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CO_2 optimized cement based on synthetic slag made of fly ash

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Abstract

Alkali-activated materials harden under the reaction of an alkaline source and a raw material reactive in such way. Different raw materials are suitable for the reaction. The use of secondary raw materials such as granulated blast furnace slags and fly ashes are favoured due to environmental aspects such as CO_2 emission and resource consumption. A disadvantage of the use of secondary resources is their limited availability or the variability of different batches.

Therefore the ASCEM cement technology goes a different way: a synthetic glass is produced under the use of fly ash and correcting materials. The advantage of this is the production of a high reactive glass with a stable quality. That glass can easily be dissolved by a lower need of hydroxide concentration compared to the fly ash. The reactive glass is milled and mixed to 50 % with fly ash as filler as well as with a dry activator. The paper gives an overview over the principle production process, some key properties and data about ecological and economic aspects compared to ordinary Portland cement.

Keywords: fly ash, alkali-activated binders, secondary resources, low CO_2 cement.

1 Introduction

The alkaline activation of reactive alumosilicate materials yields to a hardening process and the formation of a cement stone that can be used for the production of concrete. Several raw materials are suitable in this way for instance metakaolin [1, 2] , fly ashes [3-5] and slags [6-8]; but mainly fly ashes and ground granulated blast furnace slag (ggbfs) are used commercially as building materials. The reaction products of alkali-activated materials are different depending on the calcium content of the activated material. The alkaline activation of calcium-free materials such as metakaolin and some fly ashes results in the formation of amorphous to semi-crystalline three-dimensional alumosilicate networks by polycondensation [9-11]. These binders are also known as “geopolymers” as named by DAVIDOVITS [1]. The reaction product of ggbf slag have been widely investigated and can be compared to calcium silicate hydrates (C-S-H) from Portland cements, apart from incorporated tetrahedral aluminium into the dreierketten structure of the calcium silicate hydrates [12-16] and hydrotalcite if the slag contains magnesium [17].

Proposed advantages of alkaline activated binders compared to ordinary Portland cement contain beside others the lower environmental impact and especially a lower CO_2 emission. The CO_2 emission of an alkaline activated material is dominated by the nature and amount of alkaline activator as shown by DUXSON [18]. Strictly, this counts only for the use of secondary raw materials such as fly ash and blast furnace slag; if primary raw materials are utilized such as metakaolin, this can give also a dominant influence on the environmental impact as shown by WEIL [19].

Beside the different reaction products that are built by alkaline activation of calcium free and calcium containing raw materials, a main difference is also in the necessary activator concentration to a reach high level of reaction degree: calcium free materials need a higher pH value or amount of hydroxide.

If a global or local availability of the secondary raw materials is considered, than a gap of ggbf slag or high quality fly ash can often be declined. Different binder systems are for instance in competition for utilizing the resource ggbf slag like slag cements, supersulphated cements etc. Fly ashes are forced to use in cement and concrete in large amounts. But this fly ash utilization needs a certain and stable fly ash quality with especially low carbon content (mass loss). In contrast to this, large amounts of fly ash are dumped and not yet in re-use.

2 ASCEM cement technology

That was the initial starting point of the ASCEM cement technology. The following aims were considered to match:

(1) Use of secondary raw material such as fly ash,

(2) Production of a highly reactive binder with constant quality,

(3) Use of alkali-activation,

(4) Fulfilment of standard cement requirements for the production of concrete.

These aims considered were reached by a thermal treatment of the used raw material, mainly fly ash. This fly ash is melted together with correction materials to meet a certain composition in the CaO-Al_2O_3-SiO_2 ternary system to get a reactive glass. After a quick cooling of the melt the cooled glass is milled and mixed with filler. For this also fly ash can be utilized beside other fine filler material. A usual glass/filler ratio is about 1. The function of the filler can be subdivided in three main parts:

(1) Dilution of the binder for chemical and environmental reasons,

(2) pore filling effect by special grading as well as

(3) a pozzolanic effect if a reactive material such as fly ash is used.

