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TURNING RESIDUES INTO BUSINESS OPPORTUNITIES: SOME EXAMPLES

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Introduction

In the past, wastes were generally landfilled because it was the cheapest and easiest way to get rid of it. Nowadays we are more aware of the consequences and stringent regulations for landfilling are in act. Hence, costs for landfilling have increased and specific wastes are not allowed to be landfilled anymore. Moreover, the awareness of sustainability has increased strongly in the last decades. Recycling, reuse or recovery of materials and energy from wastes will reduce the need for primary resources and will contribute to a sustainable society.

Because Europe has only very limited primary resources, it is also from an economical point of view essential to make efficient use of it. Therefore, the EU policy is aimed at achieving a 'recycling society'[1]. For instance the Waste Framework Directive[2] obliges member states to modernise their waste management plans. They must recycle 50 % of their municipal waste and 70 % of their construction and demolition waste by 2020.

Waste treatment and upgrading it to new raw materials or products has become an industry of its own. It provides many new jobs and creates new technologies. Wastes can be turned into profits as will be demonstrated by three examples: blastfurnace slag, powder coal fly ash and municipal incinerator bottom ash, based on Dutch experiences.

Blastfurnace slag

Origin and composition

Blastfurnace slag is a by-product of the production of iron in a blastfurnace, where iron ore, limestone and coke are heated to about 1500 °C. In this process a layer of molten iron and on top of that a layer of molten slag is formed. The molten slag comprises mostly silicates and alumina from the original iron ore, combined with calcium oxide from the limestone. By rapid cooling of the molten slag through high-pressure water jets, granulated blastfurnace slag is produced. The size of the particles is gene-

rally less than 5 mm. The granulated slag is further processed by drying and then ground to a very fine powder.

This ground granulated blastfurnace slag (GGBS) is amorphous in structure and comprises about 85 % calciumaluminosilicates (see Table 1). Therefore, it has hydraulic properties and is very well suited for application in cement. The composition range of GGBS, Portland cement and other secondary cementitious materials in the ternary diagram CaO-SiO_2-Al_2O_3 is shown in Figure 1.

Table 1: Composition of GGBS and fly ash (FA) versus Portland cement (PC)

Constituent (wt.%)	PC	GGBS	FA
CaO	65	40	4
SiO_2	20	35	59
Al_2O_3	5	10	22
MgO	2	8	2
Fe_2O_3	3	0	8

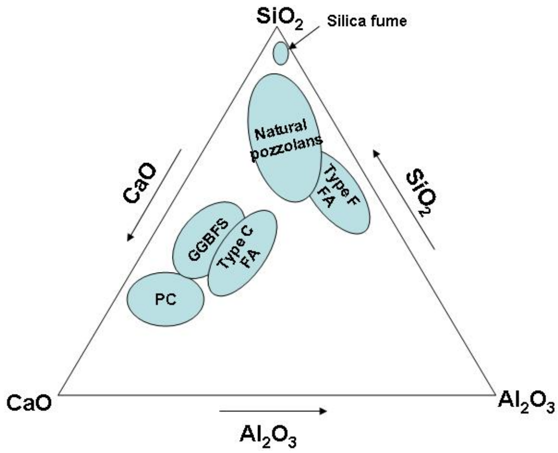

Figure 1: Composition of cementitious materials (PC=Portland cement; GGBFS=GGBS; FA=fly ash)

GGBS production and use as binder

GGBS as a cementitious binder has a long and good track record. The first commercial application of lime activated GGBS as a binder commenced in Germany in 1865. By 1880 GGBS was being used with Portland cement as the activator. The United

States commenced production of slag cements in 1896. Since then Europe, with its many blastfurnaces and steel industries has used GGBS extensively. The production of blastfurnace slag cement in The Netherlands started in 1930 by CEMIJ, using the granulated blastfurnace slag produced by its neighbour Hoogovens (now Tata Steel) at IJmuiden. The amount of GGBS used for production of Portland blastfurnace slag cement (CEM lll) by the plant in IJmuiden is shown in Figure 2. This figure also depicts the amount of GGBS used by the cement plant at Rotterdam (started production in 1964). Depending on economic situation, between 4.5 and 6 million tonnes (Mton) of cement per year is used in The Netherlands[3]. About 55 % is CEM lll cement (highest % in the world), corresponding to 1.5-2 Mton GGBS per year.

