Fig. 3. XRD pattern of sludge.

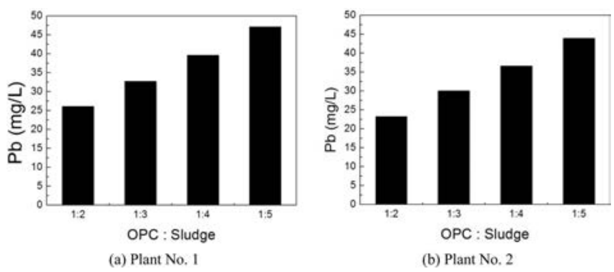


Fig. 4. Content of Pb (3 days).

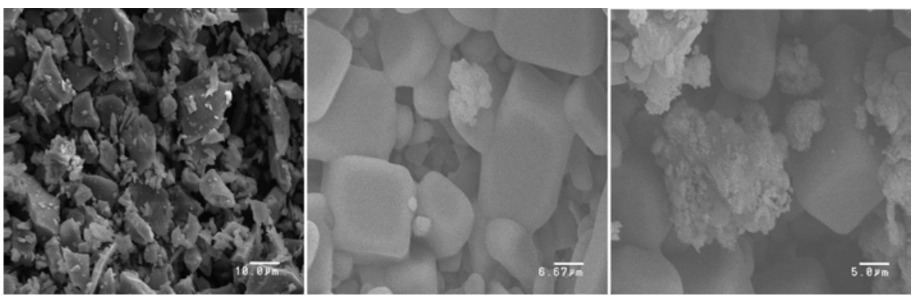


Fig. 5. Microstructure of manufactured specimen (3 days).

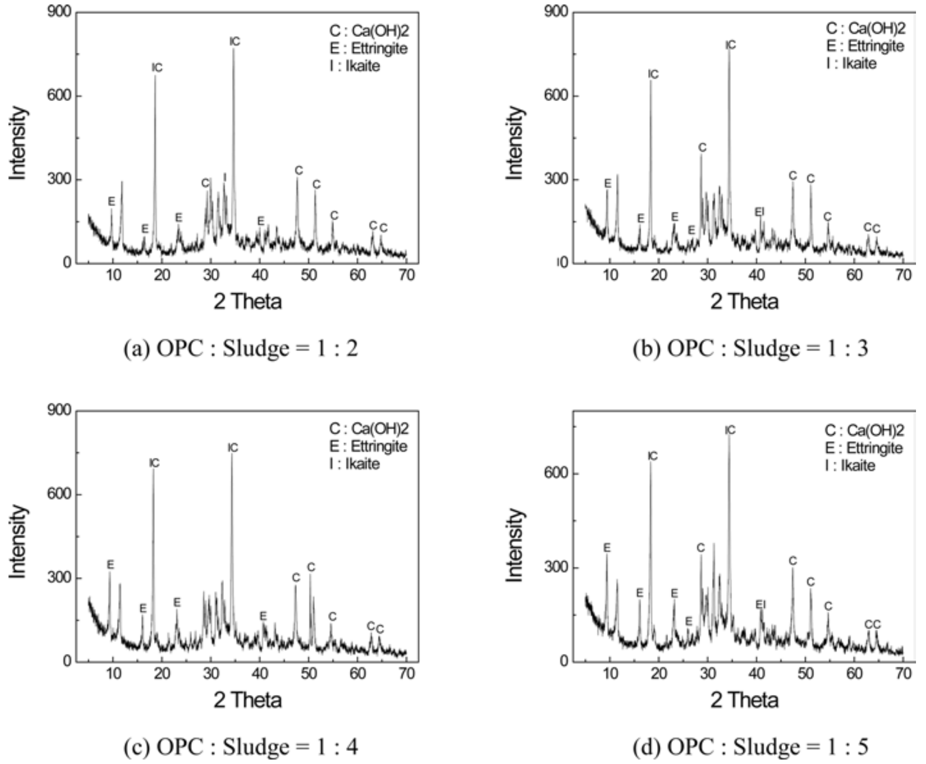


Fig. 6. XRD Pattern of manufactured specimen (Plant. 1, 3 days).