This glass/filler blend can either be mixed with a dry activator to get one-component cement (cement+) or used directly as ASCEM cement and mixed later on with a fluid activator (two-component cement).

The flow chart of the technological steps of the ASCEM cement production is given in figure 1.

3 Properties of ASCEM cement

In general, the reactivity of the ASCEM cement can either be controlled by the chemistry of the reactive glass and its grain size or be influenced by the type and concentration of the activator. Fig 2 shows the progress of reaction of ASCEM cement with the included dry activator (curve B) and with fluid activator (curve A). 7% NaOH solution is used as fluid activator, the water/cement ratio is 0.4 in each case (cement means here glass + fly ash; glass/fly ash = 1). Curve C shows a commercially available blast furnace slag (consist of 90% GGBFS, 8% Portland cement clinker and 2% lime stone) activated also with 7 m.-% NaOH solution and the same w/c ratio for comparison.

The ASCEM cement that consists of only 50% reactive glass and 50% fly ash shows a similar heat evolution as 100% GGBF slag that is accelerated by the additional clinker reaction. If activating with 7 m.-% NaOH solution, the reaction starts immediately after mixing. The start of the reaction is a little bit delayed, if using the dry activator but with a similar heat flow.

Fig. 3 shows some strength measurement results on cement mortar prisms (4×4×16 cm³). Therein the activator and/or the w/c ratio have been varied. Two different dry activators (with 4,7 % Na_2O per mass ASCEM cement; Type I is identical to the dry activator shown in Figure 2) were used as well as two different fluid activators. The fluid activator consisted either of 7 m.-% NaOH solution or a mixture of this solution with water glass solution (12.4 m.-% Na_2O, 29.4 m-% SiO_2). The amount of water glass solution added was 3% of the ASCEM cement mass. In the case of the fluid activators the added amount of Na_2O per mass ASCEM cement (glass + fly ash) was 2,3 % in case of pure NaOH solution and 2,75 % Na_2O in case of the NaOH – water glass mix.

As it can be seen, relatively high strength can be reached after one day of hardening at room temperature. The dry activator showed the highest strength gain. The 28 day strength is around 50 MPa for the dry activators as well as for the fluid activator which includes the water glass solution. The activation with pure NaOH resulted in the lowest strength after 28 days.

The structure of the hardened binder is shown in figure 4. It appears as dens, amorphous mass. The image shown in figure 4 was made of a 16 years old concrete sample. The ASCEM cement was activated with silicate solution (modul 2.1; 14 m.-% d.m. silicate per ASCEM cement), a w/c ratio of 0.45 and a cement content of 340 kg/m³ was used. In the hardening reaction a mix of alumosilicate network and calcium silicate hydrate was built (compare Figure 4 and Table 1). After that time the alumosilicate network had partly crystallized into a number of different zeolithes such as stilbite. Almost no unreacted slag grains can be seen in the matrix, but parts of fly ash particle remained unreacted in the concrete. The long term strength development of this ASCEM cement concrete is shown in Fig. 5 in comparison with similar composed concretes with state of the art OPC and GGBF slag cement in 1992. The concrete composition such as w/c ratio, cement content and aggregate amount and grading was the same. The concrete was stored indoors as well as timely under XF1 environment.

4 Ecological aspects

Worldwide, cement industry contributes to 5% of the anthropogenic CO_2 emission and in EU 3% [20]. It was estimated by IEA [21] that 9-10% of the world CO_2 emissions can be attributed to cement production by 2050. Enormous efforts were made in the last years by the cement industry to lower the CO_2 emissions.

