

# HYDRATION OF BELITE CEMENT PREPARED FROM RECYCLED CONCRETE RESIDUES

MARCELA FRIDRICHOVÁ

*Institute of Technology of Building Materials and Components, Brno University of Technology, Faculty of Civil Engineering, Veveří 95, 602 00 Brno, Czech Republic*

E-mail: fridrichova.m@fce.vutbr.cz

Submitted August 1, 2005; accepted December 1, 2006

**Keywords:** Hydration kinetics, Beta dicalcium silicate, Belite cement, Concrete recycling

*Undersize fractions occurring during the recycling of concrete waste were used for the preparation of belite clinker. The ratio of the undersizes to limestone containing a high percentage of CaO was 1 to 2.25. The mix was converted into the belite cement and its hydration properties along with those of two types of alite cements prepared from the same recycled undersizes were investigated. The hydration character of Portland cements corresponds to the kinetics of the reaction of the 1<sup>st</sup> order and its progress may be assessed from the reduction in the content of unhydrated CaO in the cement body. Quantified data characterizing the hydration products were obtained by means of the thermal analysis after standard reaction soaks of 1, 3, 7 and 28 days. The original CaO content (55 %) in the belite cement dropped to 51 % after 7 days; there was only 44 % of unhydrated CaO after a month. The original CaO content (56 %) in the ternary alite cement dropped consistently to 21 % after the hydration lasting a month; the decrease in the original CaO content (54 %) in the binary alite cement follows a similar pattern in the first 7 days, with an inflection occurring within a month and a decrease to the final value of 12 % of unhydrated CaO. The values of the velocity constants in the kinetic reaction of the 1<sup>st</sup> order were expressed statistically from the values of the residual CaO remaining after the hydration. Belite cement is characterized by the value  $k = 0.0071$  whereas the alite cements show the value  $k' = 0.225$  (ternary system), respectively  $k' = 0.326$  (binary system). This means that the belite cement prepared from recycled concrete would require an unacceptably long hydration time.*

## INTRODUCTION

It is generally known that the rate of belite hydration is lower in comparison to that of alite hydration. This fact, together with the low release of the hydration heat, can be used advantageously in special concrete technologies [1]. The increasing application of belite cements is driven by the ecological benefits they offer: low energy requirements, lower CO<sub>2</sub> emissions and the possibility of using secondary raw materials [2-4]. However, greater attention must be paid to their hydration rate [5-13]. The present investigation was stimulated by both topics. The belite clinker with the highest ratio of the undersizes to high-CaO limestone in the raw material mix is one of three Portland clinkers prepared by using undersizes originated during the recycling of concrete rejects. The results obtained during the investigation of the hydration process of belite Portland cement permitted the elaboration of the method giving a possibility to quantify the hydration rate of belite Portland cement and compare it with that of current Portland cements (usually designated as "alite cements").

## The rate of the hydration process

Theoretical data enabling the calculation of the velocity of chemical reactions were applied to the elaboration of the method:

$$v = \frac{dx}{dt} = \frac{-d(a-x)}{dt} = k'(a-x)^\alpha (b-x)^\beta \dots (a-x)^\nu \quad (1)$$

where  $v$  is the reaction rate (mole/l/s),  $dx/dt$  resp.  $-d(a-x)/dt$  are the increment in the product concentration and the drop in the reagent concentration within a unit of time (mole/l/s),  $a, b, \dots, n$  are the reagent concentrations at the time  $t = 0$  (mole/l),  $x$  is the product concentrations at any arbitrary time  $t$  (mole/l),  $(a-x), (b-x), \dots, (n-x)$  are the reagent concentrations at any arbitrary time  $t$  (mole/l),  $\alpha + \beta + \nu$  is the order of reaction and  $k'$  is the temperature-dependent velocity constant:

$$k' = A' \exp(E_a/RT) \quad (2)$$

Here  $A'$  is the frequency factor,  $E_a$  is the molar activation energy,  $R$  is gas constant and  $T$  is the temperature.

