FIBRE CEMENT: A PERFECTLY RECYCLABLE BUILDING MATERIAL

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ABSTRACT

The sustainable production of fibre cement requires that viable, and preferably also valuable, solutions are found for the recycling of the fibre cement production and construction waste, and of the installed fibre cement products after their service lifetime. To this end Redco called in the assistance of some renowned expertise centers that were assigned well described research topics, in view of developing and promoting such solutions. The paper briefly reviews some of these studies.

It was shown that air-cured fibre cement roofing slates can be used as a component in load bearing and frost-protecting road basement layers, and even can improve some of the performances of these layers. Further it has been confirmed that air-cured as well as autoclaved fibre cement waste can be used as a component of the Portland clinker raw meal. Some basic advice about the optimum way to introduce the waste into the clinker production was formulated.

Last but not least, a NIR spectroscopy based portable analysis tool too easily and quickly distinguish between asbestos cement and non-asbestos fibre cement products is briefly described. The availability of such tools is considered to be a prerequisite for the efficient recycling of fibre cement demolition waste.

KEYWORDS:

Fibre cement; recycling; road basement; Portland clinker; NIR spectroscopy

INTRODUCTION

In the European Union, all use of asbestos has been banned since 1st January 2005 (Directive 1999/77/EC, 1999) although, in practice, non-asbestos fibre cement composites have been gradually introduced into the European market since the mid 1980's. Knowing that fibre cement roofing products have been attributed a service lifetime of 60 years (BRE, 2003), it may be expected that measurable flows of fibre cement demolition waste will gradually come on stream in Europe from the mid 2020's onwards.

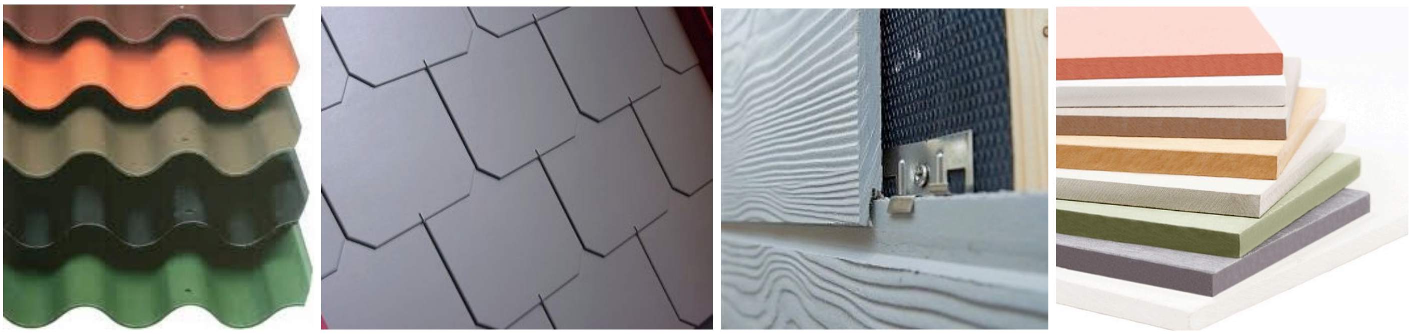
Nowadays, no matter which human activity is referred to, the need for sustainable practices is universally recognized. So, when producing fibre cement products, one should also generate sustainable, and preferably also technically valuable solutions for the recycling of these products once they will have reached the end of their service lifetime. Therefore in the past decade within Etex several studies were initiated in view of the development of such recycling routes for fibre cement products. However because aged fibre cement demolition waste is not yet readily available, these studies have been done so far with fibre cement production waste.

Of course, at the time these studies were started up, several internal and external recycling practices were in use already, but it was recognized that all of them had been introduced in a purely pragmatic way, i.e. without any research. It goes without saying that most of the applied practices concerned the addition of the crushed fibre cement production waste to some basement layer of roads, car parks or alike, in a way developed by local contractors. Without rejecting this type of applications, the studies however aimed at developing more valuable ways of recycling, or at least, to scientifically underpin, and by that hopefully optimize, and promote existing applications. This paper describes an example of both aims. First, the results of a series of studies that evaluate the potential of fibre cement recycling in road basements are briefly described. Studies which evaluate the use of fibre cement as a component of the Portland clinker raw meal are also discussed.

A topic of specific importance when studying potential recycling routes for fibre cement, concerns its great visual resemblance to asbestos cement, at least for the common man. With respect to the recycling of fibre cement production waste, this does not or should not constitute any problem since the supply chain of the waste from producer to recycler can be reliably closed to exclude any possible contamination by asbestos containing material. However, when dealing with fibre cement demolition waste, supplied from the general, i.e. rather diffuse construction market, the absence of asbestos fibres has to be undoubtedly guaranteed for all material that is delivered to a recycler. In the present paper this problem is addressed by the description of a portable analysis tool to easily and quickly distinguish between asbestos cement and non-asbestos fibre cement products.