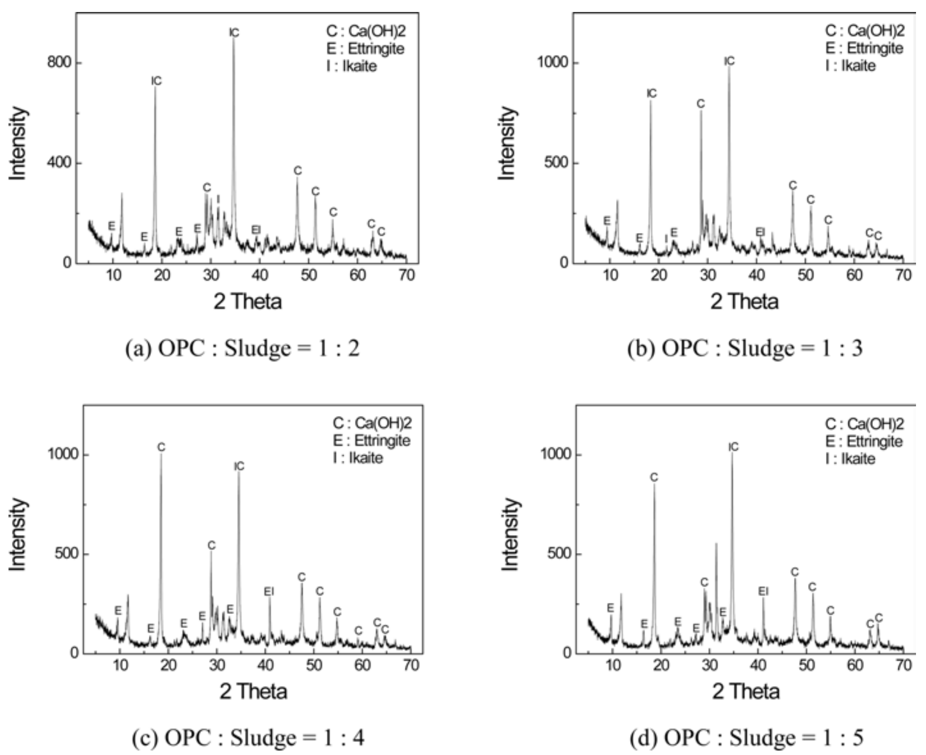
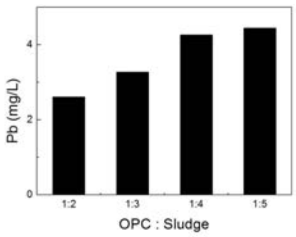
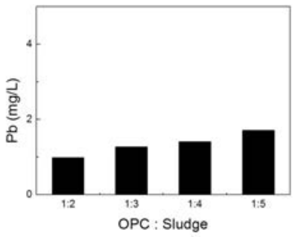


Fig. 7. XRD pattern of manufactured specimen (Plant. 2, 3 days).

thermo-hygrostat after mixing with 20 g of Ordinary Portland Cement (OPC) and 40 g, 60 g, 80 g, and 100 g of the obtained sludge from each plants's dust. The Pb elution values were 26.1 mg/L, 32.7 mg/L, 39.6 mg/L and 47.1 mg/L depending on the mixed ratio of OPC and sludge that came out of the 1st plant. The Pb elution values of the products made from 2nd plant dust were 23.2 mg/L, 30.0 mg/L, 36.6 mg/L and 43.9 mg/L. When the curation period was for 3 days, the Pb elution values of all products were significantly exceeded



(a) Plant No. 1



(b) Plant No. 2

Fig. 8. Content of Pb (7 days).

comparing with the Pb elution standard (≦ 3.0 mg/L). Fig. 5 shows the Scanning Electron Microscope photograph of the product's microstructure which was cured for 3 days.

In general, the heavy metal fixation mechanism used cement is known by the growth of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) [11]. While it grows up, heavy metals such as Pb are stuck in ettringite structure. However, it was evaluated not to fit the condition of the Pb elution standard due to the lack of the curation that is required for the ettringite formation. Figs 6 and 7 show the results of XRD pattern analysis for the 3 days of curation for the hydrates. In all the samples, hydrates such as $Ca(OH)_2$ and ettringite were observed, suggesting that the hydration progresses continuously under the constant humidity, temperature inside the thermo-hygrostat.

The comparison of Pb elution with 7 days of curation

Fig. 8 shows the Pb elution values of the manufactured products that were cured 7 days in the thermo-hygrostat after mixing with 20 g of OPC and 40 g, 60 g, 80 g, and 100 g of the obtained sludge from each plants's dust. The Pb elution values of the manufactured products followed by OPC and sludge ratio were 2.61 mg/L, 3.27 mg/L, 4.26 mg/L, and 4.44 mg/L for plant 1 and 0.99 mg/L, 1.27 mg/L, 1.41 mg/L, and 1.71 mg/L for plant 2. The Pb elution

