

## **MICROCALORIMETRIC STUDIES OF SLAG ALKALINE BINDERS**

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Calorimetric measurements were carried out on the hydration of slag activated by sodium hydroxide, sodium carbonate and water glass at 60 °C. The results can be correlated with the mechanical properties of the cured cements. The studies confirmed the applicability of calorimetry in the testing of activators used in concrete technology.

Finely ground blast-furnace slag mixed with an alkaline activator displays cementitious properties and gives concrete of high strength, high freeze-thaw resistance and high corrosion resistance. The theoretical principles of the activation of calcium and magnesium aluminosilicates by alkaline materials are given in the works by Gluchowski [1, 2]. Slags consisting mostly of glassy components and a few per cent of melilites give calcium silicate hydrate (CSH) phases, hydrogarnets and zeolites as main hydration products [3]. This activation process is influenced by the chemical composition of the slag, the content of glassy phase, and the activator used.

Microcalorimetry has previously been widely used in investigations of the hydration of Portland cement or other traditional binders [4], but not to examine the hydration of slags. This may be due to the relatively slow heat evolution at 25° during the hydration of slag, without any significant accompanying effect.

In the present study, microcalorimetric measurements were carried out during the hydration of slag from the "Huta Katowice" metallurgical plant with different activators. The calorimetric results have been related to the results of mechanical strength tests and other properties, e.g. shrinkage determination were performed on the sample giving the best heat evolution effects.

### **Experimental**

The chemical composition of the blast-furnace slag from the "Huta-Katowice" metallurgical plant used in this work was: SiO<sub>2</sub> 39.22%, CaO 43.50%, MgO 4.56%, Al<sub>2</sub>O<sub>3</sub> 6.82%, Fe<sub>2</sub>O<sub>3</sub> 2.83%, MnO 0.83% and SO<sub>3</sub> 1.83%. The specific surface was

found to be 4200 cm<sup>2</sup>/g. The basicity and activity ratios were lower than those required for the active basic slags. The glassy phase content was high, at 92.2%. The crystalline components consisted of melilites with traces of CaCO<sub>3</sub>.

The activators used in this work were sodium hydroxide, sodium carbonate and water glass with different silica ratios. The microcalorimetric measurements were made with the above activators: NaOH was added as a 3.8% or 8.6% admixture, Na<sub>2</sub>CO<sub>3</sub> as a 5% admixture, and water glass with a SiO<sub>2</sub>/Na<sub>2</sub>O ratio = 1 as a 15% admixture of the slag. For the mechanical tests, mortars consisting of granulated blast-furnace slag, sand (slag to sand weight ratio = 1:3) and 15% water glass solution (liquid phase to slag ration = 0.4) were prepared in a standard laboratory mixer. Four kinds of water glass activator, with different SiO<sub>2</sub> to Na<sub>2</sub>O ratios, were used (SR = 1.0, 1.5, 2.0 and 2.5).

The compressive and flexural strength tests were carried out on slag mortars with a water glass activator.

Two kinds of mortar curing were applied:

- standard curing in water,
- steam-curing for 4 h at 85° after heating for 2 h from 20° to 85°, and then water-curing.

## Results

The hydration of activated slags proceeded quickly at 60° and a liquid to solid ratio of 0.5, giving calorimetric curves with two or three peaks and "dormant" periods between them. The results are presented as a set of heat evolution curves in Fig. 1, together with the calculated reaction heats after hydration for 16 h.

The results of compressive and flexural strength tests are given in Tables 1 and 2.

All the mortars revealed a very low shrinkage, in the range 0.1–0.3 · 10<sup>-3</sup>, considerable stability against freezing-thawing cycles (1–9% lowering of compressive strength) and very high resistance against the corrosive action of acid and sulphate solutions (92–99% of initial strength after storage in corrosive media [5, 6]).