FIBRE CEMENT – A GENERAL DESCRIPTION OF THE MATERIAL

Within the context of this paper the term fibre cement refers to (non-asbestos) fibre reinforced cement composites produced by means of the Hatschek technology, a technology described elsewhere (Van der Heyden, 2010). It concerns relatively thin, though multilayered products (thickness mostly between ca. 4 - 12 mm, depending on the type of product). In figure 1, some examples of FC products are shown.



Corrugated sheet
Air-cured, unpressed

Slate
Air-cured, post-compressed

Siding
Autoclaved, unpressed

Decorative façade board
Autoclaved, post-compressed

Figure 1 - Illustrative examples of FC products

Next to reinforcement fibres, also process fibres are used in order to allow the formation of the individual monolayers. Within Etex, two hardening principles are applied. The first concerns ambient temperature curing of mainly Portland cement based mixtures, by which the physico-mechanical fibre cement characteristics are obtained via normal cement hydration reactions. The second principle concerns high-pressure steam curing of properly designed mixtures of Portland cement (and/or possibly lime) and quartz, also called “autoclaving”. Hereafter fibre cement will be abbreviated as “FC”, whereas the FC products corresponding with the two different hardening processes are further indicated by the terms “air-cured FC” and “autoclaved FC” respectively. In all products the process fibres are cellulosic fibres. Cellulose is also used as reinforcing fibre in the case of autoclaved FC, whereas air-cured FC contains polyvinyl alcohol and/or polypropylene reinforcing fibres. The matrix of the air-cured products is mainly composed of hydration products of Portland cement (and eventually also of pozzolan), Portland clinker relicts and carbonaceous fillers. The matrix of the autoclaved FC products consists of a mixture of well crystallized (predominantly 11Å tobermorite and hydrogarnets), cryptocrystalline and even amorphous calcium silicate hydrates. The FC board’s application determines whether it is compressed (i.e. densified) after its formation on the Hatschek machine or not. Within Etex, depending on the FC product’s application, uncoated as well as coated, air-cured or autoclaved FC products are sold.

In the figure 2 illustrative examples are given of initial compound compositions of common air-cured respectively autoclaved FC products. Of course, depending on the application, a wide variety of formulations exist differing from each other by the type(s) and amount of functional fillers used.

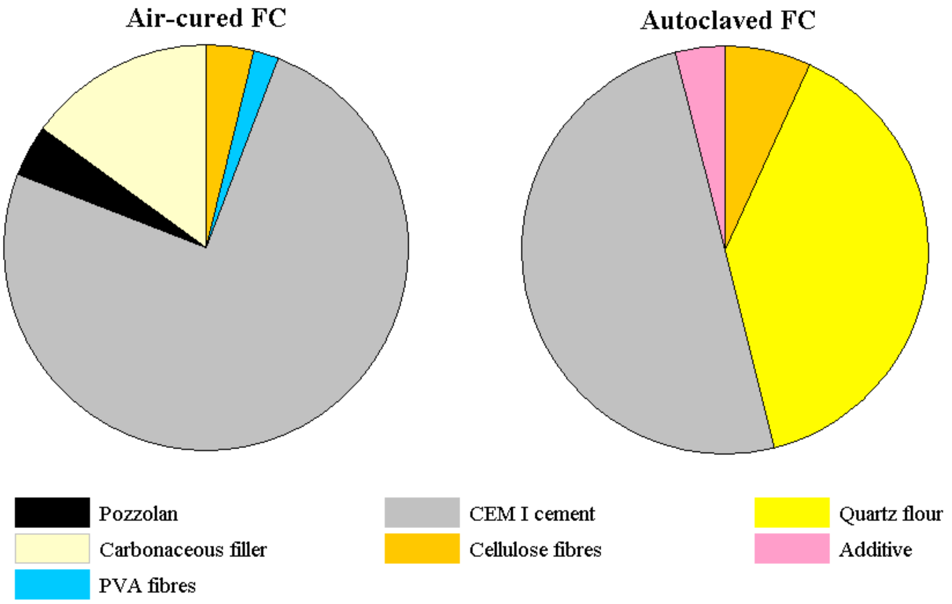
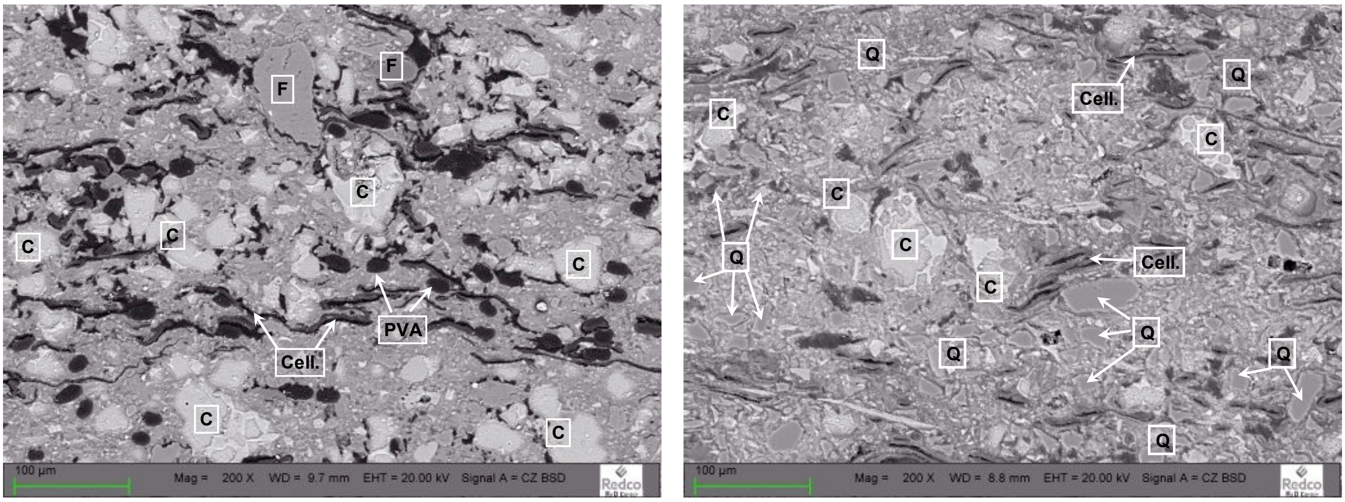