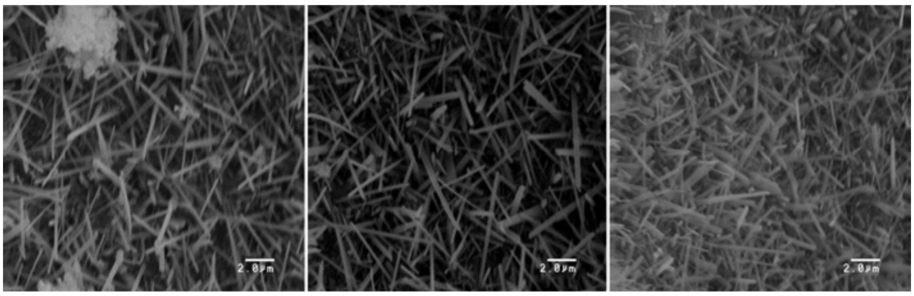
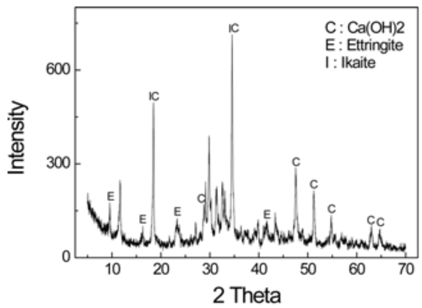
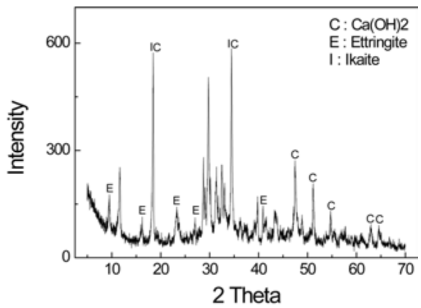


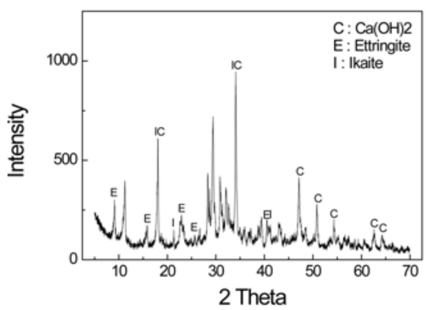
Fig. 9. Microstructure of manufactured specimen (7 days).



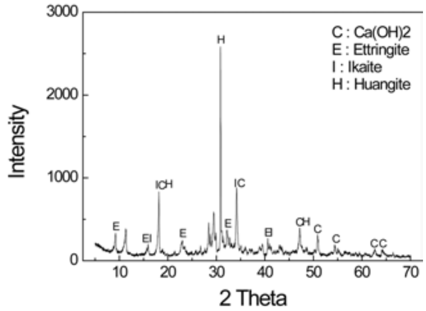
(a) OPC : Sludge = 1 : 2



(b) OPC : Sludge = 1 : 3

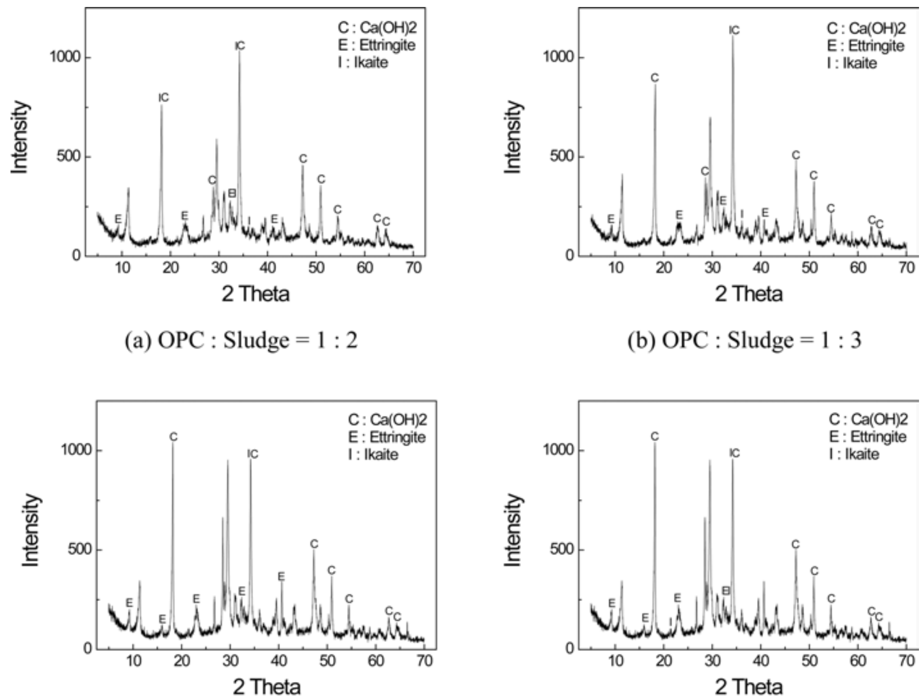


(c) OPC : Sludge = 1 : 4



(d) OPC : Sludge = 1 : 5

Fig. 10. XRD Pattern of manufactured specimen (Plant. 1, 7 days).