The mean CO_2 emissions per ton Portland cement in EU is about 0,814 t (0,861 t CO_2/t clinker [22] under consideration that CEM I contains about 94% clinker plus 0,004 t CO_2 for the clinker milling). The emissions from ASCEM cement production are far less and especially the CO_2 emission is strikingly lower. For the production of one ton cement, the CO_2 emissions for ASCEM cement are about 55% lower: 0,375 t. Fig. 6 shows that comparison, wherein also the worldwide situation and the European benchmark for Portland cement is shown (0,766 t CO_2/t clinker [23], and in analogy about 0,725 t CO_2/t Portland cement).

ASCEM contrasts favorably with the Portland cement manufacture also by the lower total weight of raw materials, which will demand less transport activities and consequently have less environmental impact. In addition, the use of a high percentage of solid waste (60-90%) avoids unwanted deposits and saves natural raw materials (Fig 7).

5 Conclusion

ASCEM cement is a new type of alkali-activated slag cement. The base of the cement is a synthetic slag/glass that is produced by melting of fly ash under addition of correction material to reach a certain composition range in the $CaO-Al_2O_3-SiO_2$ ternary system. Other production steps include the milling and mixing with filler (fly ash, standard ratio glass/fly ash=1) and a dry activator. The ASCEM cement without the dry activator can also be activated by alkaline solutions. Depending on the composition of the reactive glass and the chosen activator and its concentration one yields a spectrum of binder properties. In general the ASCEM cement is characterized by a quick reaction, a strength level of 20-30 MPa can be reached within one day of reaction.

The development of the ASCEM cement started in the 80th primarily with the aim of reutilization of fly ash. The imperative to reduce the CO_2 emission worldwide initiated the continuation of the project with high intensity. The focus of the development is set on both product and production technology. The market introduction of the ACEM cement is planned for the coming years.

6 References

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Table 1 results of EDX analysis, points indicated in Figure 4:
1 – quartz grain, 3 – fly ash, 4 – CSH matrix and 5 – alumosilicate matrix)

	Al_2O_3 m.-%	SiO_2 m.-%	CaO m.-%	K_2O m.-%	Si/ Al	Ca/ Si	K/Al
1	0	100	0	0			
3	38	60	0	2	1,4	0,0	0,0
4	11	48	37	4	3,6	0,8	0,4
5	23	67	0	10	2,5	0,0	0,5