Figure 2 - Illustrative examples of FC formulations (relative weights)

The SEM pictures in figure 3 demonstrate the microstructure of 2 hardened FC products.



Roofing slate (post-compressed air-cured FC)

Decorative façade board (post-compressed autoclaved FC)

C - residual Portland clinker
F - carbonaceous filler
Q - residual quartz
Cell. - cellulose fibre
PVA - polyvinylalcohol fibre

Figure 3 - Illustrative SEM pictures of 2 different types of FC products

The Locked Reactivity Potential of Hardened Fibre Cement

The above pictures clearly indicate the presence, and often even the abundance, of anhydrous Portland clinker and residual quartz in the hardened air-cured respectively autoclaved FC products. These relicts are embedded in reaction products, which, especially in the case of air-cured products, may be seen as one of the major reasons for the fact that they did not react completely. Therefore it seems logic to expect that, when breaking down the hardened material in such a way that free surfaces of unreacted material are generated, the material could regain some reactivity potential.

At Redco some studies were started up in order to investigate this potential. Although at present it is still too early to report on the results, hereafter some general comments are made.

So far, preliminary experiments showed that ground air-cured FC material shows only very limited hydraulic reactivity in terms of heat and strength development. In fact, the observed reactivity level is far below what one might expect based on the amount of unreacted clinker that is present in the product. Therefore the study now focuses on the exploration of different crushing and grinding techniques that might improve the liberation (and reactivity) of anhydrous clinker surfaces. In addition to mechanical activation, some chemical activation may be possible or even required.

With respect to the recycling of ground air-cured as well as autoclaved FC waste in autoclaved FC production, some positive results have been obtained already in lab studies and industrial trials. Of course the performance actually obtained, is influenced by many parameters among which are the type and composition of the FC waste, the type of FC product in which the waste is recycled, the autoclaving procedure applied. At present it is too early to make a comprehensive reporting on that.

FIBRECEMENT CRUSHING AND GRINDING

Crushing

Even without the intention of regaining any reactivity from it, the recycling of FC products requires a pre-treatment consisting of a crushing operation, which, if necessary, is followed by a grinding step.

With respect to the crushing, two aspects need attention here: the material's toughness and, in case of corrugated roofing sheets, the possible presence of polypropylene safety strips.