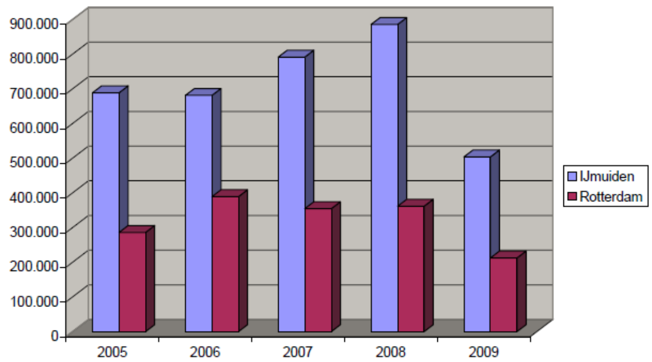

Figure 2: Annual use of GGBS by Dutch cement plants at IJmuiden and Rotterdam (drop in 2009 is due to economic recession)

The annual production of blastfurnace slag worldwide is estimated at 400 Mton. In Europe each year approximately 30 Mton of blastfurnace slag is produced, of which about 80% is granulated, i.e. 24 Mton. Approx. 80 % of the GGBS, i.e. about 20 Mton annually, is applied by the cement and concrete industries.

The European standard EN 197-1 specifies the common cements. Table 2 shows the composition limits of some of them. CEM lll/B is allowed to contain up to 80 %m/m GGBS, but in practice it usually is about 70 %m/m. GGBS can be applied to concrete by the cement or as a type ll addition at the ready mixed concrete plant. In cement GGBS is fully considered as binder, where as in type ll addition only partially (k-value of 0.6). However, based on the principle of equivalent performance of concrete[4], it is possible to value GGBS additions (in combination with specific CEM l cements) fully as a binder (k=1). This is possible in The Netherlands since 2003 and in Belgium since 2013. In the Netherlands, this concept called ‘attest’ concrete, is also possible for the ternary system: CEM l – GGBS – fly ash[5]. This ternary system provides interesting

means for optimization of concrete properties with respect to durability, sustainability and economics.

Table 2: Composition of some common cements (EN 197-1)

Cement type		Clinker	GBS	Fly ash
Portland cement	CEM l	100	0	0
Portland fly ash cement	CEM ll/A-V	80-94	0	6-20
	CEM ll/B-V	65-79	0	21-35
Portland blastfurnace slag cement	CEM lll/A	35-64	36-65	0
	CEM lll/B	20-34	66-80	0
Composite cement	CEM V/A	40-64	18-30	18-30
	CEM V/B	20-38	31-50	31-50

Distinctive properties

Portland cement (CEM l) is the most used cement in the world. Its properties are well known by concrete technologists. Portland blastfurnace slag cement (CEM lll), especially with a high percentage of GGBS (CEM lll/B), has quite different properties. Compared to CEM l cement, CEM lll:

- possesses a high resistance to chloride ingress, alkali-silica reaction, sulphate attack and similar chemical degradation mechanisms;
- has a much lower impact on the environment (more sustainable);
- has a lower heat of hydration;
- is more sensitive to curing conditions of the concrete;
- develops strength slower at early ages and at low temperatures;
- possesses less resistance to carbonation and freeze-thaw conditions with de-icing chemicals.

Although the last 3 aspects are of disadvantage for CEM lll cements, they are not decisive for most ready-mixed concrete applications. The advantage of the first 2 aspects, more durable and sustainable concrete, is of more importance. Concrete made with CEM lll cement possesses a much denser structure (more gel and less capillary pores), causing a substantial lower diffusivity and permeability. The effect of the blastfurnace slag content in CEM lll cement on the chloride and sodium diffusion coefficient is illustrated in Figure 3. A strong decrease in diffusivity is observed above 20 %m/m blastfurnace slag and very low values are obtained above 50 %m/m blastfurnace slag. Hence, ingress of aggressive species and internal deteriorating reactions