An analogous description can be also proposed for the hydration of Portland cements where the content of not yet hydrated CaO represents a reagent that characterizes the hydration conditions with a sufficient accuracy and which can be quantified with a rather good accuracy at the same time. It was demonstrated experimentally (see below) that, under standard laboratory exposure ( $T = \text{constant}$ ,  $w = \text{constant}$ ), the decrement in the not yet hydrated CaO can be described by means of an exponential dependence, i.e. with a kinetic reaction of the 1<sup>st</sup> order:

$$\frac{dx}{dt} = k(a - x) \quad (3)$$

The separation of variables and the subsequent integration yield the following expression:

$$(a - x) = ae^{-kt} \quad (4)$$

Under constant exposure conditions, the equation (4) also controls the cement hydration; this process can be described by the following expression:

$$CaO_t - CaO_0 ae^{-kt} \quad (5)$$

where  $CaO_t$  is the content of not yet hydrated CaO in the cement stone at the hydration time  $t$  (%) and  $CaO_0$  is the CaO content in the cement paste at the beginning of the hydration at the time  $t = 0$  (%).

The content of not yet hydrated calcium oxide ( $CaO_t$ ) was quantified by calculation as a difference between the content of calcium oxide in the cement paste at the beginning of the hydration ( $CaO_0$ ) and that of CaO which corresponds to individual hydration products at the given exposure time ( $CaO_h$ ):

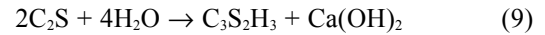
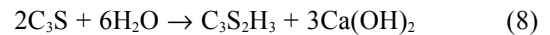
$$CaO_t = CaO_0 - CaO_h \quad (6)$$

For the determination of the  $CaO_0$  value, the total content of calcium oxide in the given cement sample ( $CaO_{\text{cem}}$ ) was taken as the basic value. It was always recalculated by taking into account the state of the respective cement paste at the given time of hydration by using the expression for the total loss-on-ignition  $\sum LOI$  (determined by thermal analysis):

$$CaO_0 = CaO_{\text{cem}} \frac{100 - \sum LOI}{100} \quad (7)$$

The total amount of calcium oxide in the hydration products  $CaO_h$  of the cement paste was calculated with the aid of the thermal analysis. The CaO content corresponding to hydroxide, respectively to calcium carbonate ( $CaO_{\text{p+k}}$ ) was expressed from the loss-on-ignition shown on the TG curve in the temperature range of 400-600°C (for  $\text{Ca}(\text{OH})_2$ ) and in the range of 600-1000°C for  $\text{CaCO}_3$ . The CaO content corresponding to calcium hydrosilicates ( $CaO_{\text{C-S-H}}$ ) was calculated from the CaO

content in the hydroxide, respectively in calcium carbonate by using stoichiometric computations made possible by following equations:



which means that the CaO content corresponding to afwillite ( $\text{C}_3\text{S}_2\text{H}_3$ ) in the alite cement is the same as that corresponding to hydroxide and calcium carbonate; however, it is three times larger in the belite cement. The CaO content corresponding to aluminocalcium hydrosulfonates, represented here by ettringite ( $\text{CaO}_E$ ), was expressed by stoichiometric computation from the loss-on-ignition on the TG curve in the temperature range of 100-300°C after subtracting the loss-on-ignition due to the dehydration of the above quantified afwillite. The total content of calcium oxide in the hydration products of the cement paste ( $CaO_h$ ) then represents the sum of all above partial contents:

$$CaO_h = CaO_{\text{p+k}} + CaO_{\text{C-S-H}} + CaO_E \quad (10)$$

## EXPERIMENTAL

Undersizes occurring in the treatment of recycled concrete rejects were used for the preparation of belite Portland clinker as one of the component of raw material powder mix because this fraction contains suitable oxides, respectively minerals even if in a somewhat different quantitative representation: the  $\text{SiO}_2$  content is higher to the detriment of the CaO content ( $\text{SiO}_2$  usually occurs as quartz). As regards the occurrence of other hydraulic and non-hydraulic oxides it is already more or less the same as that in the usual raw material mix used for firing Portland clinkers. The proposed compositional set-up of the powder mix for the belite clinker was characterized by the ratio of recycled concrete undersizes to the high-CaO limestone; it amounted to 1 : 2.25. Also two more mixes aimed at obtaining comparable alite clinkers with the ratio of 1 : 3.5 were prepared (2% Fe correction was made for the second one). All three clinkers were fired in an experimental rotary kiln under firing conditions typical for Portland clinker.

The above-mentioned firing yielded three clinkers: a binary alite clinker (designated by A - 0 % Fe), ternary alite clinker (designated by A - 2 % Fe) and a binary belite clinker (designated by B - 0 % Fe). Their phase composition was determined with the aid of the method of microscopic point integration (see Table 1).