Fig. 1 Technological steps of ASCEM cement production

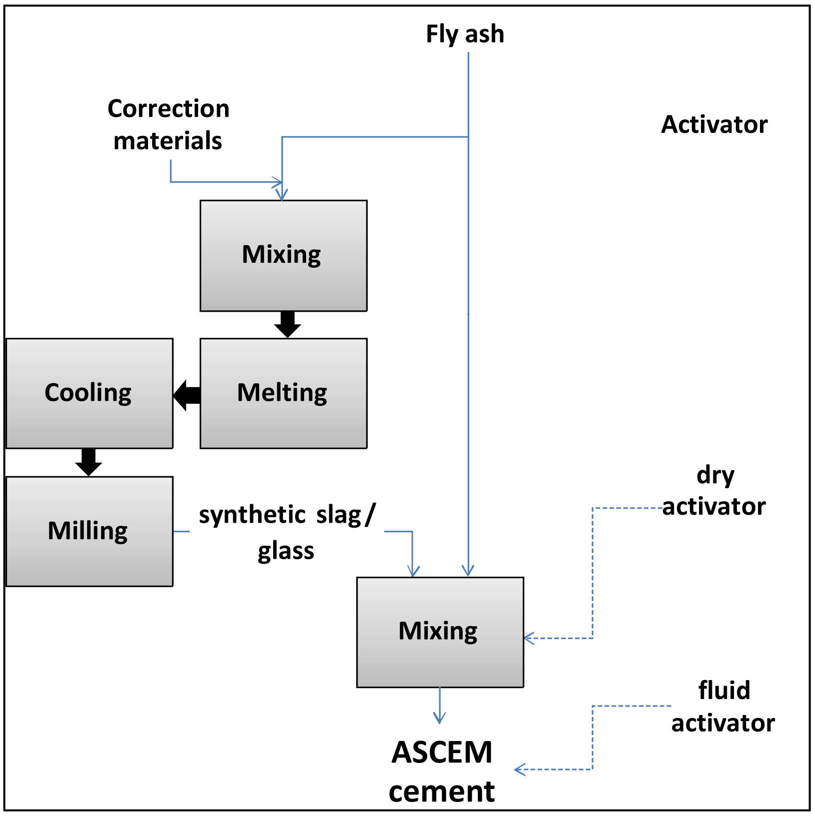

Fig. 2 Reaction progress of ASCEM cement with different activators (curve A: included dry activator, curve B: 7 m.-% NaOH) and blast furnace slag activated with 7 m.-% NaOH (curve C); w/c=0,4

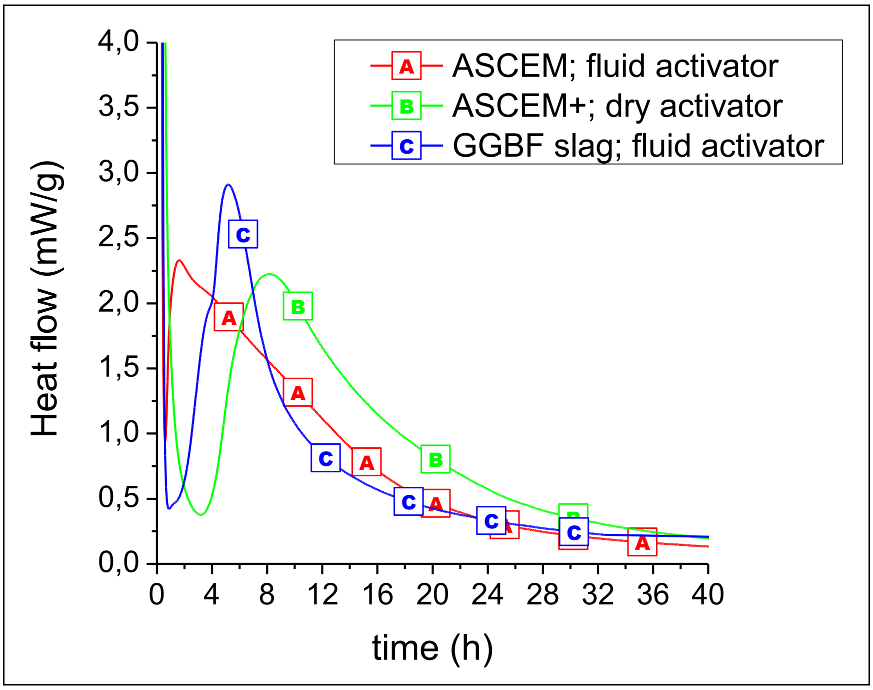

Fig. 3 Strength development of ASCEM Cement mortars with dry and fluid activators and different w/c ratios