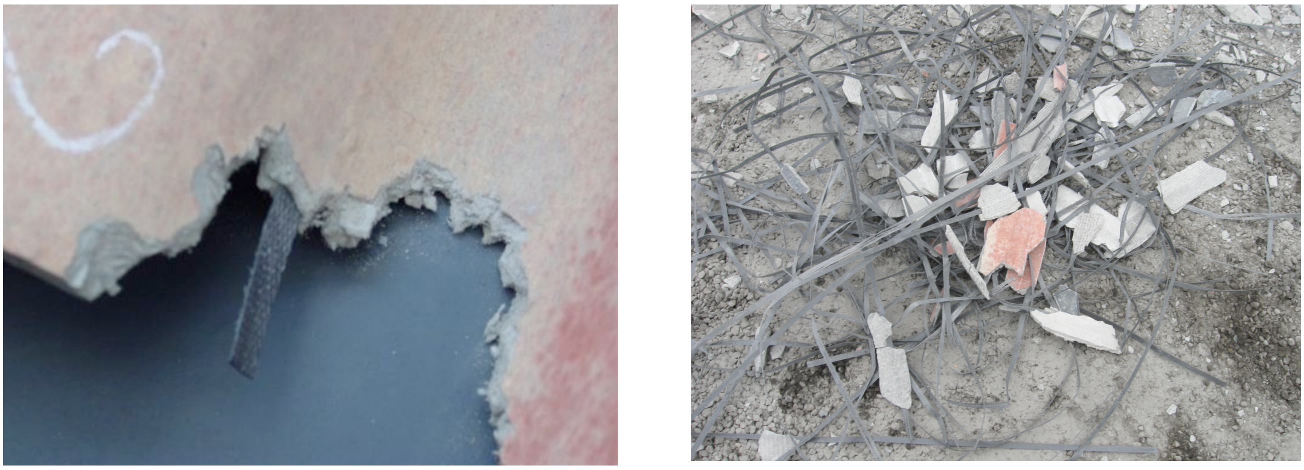
Because of the relatively high organic fibre volume (ca. 7 to 15 vol-%, depending on the product) and the absence of an aggregate phase, FC products are significantly tougher than the usual stony demolition waste such as concrete, mortar and clay brick., In practice, though it turns out that most FC products can be easily crushed by the same type of impact and hammer crushers as used for the before mentioned stony materials. For air-cured, post compressed FC slates, this was confirmed by a limited screening study at the Bauhaus-Universität Weimar, Germany, which was organized to prepare air-cured FC samples for some recycling studies. The screening revealed that jaw crushers and roller crushers are less or even not suitable because of the limited thickness of the FC products, by which material can slip through the crusher chamber without being broken down (ABW, Bauhaus-Universität Weimar, 2010a). In some cases however, i.e. uncoated FC products which have taken up too much humidity upon contact with the air, or FC products with lower density (< 1.1 kg/m^3), even impact or hammer type crushers might not be able to do the job, because of the high toughness of the product. In such cases, good results have been obtained by using a wood crusher type of machine in which the material is subjected to some cutting and tearing.

The presence of polypropylene safety strips in corrugated sheets may lead to some build-up in some parts of the crushing equipment, in case they are not cut by the machine, but remain as long, twisted and interested strips with some pieces of adherent FC material. However, many examples exist where such problems do not arise. For the time being, at Redco a more systematic study of possible FC crushing equipment is continuing. Systems in that the safety strips are removed from the product, as well as systems in that they stay part of the crushed material, are being considered. In figure 4 some pictures are shown of crushed FC, a liberated polypropylene safety strip and some nested strips that survived a crushing operation.

Because of the absence of an aggregate fraction the crushing of FC goes with an important dust generation against which the appropriate measures need to be taken.

Crusher in action

Crushed FC



Close-up of partly liberated PP strip

PP strips with adhering FC fragments

Figure 4 – Crushed FC and polypropylene safety strips

Grinding

When required by the recycling application one is aiming at, after the crushing, the FC waste is ground into a powder. With respect to the grinding, attention should be paid in order to avoid the generation of a fluffy material. Indeed, it has been shown that when not using the right grinding equipment, the cellulose fraction transforms into a woolly substance by which the whole mass of ground FC looks and behaves as an aerated wool. It has been proved that when using a ball mill, such phenomenon does not occur at all and a powdery material is obtained, in appearance similar to cement or limestone flour, notwithstanding the presence of the (crushed) organic fibres.

FIBRE CEMENT WASTE AS COMPONENT OF ROAD BASEMENT

The FC recycling practice in road basement is well established, albeit in a somewhat diffuse way. In fact, the addition of the crushed FC waste is mostly done in a non-engineered, and by that most probably non-optimized way. In an attempt to jazz up the technological level of this recycling route, Redco assigned a series of studies to the Bauhaus-Universität Weimar, Germany, with the aim to document the potential of FC waste in these applications by means of scientifically based experimental evidence.