The clinkers were then ground with a 5% addition of gypsum to obtain cements with the specific surface area of 300 m<sup>2</sup>/kg. The cements were used for the preparation of pastes characterized by the water coefficient of

w = 0.30. The pastes were hydrated in aqueous environment. The samples used for the determination of the mineralogical composition were taken after 1, 3, 7 and 28 days of hydration.

Table 1. Quantification of the phase composition of Portland clinkers.

Phase (%)	Clinker Designation		
	A - 0 % Fe	A - 2 % Fe	B - 0 % Fe
C <sub>3</sub> S	51.1	48.7	0.0
C <sub>2</sub> S	35.7	36.9	85.9
C <sub>3</sub> A	10.9	3.8	10.1
C <sub>4</sub> AF	1.8	10.2	4.0
C <sub>vol</sub>	0.5	0.4	0.0
Total	100.0	100.0	100.0

## RESULTS AND DISCUSSION

### RTG diffraction analysis

Residues of original clinker minerals as well as new hydration products were determined by XRD analysis of hydrated cement pastes:

- the alite, C<sub>3</sub>S ( $d_{h,k,l} = 0.59; 0.296; 0.278; 0.274$  nm)
- the belite, C<sub>2</sub>S ( $d_{h,k,l} = 0.296; 0.278; 0.274; 0.2405$  nm)
- the brownmillerite, C<sub>4</sub>AF ( $d_{h,k,l} = 0.724; 0.277$  nm)
- the portlandite, Ca(OH)<sub>2</sub> ( $d_{h,k,l} = 0.492; 0.3112; 0.2628$  nm)
- the calcite, CaCO<sub>3</sub> ( $d_{h,k,l} = 0.386; 0.3035$  nm)
- the ettringite, C<sub>3</sub>A·3CaSO<sub>4</sub>·32H<sub>2</sub>O ( $d_{h,k,l} = 0.98; 0.57; 0.387$  nm)
- the mono-sulfate, C<sub>3</sub>A·CaSO<sub>4</sub>·12H<sub>2</sub>O ( $d_{h,k,l} = 0.892$  nm)
- the CSH<sub>n</sub> ( $d_{h,k,l} = 0.305$  nm).

The character of diffraction patterns of all samples corresponds to usual qualitative data typical for Portland clinkers; therefore, it is not mentioned below.

### Thermal analysis

The qualitative evaluation based on the DTA curve was performed in the same manner for all three samples after all exposure times. The first endothermic peak at a temperature of 150° C in the temperature range of up to 300°C corresponded to the dehydration of calcium hydrosilicates and ettringite. Then, a predominantly shallow endothermic region attaining its maximum value at about 480°C and corresponding to the dehydroxylation of calcium hydroxide followed after a short indifferent region starting at approximately 400°C. At a temperature of 600°C this peak passed into an endothermic region characterizing the decomposition of calcium carbonate with a maximum at 820°C.

The investigated phases were quantified using the TG and DTG curves in the following way:

The CaO content corresponding to calcium hydroxide originated in result of the hydration of calcium silicates as well as CaO corresponding to calcium carbonate formed secondarily from calcium hydroxide (%):

$$CaO_{p+k} = (LOI_{400-600} \frac{56}{18} + LOI_{600-900}) \frac{56}{44} \frac{100}{m} \quad (11)$$

where  $LOI_{400-600}$  is the Loss-on-ignition corresponding to the dehydroxylation of Ca(OH)<sub>2</sub> (mg),  $LOI_{600-900}$  is the Loss-on-ignition corresponding to the decomposition of CaCO<sub>3</sub> (mg), m is the sample mass (mg).

The water content corresponding to the dehydration of calcium hydrosilicates, H<sub>2</sub>O<sub>C-S-H</sub> (mg): the quantification of the hydration products originated from alite and belite was based on the mentioned Equations (8) and (9) because the afwillite (C<sub>3</sub>S<sub>2</sub>H<sub>3</sub>) characterizes very accurately the stoichiometry of calcium hydrosilicate phases. Therefore, the water contained in these products can be calculated by using the following expressions:

- a) for the alite

$$H_2O_{C-S-H} = CaO_{Ca(OH)_2} \frac{18}{56} \frac{m}{100} \quad (12)$$

- b) for the belite

$$H_2O_{C-S-H} = 3CaO_{Ca(OH)_2} \frac{18}{56} \frac{m}{100} \quad (13)$$

Although both alite cements also contained the belite, it was shown that its presence may be neglected in the binary cement. However, the content of this phase in the ternary cement was already significant and, hence, it could not be neglected in the calculation made for the exposure time lasting 28 days. Therefore, in this case, the CaO content was split up into hydroxide, respectively calcium carbonate by taking into account the relative occurrence of both aforementioned clinker minerals.