(a) OPC : Sludge = 1 : 2 (b) OPC : Sludge = 1 : 3

(c) OPC : Sludge = 1 : 4 (d) OPC : Sludge = 1 : 5

Fig. 11. XRD pattern of manufactured specimen (Plant. 2, 7 days).

values from the 1st plant`s dust with 7 days of curation were around the waste elution standard value (less than 3mg/L) and the Pb elution values from the 2nd plant`s dust were satisfied with the standard value.

It was considered that it took a sufficient time to generate and grow the ettringite to match the fixed Pb value. Fig. 9 shows the SEM micrographs of the product's microstructure which was cured for 7 days. Compared with the curation period of 3 days, a large amount of the ettringite structure was observed. Followed, a small amount of $Ca(OH)_2$ was observed as well. It is considered that the C_3A ($3CaO \cdot Al_2O_3$) in the OPC reacted with gypsum ($CaSO_4$), showing that sufficient time is needed for the ettringite formation.[12] Fig. 10 and 11 show the XRD pattern analysis results for the condition of the 7 day curation. Compared with the results of the 3 day curation, the XRD peak intensity for ettringite was relatively high.

Conclusions

In this study, various factors were controlled to suppress the Pb elution in the obtained sludge. Especially, the mixing ratio of the obtained sludge with OPC and the number of days for curation were controlled. So, we were able to draw the following conclusion.

1) When the curation period was for 3 days with a constant temperature in a thermo-hygrostat with temperature at 23 °C and the relative humidity at 80%, the Pb elution standard values exceeded 3 mg/L in all samples. Additionally, as the sludge mixing ratio increased, the Pb elution amount also increased.

2) When the curation period was for 7 days, the amount of Pb elution were dramatically decreased. The Pb elution values from the 1st plant`s dust with 7 days of curation was around the waste elution standard value (less than 3mg/L) and the Pb elution values from the 2nd plant`s dust met the standard value.

We came to the conclusion that the amount of the Pb elution decreases when the mixed ratios of OPC and sludge are similar and the curation period gets reached longer. It was confirmed that the C_3A ($3CaO \cdot Al_2O_3$) in the OPC reacted with the gypsum ($CaSO_4$) to form ettringite, and we confirmed that the immobilization of Pb is due to ettringite. As the curation period becomes longer, the amount of Pb elution is expected to converge to 0, but when considering the value of time and money the best option is to make the OPC · sludge mixture ratio to 1 : 2 and cure for 7 days.

References

1. M. Schneider, M. Romer, M. Tschudin, H. Bolio, Cem. and Concr. Research 41 (2011) 642-650.
2. Md. S. Islam, Md. K. Ahmed, M. Raknuzzaman, Md. H.A Mamun and G. Kumar, J. of Geochem. Exploration 172 (2017) 41-49.
3. N. Gineys, G. Aouad and D. Damidot, Cem. and Concr. Composites 32 (2010) 563-570.
4. N. Gineys, G. Aouad and D. Damidot, Cem. and Concr. Composites 33 (2011) 629-636.
5. C. Lanzerstorfer, Process Safety and Environmental

Protection 104 (2016) 444-450.
6. R. Taha, A. A. Rawas, A.A. Harthy, and A. Qatan, ASCE 14 (2002) 338-343.
7. M. Achternbosch, M. Matthias, B. K. Rainer, N. Hartlieb, C. Kupsc, U. Richers and U. Peter, in “Heavy metals in cement and concrete resulting from the co-incineration of wastes in cement kilns with regard to the legitimacy of waste utilization” (Forschungszentrum Karlsruhe, 2003) p.187.
8. H.Y. Ghoraba, A. Mounir, N. Ghabrial, M. Rizk, S. Badawi and M. Khafaga, Polymer-Plastics Tech. & Eng. 43 (2004) 1723-1734.
9. Y.M. Yun, J. H. Jeong and Y.S. Chu, Korean Inst. of Res. Rec. 25 (2016) 43-48.
10. A. Roy, H.C. Eaton, F.K. Cartledge and M.E. Titlebaum, Hazardous Waste and Hazardous Mater. 8 (2009) 33-41.
11. W.A. Klemm, Portland Cement Association (1998) 68.
12. S. Speziale, F. Jiang, Z. MaO, P.J.M. Monteiro, H.R. Wenk, T.S. Duffy and F.R. Schilling, Cem. and Concr. Research 38 (2008) 885-889.