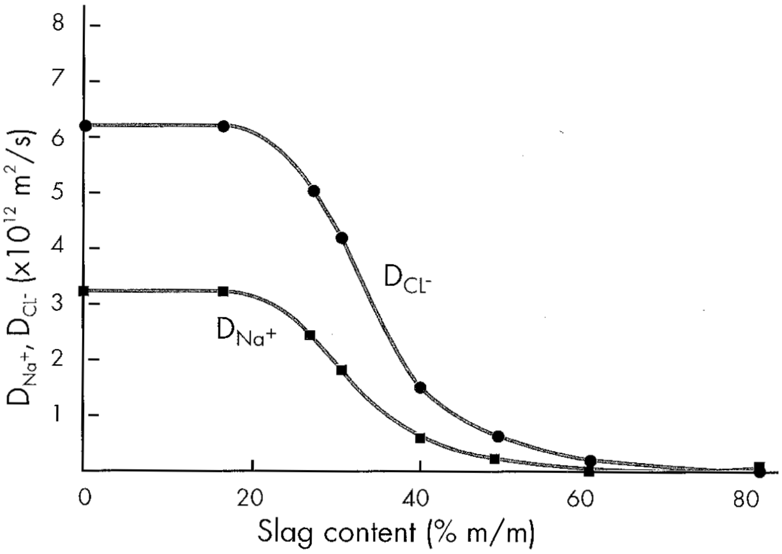

Figure 3: Effect of blastfurnace slag content on diffusion coefficient[6]

are strongly retarded. This explains the excellent durability of concrete produced with CEM lll cement in such aggressive environments[6]. That's why for over 75 years now, in the Netherlands marine and infrastructural concrete structures have been built almost exclusively with blastfurnace slag cement concrete. E.g. the Eastern Scheldt barrier (Figure 4), having a design service life of 200 years, the use of CEM lll/B cement was by far the best option. Under severe Middle East marine conditions, durable concrete structures can be achieved by using blast furnace cement as is shown by the King Fahad Causeway between Saudi Arabia and Bahrain built in 1984. The desired service life was 70 years. Chloride profile measurements over more than 12 years on a test pile of the causeway have shown that the (conservative) estimate of the service life is more than 150 years[6], which is extraordinary for that region.

Figure 4: Eastern Scheldt barrier (left) and King Fahad causeway (right)

Sustainability

The environmental impact of concrete produced with CEM lll cement is much lower (60 to 70 %) than for a similar concrete composition with CEM l cement. This is shown in Table 3 for the emission of green house gases (EGHG). In this table also data for concrete compositions with fly ash as part of the binder and municipal incinerator bottom ash (MIBA) as partial replacement (40 %m/m) of the natural aggregates are given.

Table 3: Environmental impact of different concrete compositions

Concrete (kg/m^3)	CEM l (ref)	CEM lll*	CEM l-FA	MIBA
CEM l	300	0	200	300
CEM lll	0	300	0	0
Fly ash	0	0	100	0
Water	165	165	165	165+24
River sand	616	610	610	370
River gravel	1232	1220	1220	732
MIBA	0	0	0	608
EGHG (kg CO_2-eq)	287 (100%)	116 (40%)	193 (67%)	274 (96%)

* average of Dutch CEM lll/A and CEM lll/B; EGHG of CEM lll/B is about 30% of ref.

Economics

Because the costs of granulated blastfurnace slag is lower than the costs for producing clinker, CEM lll cements in the Netherlands are somewhat lower in price than CEM l cements of the same strength class.

As described before, it is also possible to add the GGBS separately to the concrete mix at the ready mixed concrete plant, but still considered fully as binder. This is only allowed for specific combinations of GGBS and CEM l cements, which have been tested for equivalent concrete performance (‘attestation’). The market price of GGBS applied in such high valued applications is obviously dependent on specific market conditions. However, to get an impression: the price level of such GGBS is about ¾ of that for cement. Very lucrative, even when taking the costs of initial performance testing and quality assurance into account.

Powder coal fly ash

Origin and composition

Powder coal fly ash is a by-product of coal-fired power plants. The combustion of the pulverised coal at about 1200 ^{o}C results mainly in fine ash particles that rise with the flue gases. This fly ash is separated from the flue gas by electrostatic precipitators, cyclones or other particle filtration equipment and subsequently stored in silos.
Immediately after combustion, the fly ash particles are to a large extent in a molten state. When leaving the furnace, they cool down very rapidly resulting in mainly spherical and amorphous particles (see Figure 5).