The water content corresponding to the dehydration of ettringite, H<sub>2</sub>O<sub>E</sub> [mg]: owing to the fact that the first endothermic peak in the range of up to 300°C shows the loss-on-ignition corresponding only to the dehydration of calcium hydrosilicates and ettringite, the loss-on-ignition corresponds - after subtracting water due to the afwillite - to water released by the ettringite:

$$H_2O_E = LOI_{0-300} - H_2O_{C-S-H} \quad (14)$$

where  $LOI_{0-300}$  ...the loss-on-ignition corresponding to the decomposition of C-S-H phases and ettringite (mg).

The CaO content corresponding to calcium hydrosilicates (%). Using the stoichiometric formulae this content was calculated from the amount of water corresponding to the afwillite dehydration:

$$CaO_{C-S-H} = H_2O_{C-S-H} \frac{56}{18} \frac{100}{m} \quad (15)$$

The CaO content corresponding to aluminocalcium hydrosulfonates represented by the ettringite  $CaO_E$  (%). It was obtained by stoichiometric calculation from the loss-on-ignition corresponding to the water released during the hydration of the ettringite:

$$CaO_E = H_2O_E \frac{6}{32} \frac{56}{18} \frac{100}{m} \quad (16)$$

The total CaO content in the hydration products of the cement paste ( $CaO_H$ ) represents a sum of all the above described portions of calcium oxide:

$$CaO_H = CaO_{p+k} + CaO_{C-S-H} + CaO_E \quad (17)$$

The calculated values of calcium oxide corresponding to individual hydration products including the total content of calcium oxide in the hydration products ( $CaO_H$ ) are given in Table 2 for the individual hydration periods.

The contents of not yet hydrated calcium oxide ( $CaO_t$ ) corresponding to the individual periods of hydration (Table 3) and their graphical representations (Figures 1-3) were obtained on the basis of the  $CaO_H$  values shown in Table 2 and from the content of calcium oxide determined in the respective cement by means of a chemical analysis as well as on the basis of the TA values converted to the CaO content in the given state of the cement paste.

DTA curves of hydrated cement pastes after the exposure periods of 1, 3, 7 and 28 days are represented in Figures 4-6.

Application of the equation for the calculation of the reaction rate of Portland cement hydration

Using numerical methods the Equation (5) was modified; the values characterizing the content of not yet hydrated calcium oxide ( $CaO_t$ ) and the respective hydration time shown in Table 2 were applied to this purpose. The following specific expressions could thus be obtained for individual types of cement:

- binary alite cement A - 0 % Fe:  $CaO_t = 75.8 \cdot e^{-0.326 \cdot t}$ ,
- ternary alite cement A - 2 % Fe:  $CaO_t = 68.7 \cdot e^{-0.225 \cdot t}$ ,
- binary belite cement B - 0 % Fe:  $CaO_t = 53.1 \cdot e^{-0.0071 \cdot t}$ .

In addition to the fact that the initial  $CaO_0$  content calculated experimentally in the cement paste drops in dependence on the belite content (as actually observed in the practice) it is also evident from the respective velocity constants that the reaction rate of the Portland cement hydration decreases the more, the less alite the cement contains.

Table 3. Quantification of unhydrated CaO.

Duration of Hydration (days)	Content on unhydrated $CaO_t$ (%)		
	A - 0 % Fe	A - 2 % Fe	B - 0 % Fe
0	53.55	55.69	54.42
1	34.11	45.47	51.65
3	32.49	33.25	51.17
7	26.84	30.28	51.12
28	11.84	21.35	43.47

Table 2. CaO content in hydration products.