In a first study, the potential of crushed FC roofing slate was evaluated for its potential as a component of unbound road foundations which nowadays are already based on recycled concrete aggregate. A FC slate production waste was crushed and a 0/8 mm fraction was prepared from the crushed material. Out of this fraction, 4 additional fractions were generated: 0/2 mm, 0/4 mm, 2/4 mm and 2/8 mm. The recycled concrete material, with which the FC was combined, concerned a 0/32 mm fraction. A total of 8 different mixtures were studied. In a first group, 4 mixes were considered, corresponding with varying substitution ratios of the recycled concrete aggregate: 1, 2, 5 and 10 weight-% of the 0/8 mm fractions FC were used respectively. The second group of 4 mixtures was obtained by substituting 5 weight-% of the recycled concrete aggregate by 0/2 mm, 0/4 mm, 2/4 mm respectively 2/8 mm fraction FC.

The so obtained mixtures were evaluated for granulometry, density, porosity, water absorption, frost-thaw resistance, toughness and abrasion resistance (Los Angeles test), Proctor density and water content, and the load bearing power as measured in the CBR test (California Bearing Ratio test).

Unlike expectation, it was found that the frost-thaw resistance of the crushed FC on its own, was at least as good as that of the recycled concrete aggregate. Also the FC's toughness and resistance against abrasion were better.

When evaluating the mixtures containing the 0/8 mm fraction, it was found that up till 5% (frost-thaw test) resp. 10% (LA test) no changes were observed in comparison with the 100% recycled concrete aggregate based reference foundation material. Because of that, the study concluded that up till substitution ratio of 5%, the FC 0/8 mm fraction can be applied without any problem.

Last but not least, the study indicated that the addition of the crushed FC led to higher Proctor densities and clearly higher load bearing capacities, irrespective of the crushed FC fraction used. With respect to the latter characteristic, the highest increase (+21%) was obtained by adding 10% of the 0/8 mm fraction.

More information about this study can be found in (ABW, Bauhaus-Universität Weimar, 2010a; Müller, A., 2010; Müller, A., 2011b)

In a second study, FC slate production waste was mixed up with partially crushed concrete demolition rubble at 2 addition ratios, 5 and 10 % respectively. The mixtures were presented to an impact crusher and the resulting crushed mixes were evaluated for the same characteristics as in the first study. The study revealed that the combined crushing led to a lower degree of size reduction of the FC material than in the case of separate crushing, and also compared to the concrete rubble. This observation is in line with the results of the Los Angeles tests which show an increasing abrasion resistance with increasing FC content. Apart from the visually less optimum appearance, the different degree of size reduction of FC and concrete rubble, also led to the fact that the different granulometric fractions of the composed mixtures, exhibited different FC contents. By that, not all of the performance characteristics were influenced in the same way. (ABW, Bauhaus-Universität Weimar, 2010b).

In a third study, the above described combined crushing was applied in an industrial operation. As in the lab study, this way of crushing led to a different degree of size reduction for the FC and concrete rubble fraction. The construction performance characteristics of the mixtures as measured in the lab were hardly influenced by the FC addition. It seems that, at least up to 10% FC addition, the influence of the crushed concrete rubble fraction is overruling. With the produced mixtures also some experimental test fields were made on which load bearing tests were executed. These tests indicated an increased load bearing capacity when FC waste was used. (ABW, Bauhaus-Universität Weimar, 2011). Figure 5 shows some pictures of one of the test fields.

Figure 5 – Real scale road basement test with mixture composed of concrete rubble and 10 weight% crushed FC

In general this study on industrial scale, confirmed the lab tests: FC waste can be used in load bearing and frost-protecting road basement layers, and even can improve some of the performances of these layers. Though the test also confirmed that when combined crushing is applied, FC fragments stay clearly visible in the end product (mainly due to their platy fragment morphology). It is believed that this visibility is a disadvantage for the acceptance of the application (since it resembles asbestos cement). Therefore it seems preferable to crush FC to particle sizes below 8 mm. This requires separate crushing of the FC waste.

FIBRE CEMENT WASTE AS COMPONENT OF THE PORTLAND CLINKER RAW MEAL

The Logic

Since hardened air-cured FC mainly consists of partially carbonated Portland cement hydrates, residual anhydrous clinker and carbonaceous filler, the recycling of hardened FC in the production of Portland clinker seems to be its most obvious recycling solution, irrespective of whether it concerns production, construction or demolition FC waste. The two other components, cellulose and PVA even have some caloric value.

The data in table 1 clearly illustrate the striking similarity between the chemical composition of Portland clinker or its ignited raw meal, and that of ignited air-cured FC.