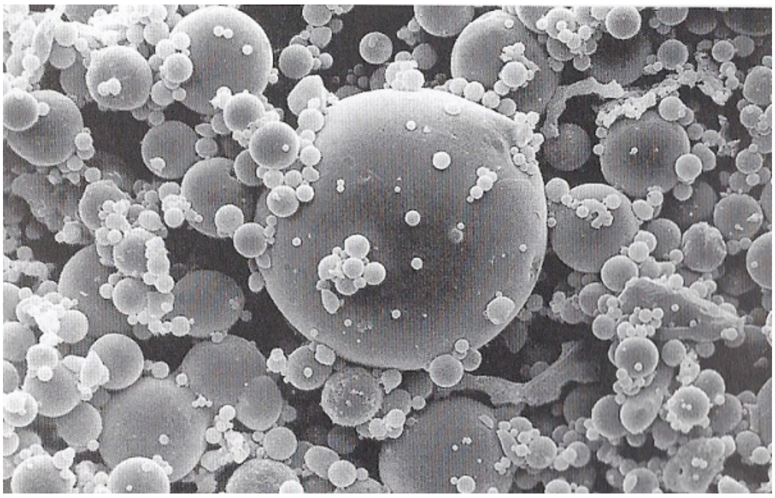

Figure 5: Fly ash (type F)

The burning of anthracite and bituminous coal typically produces type F fly ash. This fly ash is pozzolanic in nature. Fly ash produced from the combustion of younger lignite or sub-bituminous coal, is called type C fly ash, which in addition to having pozzolanic properties, also has some self-cementing properties. In Figure 1 the typical composition range of both fly ashes are shown. The average composition of the Dutch fly ash is given in Table 1.

Although type C fly ash also has interesting possibilities for application as a binder in concrete, the remainder of this section is related to type F fly ash.

Fly ash production and use as binder

Fly ash is used successfully in concrete for over 70 years now. The initial use of fly ash in concrete was mainly as an additive (filler), but its contribution to the improved performance of the concrete due to its pozzolanic nature was swiftly recognized. In the mid seventies the generation of electricity by burning powder coal increased strongly, resulting in large amounts of fly ash production. The cement industry anticipated on these developments by introducing Portland fly ash cement in the early eighties[7]. In this application fly ash is fully accounted as cementitious material. For fly ash used as an additive the k-value concept was subsequently developed, in which the fly ash is partly (the k-value) considered as a binder[4]. Based on the principle of equivalent performance, the possibility of using a specific fly ash in combination with a specific cement as a binder in concrete was developed in 1992 and since then successfully applied in the Netherlands.[8] In this application, called ‘attest’ concrete, the fly ash is fully accounted as cementitious material (‘k-value’ = 1), similar to Portland fly ash cement. A similar system will be introduced in Belgium this year.

In the Netherlands about 1 Mton of fly ash is produced each year, which is almost entirely used in cement and concrete. Due to the success of ‘attest’ concrete, fly ash from Germany is imported to meet the demand. A similar situation is developing in Belgium, which has a national production of fly ash of only 0.5 Mton per year.

The annual production of fly ash worldwide is more than 400 Mton. Most fly ash is landfilled; only a very small part is used for high end purposes such as binder in concrete. In Europe each year about 30 Mton of fly ash is produced of which only 8 % is disposed off[9]. Approximately 30 % of the fly ash is applied in cement and concrete. Hence, big challenges as well as opportunities lie ahead to achieve a similar level of high end applications as in the Netherlands.

Distinctive properties

The successful application of fly ash in concrete in the Netherlands is based on an extensive research programme in the 1980’s, which is summarized in CUR-report 144[10]. At early age (first few weeks) the contribution of the fly ash to the performance of concrete is limited to its physical properties: filler effect due to its fineness and lower water demand due to its spherical shape. The formation of cementitious hydrates by pozzolanic reactions (its chemical contribution) occurs at a later age. Replacement of 25 % of cement by fly ash at the same water/binder ratio (binder = cement + fly ash) will result in an initially lower compressive strength, but will be at the same or even higher level at an age of 90 to 180 days. The pozzolanic reaction of fly ash causes an ongoing densification of the concrete matrix. Coarse capillary pores are transformed into finer gel pores, slowing down the transport of aggressive spe-

cies in(to) the concrete more and more and therefore making the concrete more durable. In about 1 year fly ash concrete has about the same dense structure as blastfurnace slag cement concrete and hence a similar or even better durability[11]. This is illustrated by the decrease of the chloride diffusion coefficient with time as shown in Figure 6.

