

HEAT EVOLUTION IN ALKALI ACTIVATED SYNTHETIC SLAG–METAKAOLIN MIXTURES

Wiesława Nocuń-Wczelik*

Faculty of Material Science and Ceramics, University of Science and Technology AGH, al. Mickiewicza 30, 30-059 Cracow, Poland

In this study the calorimeter was applied to follow the early hydration of mixtures produced using three different synthetic slag vitreous materials, differing with alumina to silica ratio and mixed or not with synthetic two different metakaolin additions (kaolin heated with sodium containing admixture or without admixture). These mixtures were processed with sodium/potassium hydroxide solutions and placed inside the chamber of calorimeter. The kinetics of hydration process was thus characterized and the hydraulic properties of slag–metakaolin mixtures were very well assessed. Substantial heat evolution was found in the presence of activators, in many cases exceeding 100 J g^{-1} for 24 h process; heat evolved on hydration with water only was very poor, below 20 J g^{-1} after 24 h. The rate of heat evolution vs. time plots showed specific shape, more or less similar to the typical heat evolution curves reported for cements. Finally, some conclusions were drawn and the amount/concentration of activators was selected for further studies.

Keywords: alkaline activation, heat of hydration, slag–metakaolin mixture

Introduction

The kinetics and mechanism of hydration in cementitious systems can be investigated by use of calorimetry [e.g. 1–4]. Calorimetry has been also successfully used in the investigations of non-clinker hydrating mixtures with different activators [5, 6]. In cement technology different materials are mixed with cement clinker to produce binding materials; the wastes from metallurgy and power industry are generally used for this purpose.

Among the wastes from metallurgical processes, the blast furnace slag, composed mainly of silica, alumina, calcium and magnesium oxides, is the most widely investigated as cement additive/cement replacement. This material has been appeared as the most effective one, among the other wastes/by-products used in cement and concrete technology. The production of cements with high waste material content or even without clinker but with the other industrial wastes/by-products has been grown for last decades. The hydraulic properties of slag (it means the ability to form, as a result of reaction with water only, the product, in which setting and hardening takes place) are poor. In blended cements the cement clinker phases act as slag activator, releasing the calcium and alkaline ions into the liquid phase. In non-clinker materials the sodium compounds play usually the role of activators. These alkaline components break down the Si–Si–(Al)

bonds in slag structure and subsequently the transformation to the hydration products takes place easily. The effectiveness of this process is strongly bound with the nature of slag material – it must occur as glassy phase, with excess energy. Rapidly cooled slag has a form of vitreous matter which, after mixing with water and in the presence of alkaline activator, transforms into hardened material. In practice the relationship between the parameters of slag/activation process and properties of hardened material is very complex, because the potential hydraulic properties of slag containing mixture are determined by many factors: the chemical composition of slag, type of activator, time/temperature/pressure of curing. Among the ‘chemical’ criteria the so-called modulus of slag activity, calculated as alumina to silica ratio is used.

The hydration process can be successfully initiated by use of ‘seeds’ initiating the formation of hydration products. In this work the addition of easily hydrating material – the metakaolin originating from thermal decomposition of kaolin clay was used. This material transforms into calcium silicate/calcium aluminate hydrates in alkaline environment and the further precipitation of hydration products (from slag in this case) goes more effectively. When some amount of slag is replaced by this admixture, one can observe that the rate of hydration process/rate of heat evolution increases less or more, depending on the composition/reactivity of hydrating mixture.

* wiesia@uci.agh.edu.pl

Experimental

Three synthetic slag samples with Al_2O_3 to SiO_2 ratio corresponding to 0.66; 1.00 and 1.20 respectively, were produced. Among them:

1. The two gehlenite-type synthetic slag glass:
 - with Al_2O_3 to SiO_2 ratio 1 (corresponding to the stoichiometric gehlenite – $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$)
 - with Al_2O_3 to SiO_2 ratio 1.2 (corresponding to the non-stoichiometric gehlenite phase – $2\text{CaO}\cdot 1.2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$).
2. The melilite slag glass – corresponding to the solid solution between $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$ mixed at the ratio 0.66 (that is corresponding to the Al_2O_3 to SiO_2 ratio 0.66; this proportion is found in many industrially produced materials).

The initial batches (analytically pure calcium carbonate, aluminium hydroxide, magnesium hydroxide and silica-gel) were heated to the melting point and subsequently quenched by pouring to the water. After this the materials were dried and ground to the specific surface ca. $4000\text{ cm}^2\text{ g}^{-1}$.