	Chemical composition [M%] of			Initial fibre cement compound composition [M%]		
	clinker or the **ignited clinker raw meal**	**ignited fibre cement**		**Mix component**	**slate**	**corrugated sheet**
		slate	**corrugated sheet**			
CaO	65 - 68	65.7	64.3	**Cellulose**	3.4	3
SiO_2	20 - 23	22.5	24.2	**PVA**	1.8	1.9
Al_2O_3	4 - 6	4.3	4.2	**CEM I**	75.8	74.1
Fe_2O_3	2 - 4	3.1	3.0	**Limestone flour**	15	15
MgO	1 - 5	1.6	1.5	**Cond. silica fume**	4	6
SO_3	0.1 - 2	2.0	2.0			
K_2O	0.1 - 1	0.5	0.5	Total	100	100
Na_2O	0.1 - 0.5	0.3	0.3			

Assumptions made on the chemical composition of IGNITED raw materials:

- ignited cement: 65.22 % CaO, 21.17 % SiO_2, 5 % Al_2O_3, 3.60 % Fe_2O_3, 1.77 % MgO, 2.33 % SO_3, 0.59 % K_2O, 0.32 % Na_2O
- ignited carbonaceous filler: 100 % CaO
- ignited condensed silica fume: 95 % SiO_2, 0.3 % Al_2O_3, 0.1 % Fe_2O_3, 0.5 % MgO

Table 1 – Illustration of the striking similarity between chemical composition of ignited clinker raw meal and ignited FC

Additionally, as has been shown elsewhere (Etex, 2010), even for the air-cured FC products that contain carbonaceous fillers in their formulation and/or exhibit high degree of carbonation due to ageing, the amount of CO_2 that is generated per mass unit of CaO upon calcination, is significantly lower than in the case of common Portland clinker raw meal.

The Current Practice

These considerations have made that in 2001; Redco started a development project with the Belgian cement company CBR N.V. (Heidelberg Cement Group) in order to evaluate the feasibility of the recycling of FC production waste as a component of the Portland clinker raw meal. In 2003, this development resulted in the practical implementation of the routine recycling of air-cured FC waste from the Belgian Etex FC works in the CBR clinker plant in Antoing, Belgium.

Figure 6 – Crushed FC slate waste as it is delivered to the clinker plant

In 2005, a similar recycling operation was started in a German Heidelberg Cement cement works using FC production waste from a German Etex FC works. Until now, in both clinker plants, the FC recycling is limited to production waste. This also explains that nowadays, in both plants the FC waste dosage in the clinker raw meal is very limited: only 0.3 and 0.4 weight% on average. Both recycling operations have been described already in more detail elsewhere (Etex, 2010; Baulinks.de, 2010). Here we just remark that in both cases, the FC production waste is presented at the cement works' gate as a pre-crushed material (maximum fragment size ca. 40 à 50 mm) and is mixed up with the other clinker raw meal components before being fed to the raw meal mill. The pre-crushing is done to assure a smooth handling

Scientific Studies

In a way, the fact that nowadays, cement plants are very eager to use alternative raw materials and fuels, should facilitate the wide introduction of FC waste in the Portland clinker production. But on the other hand, by the fact that already today, in many plants a varied portfolio of secondary raw materials and fuels has been installed, some of these cement plants hesitate to introduce yet another secondary raw material. Next to the argument that this would further complicate their operations, the fact that FC holds some organic fibres is often brought up as an argument (or excuse) for not starting up such recycling operation. Indeed, some risk would exist that only partially decomposed organic substances might end up in the stack, via the air leaving the raw meal mill and/or via the preheater tower, in an amount by which VOC limits for the exhaust gases might be surpassed. In order to get a scientifically based view on the thermal decomposition phenomena, last year, Redco decided to assign a fundamental study to the renowned Research Institute of the German Cement Industry, VDZ (Düsseldorf, Germany). Though, the study was supposed to also give a technico-scientifically based view on the possible impact of FC on process operation and the clinker product quality. Additionally the study was expected to bring an indication of the maximum dosage of FC waste one could use in the Portland clinker raw meal, without having to implement major changes to the nowadays existing layout and way of operation of Portland clinker kilns. The latter question was triggered by the knowledge that within few decades, especially in Europe, an appreciable amount of FC demolition waste will gradually come on stream. Trying to recycle that demolition waste in Portland clinker will definitely increase the FC waste dosage in the clinker raw meal.

Simultaneously with the preparation of the VDZ study, Redco was invited to participate as industrial partner in a PhD study at the Ghent University, Belgium, in that the recycling of different waste streams in Portland clinker kilns would be studied. Redco was asked (and did confirm) to assist in the practical design and execution of that part of the study which deals with FC waste.

Hereafter the general setup of the 2 studies is roughly sketched and a selection of findings of the VDZ study (VDZ, 2012a), and of that obtained in the PhD study so far, are briefly commented upon. At the time of writing the present paper, 2 other articles are under redaction, each of which deals with a more extensive and documented summary of the respective studies (VDZ, 2012b; Schoon J., 2012).