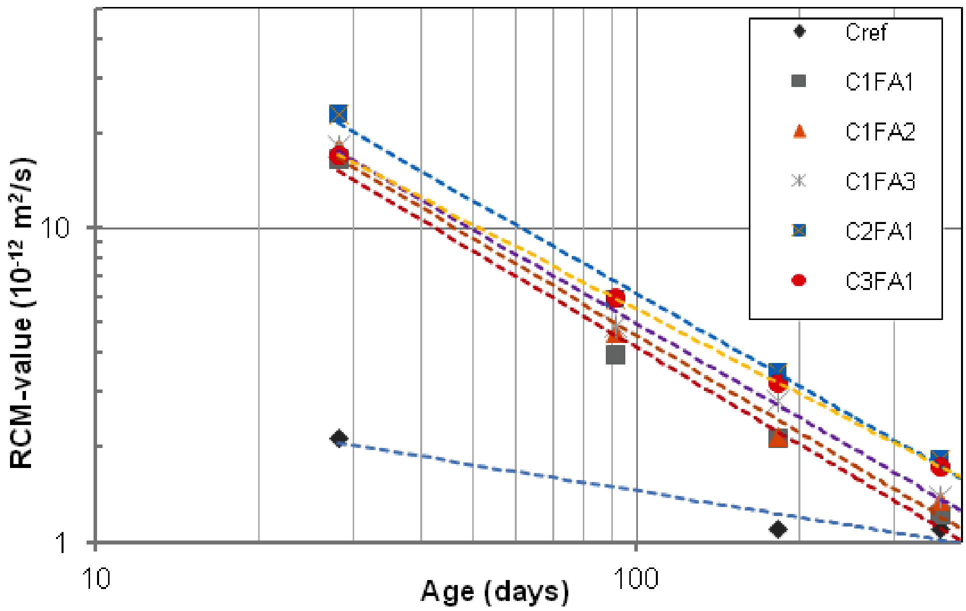

Figure 6: Decrease of chloride diffusion coefficient in time of FA concretes (=CiFAi) versus GGBS concrete (=Cref), illustrating pozzolanic effect of FA

The resistance of fly ash concrete against carbonation and freeze-thaw attack with deicing chemicals is significantly better than for blastfurnace slag cement concrete.

Sustainability

In 'attest' concrete about 1/3 of the CEM I is replaced by fly ash. This means a reduction in the emission of the green house gases (EGHG in Table 3, 4th column) of 33 % compared to the reference concrete with CEM I. Hence, the use of fly ash as cementitious binder in concrete is also of benefit from an environmental point of view.

Economics

Fly ash meeting the requirements of EN 450-1 can partly (k-value) replace cement in concrete and has a positive but limited economic value. However, for specific combinations of fly ash and CEM I cements, which have been tested for equivalent concrete performance (attest concrete), the fly ash can be fully considered as

cementitious binder. This means a much higher economic value, which can be at a level of about ½ of the market price for cement.

In the 1970's fly ash produced in the Netherlands was landfilled at a cost of about 10 Guilders per tonne. 10 Dutch Guilders in 1970 is equivalent to about 20 Euro nowadays. Hence, fly ash has changed from a waste material into a very profitable, high valued cementitious binder.

Municipal incinerator bottom ash

Origin and composition

Inhabitants of the EU produce on average about 0.5 tonnes of household waste each year. Of the EU municipal waste, which amounts approximately 350 Mton per year, about 40 % is recycled or composted, 25 % is incinerated and 35 % is landfilled. Municipal waste is often incinerated to recover energy and to reduce the volume of the waste. Bottom ash obtained from such a plant is called municipal solid waste incinerator bottom ash or more briefly: municipal incinerator bottom ash (further abbreviated as MIBA). In the Netherlands about 15 Mton of municipal waste is produced annually, of which 50 % is incinerated, resulting in 2 Mton MIBA per year.