The metakaolin used as an addition was produced by heating of naturally occurring kaolin clay at 750°C . The pure, white clay samples (containing 80% of kaolinite – $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$ mixed with quartz 9% and illite 9%) were soaked or not with sodium silicate suspension (so-called water glass) before the thermal treatment. (Sodium silicate is used as very effective activator of setting and hardening, particularly in case of non-portland cements and different rapidly setting mixtures). In case of this sodium activation the amount of sodium silicate added was to give ca. 8% Na_2O by mass of dry final metakaolin sample. The dried metakaolin samples thus produced show very

disordered structure and can be easily ground to give very fine powder. The main chemical components of this nearly amorphous material are: SiO_2 (ca. 58%) and Al_2O_3 (ca. 35%).

The following types of cementitious material were taken into account:

- pure slag glass,
- slag glass with 5, 10, 20% metakaolin activated additionally with sodium silicate or not.

The solid samples were mixed with NaOH or KOH solutions; the concentrations of alkaline solutions changed in the range from 0.75 m up to 15 m.

The rate of heat evolution was followed in the differential BMR microcalorimeter, constructed in the Institute of Physical Chemistry, Polish Academy of Science (Warsaw). Hydrating pastes were prepared at liquid to solid ratio 0.5 on 5.00 g solid samples; the initial temperature was kept constant at 25°C .

Results and discussion

The heat evolved values were computed and they are given in Tables 1–3; the heat evolution curves are shown in Figs 1–7. The following abbreviations were used: Mk – metakaolin; MkNa – metakaolin modified with sodium silicate. For further discussion, in Fig. 2 the typical calorimetric curve for ‘pure’ portland cement of good quality is plotted.

It has been found that in the hydrating pastes produced from:

- ground calcium/magnesium aluminate/silicate glassy materials, corresponding to melilite or gehlenite slag vitreous components

Table 1 Heat evolved values on hydration of slag systems; activity modulus of slag calculated as alumina to silica ratio=0.66

Sample code	Slag replacement	Hydration in solution	$Q(t)/\text{J g}^{-1}$ after 24 h hydration
1/0.66	–	0.75 M NaOH	55
2/0.66	–	2.25 M NaOH	81
3/0.66	–	4.5 M NaOH	121
4/0.66	–	0.75 M KOH	62
5/0.66	–	2.25 M KOH	92
6/0.66	–	4.5 M KOH	143
7/0.66	5% MkNa	2.5 M NaOH	86
8/0.66	5% MkNa	15 M NaOH	93
9/0.66	10% MkNa	2.5 M NaOH	88
10/0.66	10% MkNa	15 M NaOH	97
11/0.66	20% Mk	0.75 M NaOH	65
12/0.66	20% Mk	2.25 M NaOH	96
13/0.66	20% Mk	4.5 M NaOH	122
14/0.66	20% MkNa	4.5 M NaOH	128

Table 2 Heat evolved values on hydration of slag systems; activity modulus of slag calculated as alumina to silica ratio=1.00

Sample code	Slag replacement	Hydration in solution	$Q(t)/J\ g^{-1}$ after 24 h hydration
1/1.00	–	0.75 M NaOH	89
2/1.00	–	2.25 M NaOH	103
3/1.00	–	4.5 M NaOH	140
4/1.00	–	0.75 M KOH	90
5/1.00	–	2.25 M KOH	131
6/1.00	–	4.5 M KOH	147
7/1.00	20% Mk	0.75 M NaOH	94
8/1.00	20% Mk	2.25 M NaOH	118
9/1.00	20% MkNa	0.75 M NaOH	117
10/1.00	20% MkNa	2.25 M NaOH	126
11/1.00	20% Mk	4.5 M NaOH	156
12/1.00	20% MkNa	4.5 M NaOH	168

Table 3 Heat evolved values on hydration of slag systems; activity modulus of slag calculated as alumina to silica ratio=1.20

Sample code	Slag replacement	Hydration in solution	$Q(t)/J\ g^{-1}$ after 24 h hydration
1/1.20	–	0.75 M NaOH	98
2/1.20	–	2.25 M NaOH	124
3/1.20	–	4.5 M NaOH	141
4/1.20	–	0.75 M KOH	112
5/1.20	–	2.25 M KOH	138
6/1.20	–	4.5 M KOH	135
7/1.20	20% Mk	0.75 M NaOH	107
8/1.20	20% Mk	2.25 M NaOH	132
9/1.20	20% MkNa	0.75 M NaOH	108
10/1.20	20% MkNa	2.25 M NaOH	139
11/1.20	20% Mk	4.5 M NaOH	115
12/1.20	20% MkNa	4.5 M NaOH	122

- metakaolin (dehydrated kaolin) modified or not with some sodium silicate
- NaOH or KOH solutions

the intensive hydration process takes place within a few hours after mixing, followed by setting and hardening (samples removed from the calorimetric vessel are hardened). Hydration is accompanied by significant heat evolution. The heat evolution curves differ from those for portland cements – the high and broad first peak is generally observed; there is no so-called ‘dormant period’. The second peak usually occurs as a shoulder, either as more or less extended ‘plateau’.