VDZ Study

The VDZ study was limited to 2 types of air-cured FC products: decorative façade boards and corrugated sheets. A total of 20 samples were considered for the extensive chemical characterization in view of obtaining the necessary parameters for the feasibility assessment of possibilities for the partial substitution of standard clinker raw meal by this FC waste. Out of the 20 samples, 15 samples had been taken from stock, and represent, with respect to the material chemistry and mineralogy, production waste. The other samples were added to the sampling plan in an attempt to get a first indication of the possible impact ageing might have on the FC's recycling potential in a clinker kiln. 3 of these samples were taken from a natural exposure site (3 and 4 years of outside exposure). The other 2 samples concerned artificially aged FC (fully resp. partially carbonated).

For the assessment, use was made of a process engineering model developed by the Research Institute of the German Cement Industry. Essentially it describes the process from the kiln meal feed to the clinker output from the cooler. It is made up of individual models, each of which corresponds with a specific plant component: preheater, calciner, bypass, rotary kiln and grate cooler. All the individual models can be linked mathematically with one another, which make it possible to determine a steady-state condition for the entire rotary kiln plant. Because of the modular structure, the different plant circuits can be easily and flexibly mathematically simulated comparatively. The individual plant sections can also be defined geometrically so that different plant sizes can be simulated. Further inputs relate to the composition and mass flows of the raw materials and fuels as well as the volumetric flows of cooler inlet air, secondary air and, where appropriate, tertiary air. The calculations themselves cover the energy and material balances for the flows of fuel, dust and gas. Not only the combustion calculations for the fuels and the heat transfer, but also the relevant chemical and mineralogical solid phase and gas phase reactions as well as the gas-solids reactions are taken into account. The result is that the calculations do not only provide comprehensive process variables such as mass and volume flows and their compositions, gas and solids temperatures and heat losses, but also the specific energy requirement for burning the clinker. The model allows quantification of the influence of individual operational parameters via mathematical modeling. Furthermore extreme operational modes can be checked without the risk of damage at the kiln plant and the modeling can be used when operational experiences are missing. (VDZ, 2012a).

The starting point of the model describes a so-called BAT (Best Available Techniques) plant with an energy consumption of 3445 kJ/kg clinker at a production capacity of 3000 t/d. The plant consists of a rotary kiln with a five-stage cyclone preheater, a calciner with tertiary air duct and a grate cooler. The fuel input is divided into 70 % alternative fuel (mixture of solid recovered fuels, dried sewage sludge, animal meal) and 30 % coal. On the basis of this operating condition, referred to as “reference condition”, numerous variations were simulated with different application of FC amount and composition, in order to examine the influence on the clinker forming process.

The study concluded that by blending the alternative resource with pure correctives the FC production waste can theoretically amount to between 64 and 93 % in the raw material mixture from a material chemistry point of view.

But, since the organic compounds of the fibres volatilize in the clinker manufacturing process (see table 2 and figure 7), and a safe decomposition of the vaporized organic compounds is not guaranteed at temperatures below 900 °C, when entering the FC material via the normal kiln raw meal flow, the substitution ratio would have to be less than 1%.

		Air-cured Façade board		Air-cured Corr. sheet		Air-c., aged Corr. sheet	
volatile organic carbon analysis w/o polypropylene strips							
VOC 30-1000 °C	mg C/kg	8124	9162	6071	5035	6754	5212
carbon contribution by polypylene strips							
PP strips in sample	% (w/w)	0,00	0,00	0,17	0,17	0,17	0,16
C contribution by PP	mg C/kg	0	0	1332	1363	1333	1271
sum VOC till 1000 °C i	mg C/kg	8124	9162	7393	6390	8075	6474
change in kiln feed comp. per 1 perc. point usage of FC products							
carbon dioxide CO_2	%-pt./%-pt.	-0,27	-0,27	-0,19	-0,26	-0,15	-0,12
water H_2O	%-pt./%-pt.	0,14	0,16	0,17	0,20	0,14	0,14
change in VOC conc. in preheater exit gas per 1 % usage of FC products							
VOC @ 0.85 Nm¤/kg kiln feed	mgC/Nm¤ %-pt.	96	108	87	75	95	76
VOC @ 1.1 Nm¤/kg kiln feed	mgC/Nm¤ %-pt.	74	83	67	58	73	59

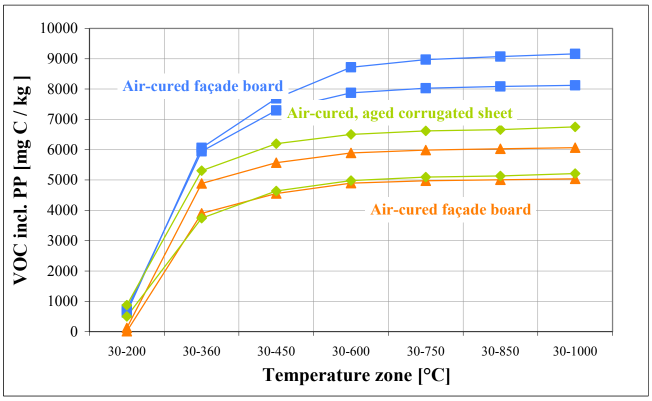


Table 2 – Selection of data on VOC content of FC waste. **Figure 7 – VOC as function of heating**

Indeed, the study indicated that already at a 1% substitution ratio the expected emissions are beyond the limit values according to German and European legislation. Therefore, large(r) quantities of FC waste would have to be fed to the kiln inlet, where the fibres are completely destroyed due to high temperatures and long residence times.