Duration of hydration (days)	A - 0 % FeO			
	$CaO_{p+k}$ (%)	$CaO_{C-S-H}$ (%)	$CaO_E$ (%)	$CaO_H$ (%)
1	8.6	8.6	2.2	19.4
3	10.3	10.3	3.0	23.6
7	11.6	11.6	3.8	27.0
28	15.6	19.3	4.1	39.0
Duration of hydration (days)	A - 2 % FeO			
	$CaO_{p+k}$ (%)	$CaO_{C-S-H}$ (%)	$CaO_E$ (%)	$CaO_H$ (%)
1	7.1	7.1	0.8	15.0
3	9.9	9.9	2.6	22.4
7	10.4	10.4	3.2	24.0
28	11.8	15.2	4.0	31.0
Duration of hydration (days)	B - 0 % FeO			
	$CaO_{p+k}$ (%)	$CaO_{C-S-H}$ (%)	$CaO_E$ (%)	$CaO_H$ (%)
1	1.1	3.3	0.6	5.0
3	1.3	3.9	0.4	5.6
7	1.2	3.6	0.8	5.6
28	3.2	9.6	0.6	13.4

CONCLUSION

The minimum time of hydration of investigated cements that is particularly important from the view-point of the envisaged use of belite cement was calculated for Portland cements prepared on the basis of recycled concrete rejects by using the proposed method based on the calculation of the reaction rate of the hydration process.

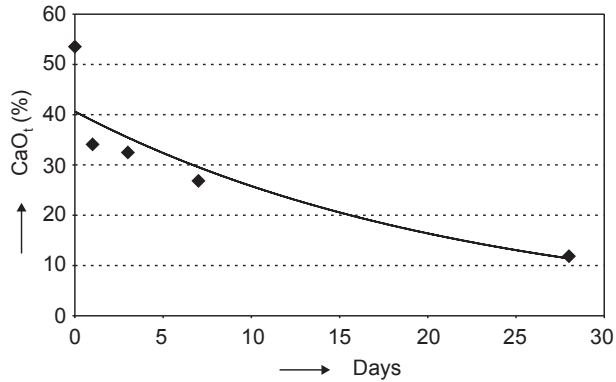


Figure 1. Content of unhydrated CaO<sub>t</sub> vs. hydration time. A - 0 % Fe.

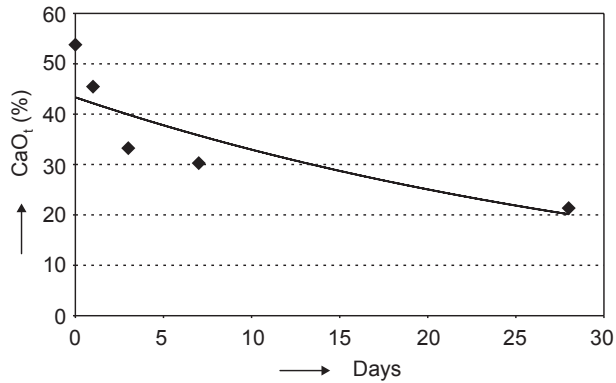


Figure 2. Content of unhydrated CaO<sub>t</sub> vs. hydration time. A - 2 % Fe.

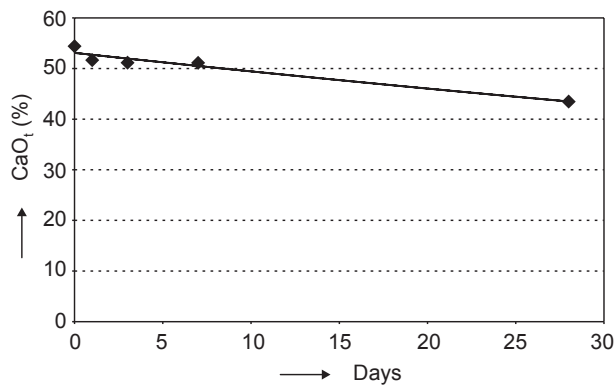
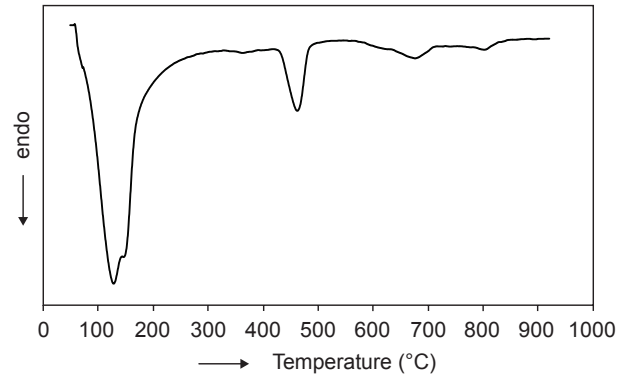
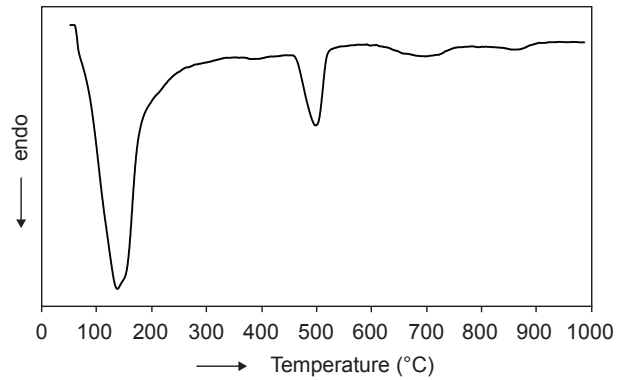