The MIBA as produced, is very inhomogeneous and contains unburned material, metals, glass, minerals, slag, etc. Such bottom ash is not suitable for any application.

Present treatment and applications

The raw bottom ash of the incinerator plant is standard treated by sieving, separation of ferrous (magnetic) and non-ferrous (Eddy current separator) metals and handpicking. In this way it can be made suitable for application as embankments (noise barriers) or (un)bound base courses for roads.

Appropriate utilization of this bottom ash has gained much attention over the last decades, especially in Europe where the EU policy is strongly aiming at resource-efficiency. The EU Waste Framework Directive[2] specifies that member states must achieve 50 % re-use and recycling of municipal waste materials/residues by 2020.

In the Netherlands, nowadays, application of unbound MIBA in road construction and noise barriers is discouraged because of environmental issues. Consequently, producers/suppliers of this bottom ash have been looking for alternative and more added value applications, especially in concrete. Stimulated by the increased market value of metals, commercial wet and a dry treatment processes for MIBA have been developed, which also improve the quality of the remaining mineral fractions.

Upgrading quality

The basic quality of MIBA can be upgraded by a wet or a dry additional treatment. The wet process is similar to the traditional washing of polluted soil. In the washing process the bottom ash is separated in the fractions 4-40 mm, 0.1-4 mm and residue. In both fractions 4-40 mm and 0.1-4 mm ferrous and non-ferrous metals are additionally removed. In the residue the very fine and low density particles are collected. The dry process has been developed by the University of Delft and this technology, called ADR, and is patent protected. It is based on ballistic principles to break the water bond that is formed by the moisture associated with the fine particles. Both processes not only increase the amount of metals recovered but also separate the very porous particles, especially for the smaller grain sizes. This improves the quality of the mineral fractions, which is very important for application in higher valued concrete products. Moreover, the suitability of this fine fraction separated from the MIBA is now being researched as a possible raw material for cement production.

Application as aggregate in concrete

Table 4 summarises the properties of upgraded MIBA, obtained by the wet as well as the dry process[12].

Table 4: Properties upgraded MIBA

Property	Units	Dry process		Wet process		
		0-2 mm	2-12 mm	0-2 mm	2-12 mm	12-40 mm
Density	kg/m^3	2090-2230	2070-2210	2230	2290	2260
Water abs. (24 h)	%m/m	7.1-11	5.9-10	5.7	4.8	5.4
Loss-on-ignition	%m/m	3.7-5.6	1.8-3.4	1.9	0.82	0.52
Chloride (Cl)	%m/m	0.26-0.53	0.10-0.28	0.05	0.03	0.03
Sulphate (SO_3)	%m/m	1.6-2.4	0.76-1.4	1.4	0.53	0.34
Alkalis (Na_2O-eq)	%m/m	0.44-0.77	0.23-0.44	average 0.1		
Metallic Al+Zn	%m/m	0.32-0.64	1.0-1.4	average 0.7		
Fines (<63 µm)	%m/m	5-10 range		3.2	1.0	0.3

The content of undesired constituents, like chlorides, sulphates, alkalis, loss-on-ignition and fines, in upgraded bottom ash from the wet process is low and meets the requirements for application in concrete. As can be expected the dry process results in bottom ashes with higher content of these constituents. Especially the sulphates and metallic Al+Zn need attention for application as aggregate in concrete. Their values should be less than 0.8 %m/m and 1.0 %m/m respectively. A low density, which corresponds to a high water absorption, of the particles results in

inferior concrete. For structural concrete a particle density less than 2100 kg/m^3 is not desirable.

Upgraded MIBA can replace 20 %V/V of fine and/or coarse aggregate in concrete. In concrete made with hard and dense aggregates having good flow properties, the partial replacement will result in a decrease in compressive strength of about 10-20 % (see Figure 7)[12]. In dry concrete mixes such as used for the production of concrete paving blocks and flags, the partial replacement (up to 40 %m/m) of the natural aggregate by upgraded MIBA does not result in any decrease in strength. This is because of the angular shape of the bottom ash particles.