## Conclusions

These studies were carried out to show the applicability of calorimetry in preliminary investigations of activators used in slag binder preparation. The shapes of the heat evolution curves depend strongly on the activator used. Water glass was the best activator, strongly accelerating the heat evolution process. This means that

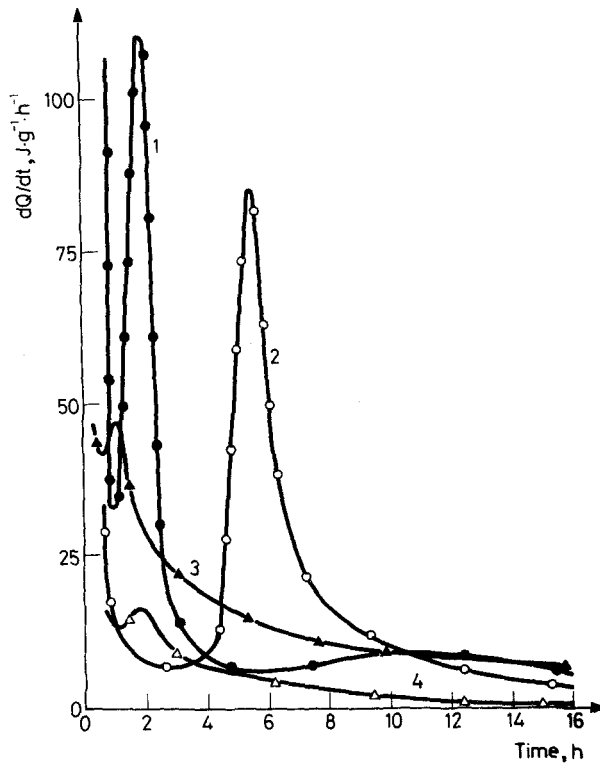


Fig. 1 Microcalorimetric curves of activated slag hydrated at 60 °C.

Activator:  $Q_{16h}$ ,  $Jg^{-1}$

1. Water glass 142

2. 5%  $Na_2CO_3$  138

3. 3.8% NaOH 38

4: 8.6% NaOH 131

able 1 Compressive and flexural strengths of activated slag mortars cured in water

Silica ratio of water glass	Curing time, days				Curing time, days			
	3	7	28	90	3	7	28	90
	Flexural strength (MPa)				Compressive strength (MPa)			
1	6.0	6.9	7.3	11.1	51.7	44.5	87.2	101.9
1.5	3.6	6.2	6.8	6.9	18.2	41.2	65.0	69.8
2.0	—	2.4	6.3	7.4	8.2	17.5	55.3	62.1
2.5	—	2.2	5.9	6.2	6.5	16.6	39.7	42.8

**Table 2** Compressive and flexural strengths of activated slag mortars subjected to steam-curing

Silica ratio of water glass	Steam-curing and storage period, days				Steam-curing and storage period, days			
	SC	7	28	90	SC	7	28	90
	Flexural strength (MPa)				Compressive strength (MPa)			
1.0	9.8	9.8	9.7	9.9	85.2	80.0	84.3	89.1
1.5	8.7	8.3	8.4	8.6	73.7	70.6	72.9	77.2
2.0	7.4	7.2	7.0	7.4	62.0	60.8	61.4	63.2
2.5	6.8	6.0	7.0	7.1	57.0	44.6	60.7	61.2

hydration occurred very quickly, during the first few hours of thermal treatment corresponding to the steam-curing operation. New cementitious material used in the production of slag can thus be obtained, with a very high compressive strength, in the range 80–100 MPa. The other properties of slag mortars activated by water glass are also very good. Our calorimetric measurements confirmed that concretes with a compressive strength below 50 MPa [1, 2] are produced through the use of sodium hydroxide or sodium carbonate-containing activators, which have a lower influence on the hydration process.

## References

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**Zusammenfassung** — Die Hydratation von Schlacke bei 60 °C und Aktivierung mit Natriumhydroxid, Natriumcarbonat oder Wasserglas wurde durch kalorimetrische Messungen verfolgt. Die Ergebnisse lassen sich mit den mechanischen Eigenschaften der erhärteten Zemente korrelieren. Die Untersuchungen bestätigen die Brauchbarkeit der kalorimetrischen Methode zum Testen von Aktivatoren in der Betontechnologie.

**Резюме** — Проведены calorimetрические измерения гидратации шлаков, обработанных при 60° гидроокисью натрия, карбонатом натрия и жидким стеклом. Полученные результаты коррелировались с механическими свойствами отвержденных цементов. Проведенное изучение подтвердило применимость calorimetрического метода для контроля активаторов, используемых в какой-либо конкретной технологии.