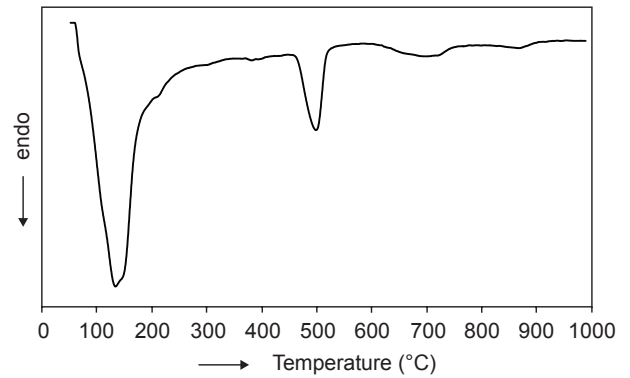
Figure 3. Content of unhydrated CaO<sub>t</sub> vs. hydration time. B - 0 % Fe.



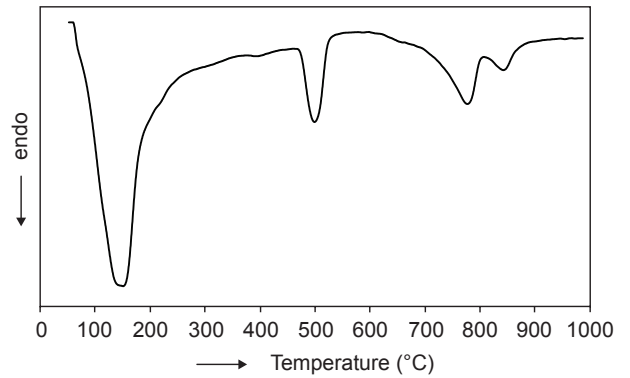
1 day



3 days



7 days



28 days

Figure 4. DTA of hydrated cement A - 0 % Fe.