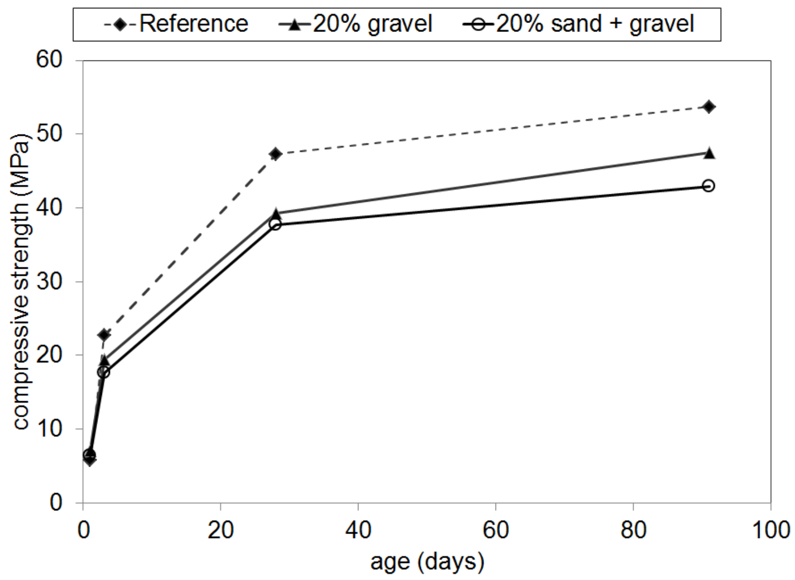

Figure 7: Compressive strength of concrete with 20 %V/V replacement of natural aggregate by upgraded MIBA

At the same compressive strength, the structural properties (tensile strength, E-modulus, strain at fracture, shrinkage, creep) of concrete with up to 20 %V/V upgraded MIBA are similar to concrete with no replacement in aggregates. However, the shrinkage and creep of concrete with 20 %V/V of fine and coarse aggregate replacement can be substantially higher. This must be taken into account for specific applications which are sensitive to shrinkage or creep.

The durability of concrete with 20 %V/V upgraded MIBA is similar to the concrete without this bottom ash, except for the chloride diffusion coefficient, which is about 50 % higher.

Sustainability

Concrete in which 40 %m/m of the natural aggregate is replaced by the upgraded MIBA shows a reduction in the emission of the green house gases of 4 % (EGHG in Table 3, 5th column). Although it is only a small difference, it is a positive one.

Concrete with MIBA as aggregate can be used in a second life. The recycled aggregates made of this concrete are of similar (structural) quality as the recycled aggregates from ordinary concrete.

Economics

Taxes on landfilling of municipal incinerator bottom ash in EU amount on average to 80 €/ton. Some member states have landfill ban for wastes that are suited for incineration. Total costs for landfilling can be as high as 180 €/ton (CEWEP data)[13]. Although these costs vary strongly between different member states of the EU, it is clear that there is sufficient margin to upgrade MIBA.

Only a few percent of the bottom ash is metals. But the high price for secondary metals, especially non-ferro, makes it worthwhile to recuperate it. This almost fully covers the costs of upgrading.

The use of (unbound) MIBA in embankments and road construction generally requires additional measures to prevent leaching and therefore results in a negative price for the MIBA of about -10 €/ton. Applied as aggregate in concrete, a market price of about half of the natural aggregates is possible for the upgraded MIBA.

Conclusions

The three examples described in this paper clearly demonstrate that mineral residues can be turned into valuable raw materials for the concrete industry. Some of such residues even improve the performance of concrete significantly, as was shown for the GGBS and powder coal fly ash. Not only from a materials but also from a sustainability and an economic point of view. Residues of lesser quality than present day raw materials for concrete, need upgrading before they can be used in concrete. Depending on their performance a specific market price will establish. In general this will be a positive value, making the process of upgrading feasible.

In order to successfully implement new applications for mineral residues in concrete, it is necessary to fully characterize the specific mineral residue as a raw material for concrete and to determine its effect on all relevant properties of the concrete. Based on this knowledge regulation for the specific application(s) have to be drawn up. This

regulation is the basis for the quality assessment (certification) of the mineral residue for the intended application(s). These are the key success factors to bear in mind.

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