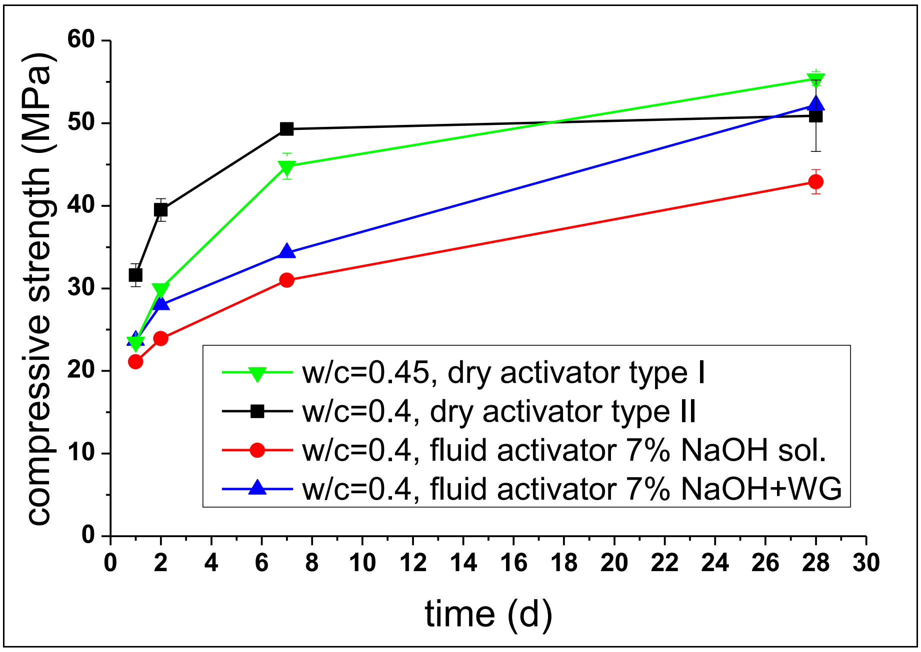

Fig. 4 Structure of ASCEM cement concrete, activated with silicate solution, 16 years old (points indicate EDX analysis, see also Table 1:
1-quartz grain, 3-fly ash, 4-CSH matrix, 5-alumosilicate matrix)

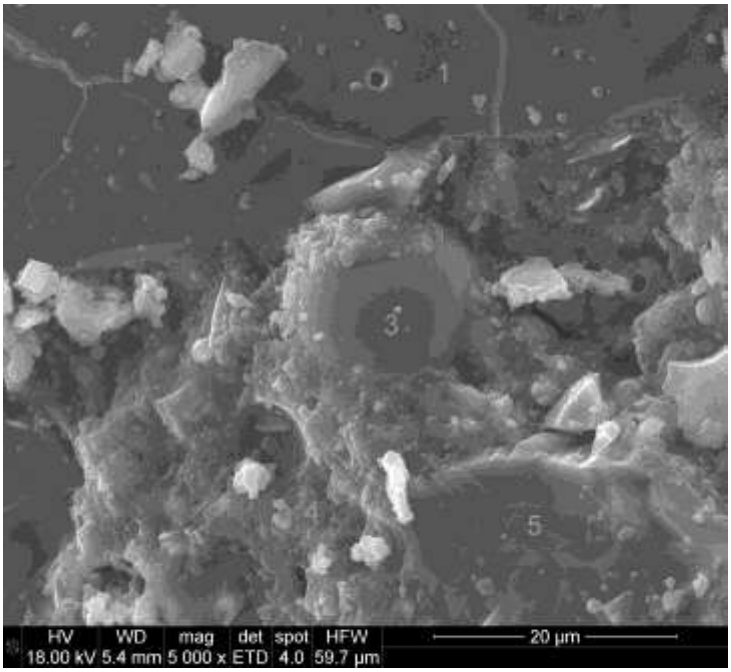

Fig. 5 long term strength development of ASCEM concrete, activated with water glass solution (modul 2.1; 14 m.-% d.m. silicate per ASCEM cement); w/c ratio of 0.45 and cement content of 340 kg/m³ASCEM