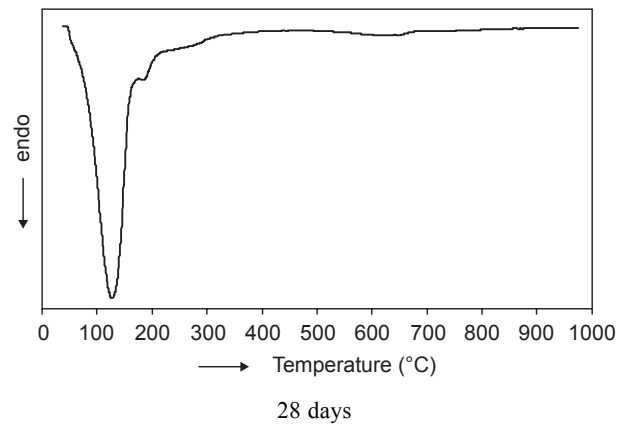
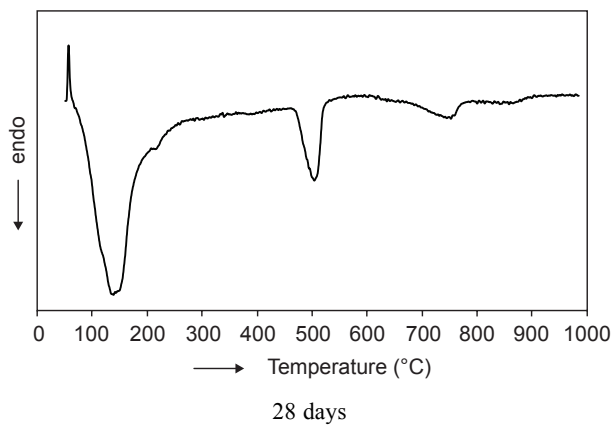
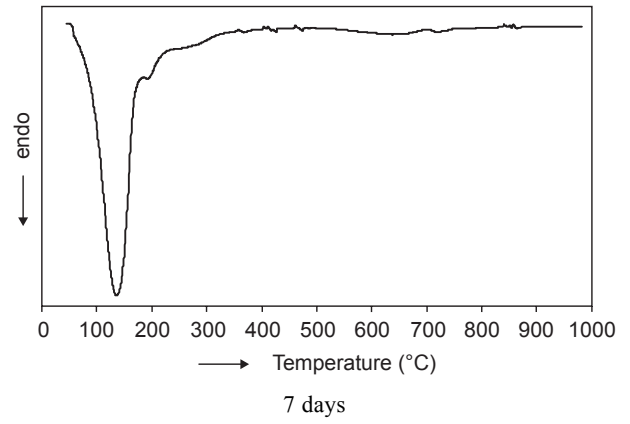
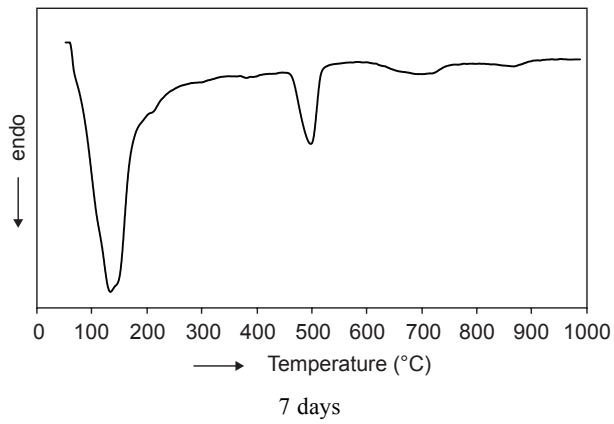
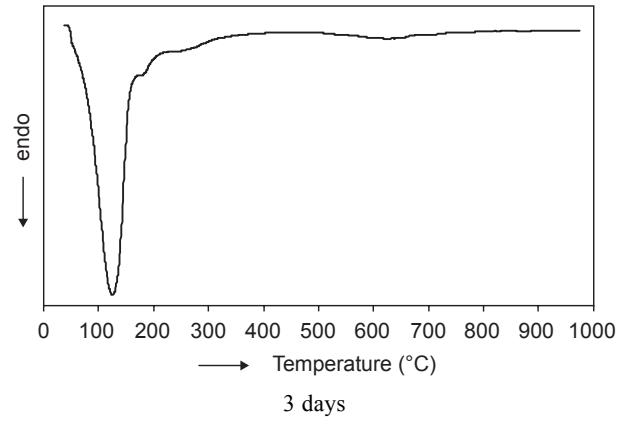
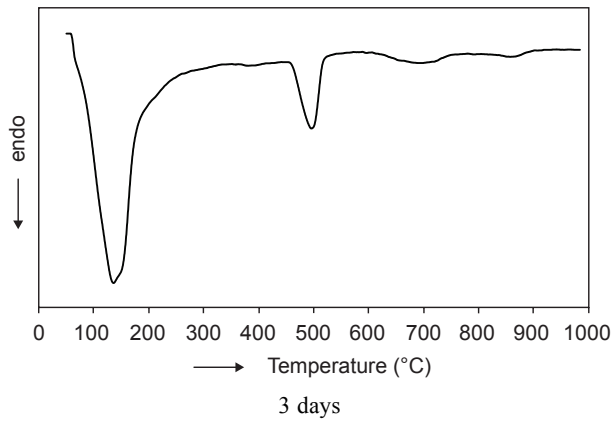
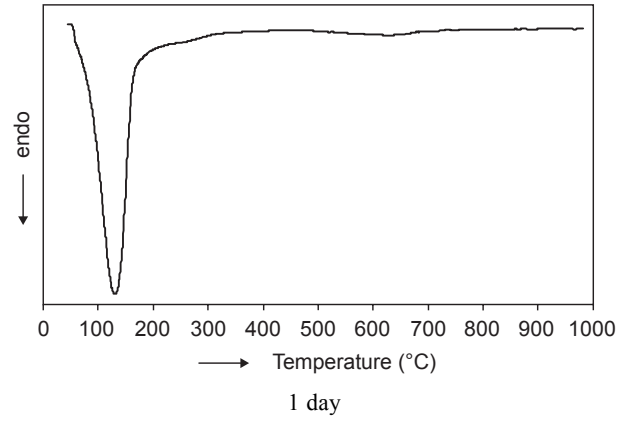
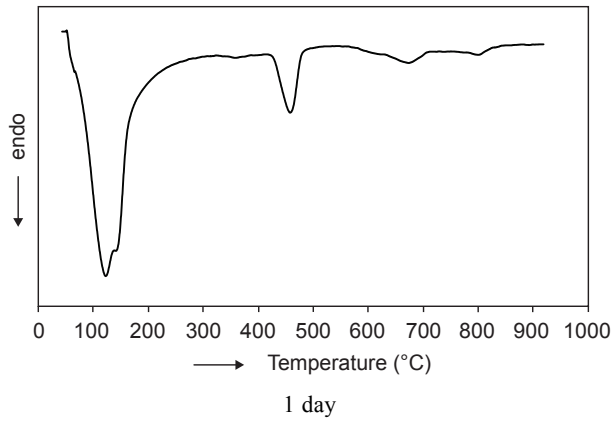