The heat evolved values for mixtures processed with alkaline solutions are in the range from over 50 to almost 170 J g⁻¹ (for 24 h hydration); this upper value is close to those found for many cements. Taking into account the heat effects attributed to the reaction between slag and water, not exceeding 20 J g⁻¹ (it is only the surface wetting), one can conclude that in

alkaline environment the transformation of slag glassy substance into hydration products is significantly accelerated. Generally, the effect of variable parameters on heat evolution/kinetics of hydration can be summarized as follow:

- reactivity of melilite slag with lower alumina to silica ratio ($Al_2O_3/SiO_2=0.66$) and Mg is somewhat lower than the reactivity of gehlenite slag ($Al_2O_3/SiO_2=1$ or more), without Mg
- solid active additions affect the kinetics of hydration/heat evolution of slag; it seems that they are more active components of mixtures, as it results from the data for growing percentage (5 to 20%) – their reaction with alkaline solutions is the first step and obviously gives first amount of products which can play a role of ‘nuclei’
- metakaolin with Na is a little better modifier than ‘pure’ metakaolin

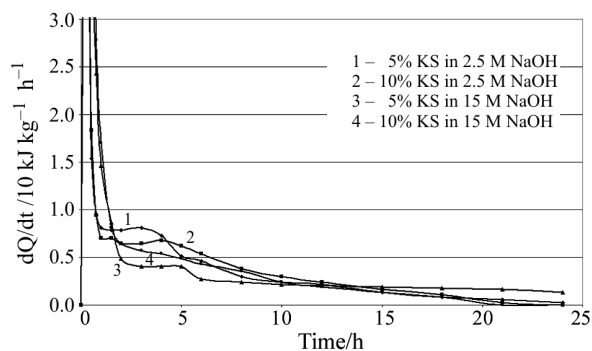


Fig. 1 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 0.66) with metakaolin addition, processed with NaOH solutions of different concentrations

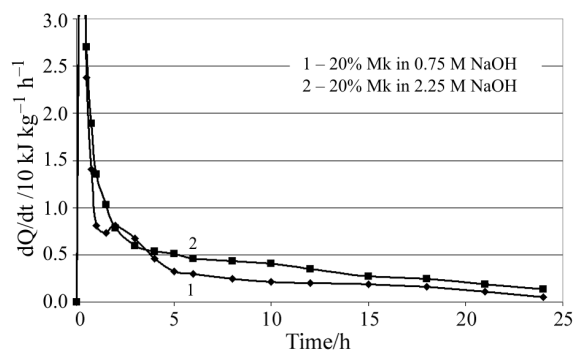


Fig. 4 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 1.00) with metakaolin addition, processed with NaOH solutions

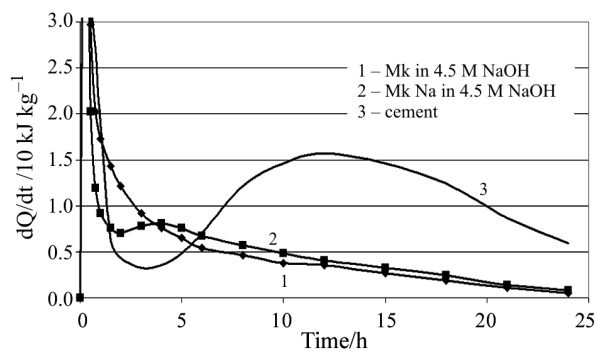


Fig. 2 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 0.66) with metakaolin and sodium modified metakaolin addition, processed with 4.5 M NaOH solutions

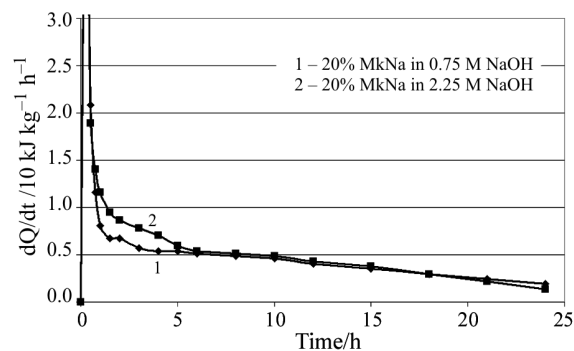


Fig. 5 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 1.00) with sodium modified metakaolin addition, processed with NaOH solutions