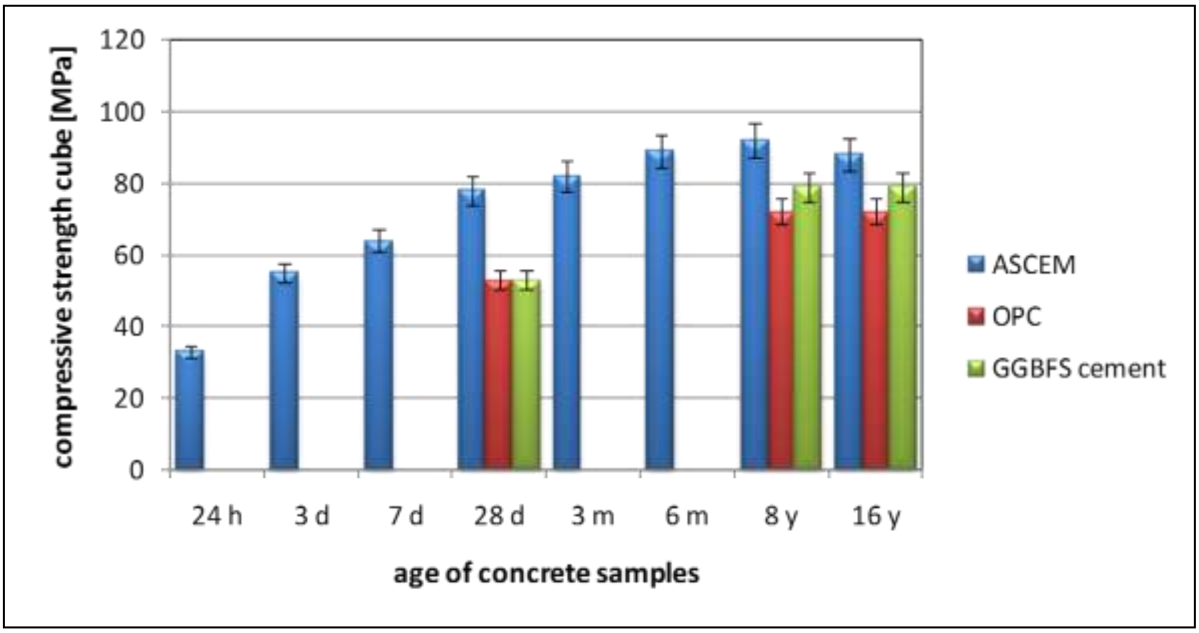

Fig. 6 Comparison of the CO_2 emissions caused by the production of Portland cement und ASCEM® cement

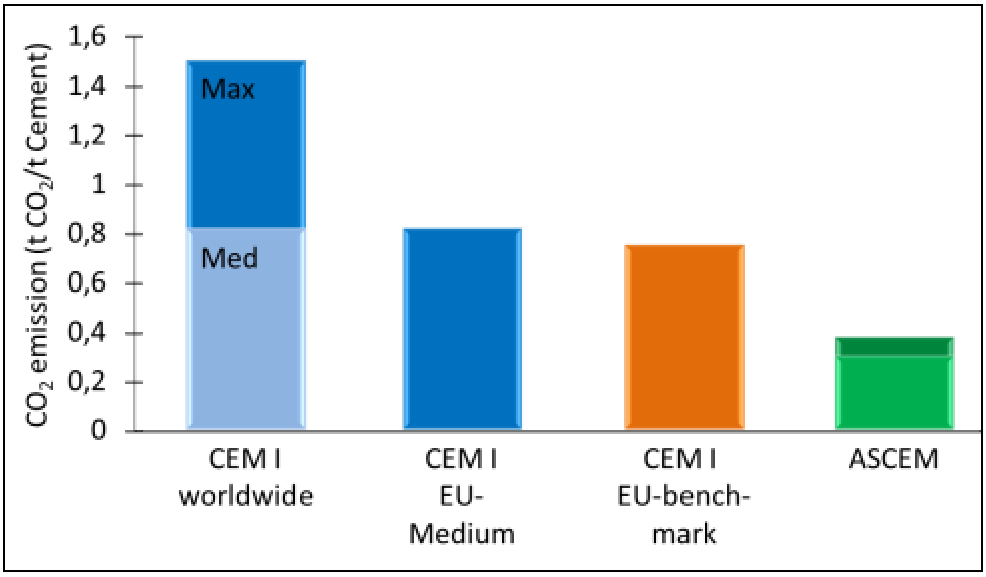

Fig. 7 Utilization of (primary and secondary) resources for the production of 1 ton ASCEM® cement compared with 1 t Portland cement