Figure 5. DTA of hydrated cement A - 2 % Fe.

Figure 6. DTA of hydrated cement B - 0 % Fe.

The calculated time of hydration is unacceptably long for prepared belite Portland cement. The future investigation should focus the possibility to modify the belite Portland cement prepared from recycled concrete rejects in such a way that should bring the acceleration of the hydration process.

#### References

1. Jinyu L., et al.: *J.Chin.Ceram.Soc.* 32, 364 (2004).
2. Fa-Tang L., et al.: *Hebei J.Indus.Sci.Tech.* 20, 57 (2003).
3. Popescu C. D., et al.: *Cem.Concr.Comp.* 25, 689 (2003).
4. Guerrero A., et al.: *Envir.Sci.Tech.* 38, 3209 (2004).
5. Šatava V.: *Physical Chemistry of Silicates*, ICT Prague, Prague 1991.
6. Young-Min K., Seong-Hyeon H.: *J.Am.Ceram.Soc.* 87, 900 (2004).
7. Richardson I.G.: *Cem.Concr.Res.* 34, 1733 (2004).
8. Nakshatra S. B., et al.: *J.Am.Ceram.Soc.* 85, 2171 (2002).
9. Black L., et al.: *Cem.Concr.Res.* 33, 1561 (2003).
10. Livingston R. A.: *Trans.Am.Nucl.Soc.* 87, 486 (2002).
11. Hela R.: *Proc. Our World in Concrete and Structures*. Singapore 2003.
12. Fridrichová M., Fenrich J.: *Cement International*, Erkrath 2005.
13. Fridrichová M.: *Proc. XVII<sup>th</sup> Termanal*, Slovak University of Technology, Bratislava 2005.

#### HYDRATAČE BELITICKÉHO CEMENTU PŘIPRAVENÉHO Z RECYKLÁTŮ BETONU

MARCELA FRIDRICHOVÁ

*Ústav technologie stavebních hmot a dílců,  
Vysoké učení technické v Brně,  
Fakulta stavební,  
Veveří 95, 602 00 Brno*

Pro přípravu belitického slinku byly použity propady z výroby betonových recyklátů v poměru 1 : 2,25 s vysokoprocenním vápencem. Po následném převedení na belitický cement studovány jeho hydratační vlastnosti paralelně se dvěma typy alitických cementů, připravených ze stejných recyklátových propadů. Průběh hydratace portlandských cementů odpovídá kinetice reakce I. řádu a její postup lze sledovat ze snižování obsahu nezhydratovaného CaO<sub>i</sub> v cementovém kameni. Hydratační produkty kvantifikovány pomocí termické analýzy po standardních reakčních prodlevách 1, 3, 7 a 28 dnů. V belitickém cementu původní obsah 55 % CaO klesal do 7 dnů na 51 % a po měsíci jen na hodnotu 44 % nezhydratovaného CaO. V trojsložkovém alitickém cementu původní CaO z 56 % klesá pravidelně na 21 % po měsíci hydratace, ve dvojsložkovém alitickém cementu původní obsah 54 % CaO klesá obdobně do 7 dnů se zlomem do 1 měsíce až na konečnou hodnotu 12 % nezhydratovaného CaO. Z hodnot zbytkového CaO po hydrataci statisticky vyjádřeny hodnoty rychlostních konstant pro kinetickou rovnici I. řádu. Belitický cement vykazuje hodnotu  $k'=0,0071$ , zatím co alitické cementy vykazují hodnoty  $k'=0,225$  pro trojsložkový, případně  $k'=0,326$  pro dvojsložkový cement, což znamená pro belitický cement připravený z betonových recyklátů neúnosně dlouhou dobu hydratace a je nutno jej modifikovat k urychlení tuhnutí.