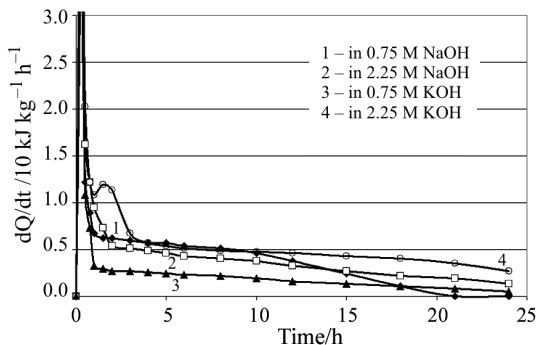


Fig. 3 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 1.00) without metakaolin addition, processed with NaOH and KOH solutions

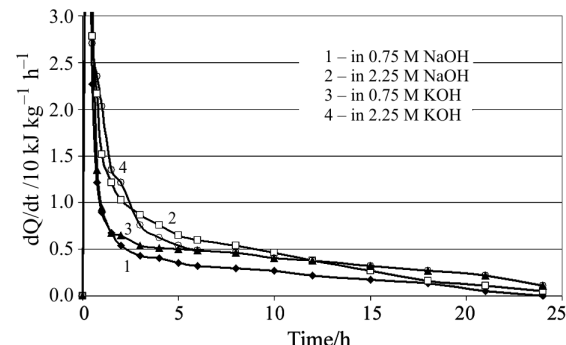


Fig. 6 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 1.20) without metakaolin addition, processed with NaOH and KOH solutions

- the concentration of alkali hydroxide is an important factor: *i*) heat evolution/hydration is accelerated with increasing concentration in the range of 0.75/4.5 M, *ii*) however, in highly concentrated solutions (15 M) further acceleration is not observed. This effect can be attributed to the formation of very dense gel-like hydration product (calcium silicate hydrate; so-called C-S-H phase) covering the surface of hydrating grains, just after mixing with

- strong, basic solution. Such an effect is known in cement chemistry and it must be overcome by diffusion through this layer of hydration products
- calorimetric method does not exhibit any significant difference between the effect of NaOH and KOH. However, it seems that at early age (see the data for 4.5 M solutions) KOH acts as better dissolution promoting agent but the layer of products precipitating soon after hampers further hydration.

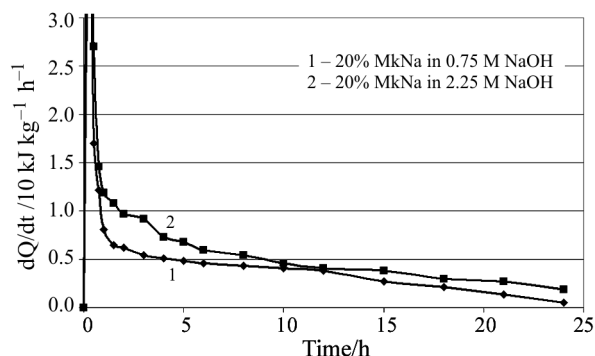


Fig. 7 Heat evolution on hydration of slag (activity modulus calculated as alumina to silica ratio 1.20) with sodium modified metakaolin addition, processed with NaOH solutions

These preliminary studies were followed by the other standard measurements, which allowed to optimize the scale of slag activation in terms of standard requirements.

Conclusions

- Calorimetric data indicate well the role of slag and alumina-silica containing poorly ordered material in cementitious mixtures.
- Metakaolin or metakaolin doped with sodium can be successfully used as heat evolution/hydration accelerating addition in alkali activated slag mixtures.
- The rate of heat evolution and heat evolved is dependent upon the concentration of alkaline activator. An acceleration of hydration process can be easily observed with growing concentration. At very high concentration the heat evolved/hydration rate can be slightly reduced because of the barrier

of hydration products deposited immediately on the surface of initial material.

- The gehlenite type slag vitreous materials doped with 20% metakaolin and processed with 4.5 M hydroxide solution reveal the best hydraulic activity within the first hours of hydration.

Acknowledgements

The financial support from the former Polish Scientific Research Committee (grant No:4 T08D 027 23/2002-2005) is acknowledged.

References

- 1 W. Nocuń-Wczelik, *J. Therm. Anal. Cal.*, 65 (2001) 613.
- 2 B. Pacewska, I. Wilińska, M. Bukowska, G. Blonkowski and W. Nocuń-Wczelik, *J. Therm. Anal. Cal.*, 77 (2004) 133.
- 3 W. Roszczynialski and W. Nocuń-Wczelik, *J. Therm. Anal. Cal.*, 77 (2004) 151.
- 4 W. Nocuń-Wczelik and Z. Pytel, *J. Therm. Anal. Cal.*, 77 (2004) 159.
- 5 J. Małolepszy and W. Nocuń-Wczelik, *J. Thermal Anal.*, 33 (1988) 431.
- 6 J. Deja and J. Małolepszy, *Ann. Chim.-Sci. Mat.*, 28 (2003) 51.

Received: September 2, 2005

Accepted: September 27, 2005

OnlineFirst: June 27, 2006

DOI: 10.1007/s10973-005-7313-4