However, in practice, even when added at that kiln inlet, the above mentioned “theoretically” possible high FC dosages would still not be possible. This is related to the release of large amounts of chemically bound water which is present in the cement matrix. Its evaporation causes a considerable heat shifting from the rotary kiln to the calciner. As the FC material is a more calcined material (than limestone or marl is) the shifted heat cannot efficiently be used in the calciner and the preheater any more, so process temperatures increase and cause thermal stress to the (calciner and preheater) refractory. Therefore, due to this risk for overheating, the dosage of FC materials would be limited to about 15 to 20%. Furthermore, the rotary kiln has to provide the heating up and the release of chemically bound water in addition to the sintering and clinker phases formation. Rotary kiln length and residence time affect the conversion of the kiln feed to clinker. At a substitution ratio of 20% or more no complete conversion takes place any more in the calciner, which may result in a too high free lime content of the clinker. Potentially higher ratios can be achieved in conventional kiln lines as longer rotary kiln length benefits the material conversion. The higher ratios are possible, but would go together with a considerable decrease of the kiln output. (VDZ, 2012a).

Even air-cured FC that contains carbonaceous filler in its formulation, and which has been carbonated during its exposure, still exhibits significantly lower CO_2 content than traditional kiln feed. Further less energy is required for the calcination of the FC material, which in its turn decreases the fuel related carbon dioxide emissions. The study found that at a standard clinker meal substitution ratio of 20% by FC, a carbon dioxide saving of around 10% is achieved. As less energy for the calcination is required the total energy consumption for the cement clinker manufacturing is lowered of by around 300 kJ/kg clinker (Table 3) (VDZ, 2012a).

Point of addition		**-**	**raw meal mill**	**kiln inlet**			
Type of FC corrugated sheet waste added		**-**	**aged**	**non-aged**			**aged**
Classic raw meal substitution by FC		**0 %**	**1%**	**5%**	**15%**	**20%**	**15%**
KEY ENERGY FIGURES							
preheater extit gas	kJ/kg cl.	986	991	918	1053	1127	1086
reaction enthalpy of kiln feed	kJ/kg cl.	1703	1706	1639	1448	1343	1527
total energy consumption	kJ/kg cl.	3445	3453	3254	3207	3151	3291
main burner energy input	MW	42	42	52	54	61	61
calciner burner energy input	MW	56	56	58	57	49	50
energy splitting calciner/main burner	%/%	57/43	57/43	47/53	49/51	45/55	45/55
COMPOSITIONAL DATA EXIT GAS							
humidity	% (v/v)	11,0	11,2	11,8	14,3	15,0	13,1
carbon dioxide CO_2	% (v/v)	27,0	26,9	27,3	25,9	25,0	26,2
specific CO_2 emission	kg/kg cl.	0,85	0,85	0,81	0,78	0,76	0,81
CO_2 saving versus reference	%		0,3	4,0	8,2	10,6	4,9

Table 3 – Selection of key energy figures and compositional data of exit gas

The overall conclusion of the study states that air-cured FC production waste, and most probably also air-cured FC demolition waste, are valuable (partial) substitutes for Portland clinker raw meal. Due to organic emissions caused by the FC material it should preferably be added at the kiln inlet. Process conditions and clinker quality limit the standard raw meal substitution ratio by air-cured FC material to about 15 to 20%.

PhD-Study

In this study 2 air-cured and 2 autoclaved FC products have been considered, in both cases one product being an unpressed, the other a post-compressed product. For a period of 24 consecutive weeks, each week a sample was taken from the respective production lines. For each product, out of the sample taken in week (i) and that taken in week (i+1), with i being an odd integer varying from 1 till 23, a homogeneous composite sample was produced. All these composite samples, a total of 12 samples per product, were analyzed for the chemical parameters commonly used for clinker raw meal analysis. Additionally, for a selection of them, a more extensive series of analyses were done in view of getting more information on the products' mineralogy, decomposition substances upon heating and their caloric value. Indeed, in the study special attention is given also to the possible effects of the FC waste on the emissions and the energy consumption. In the study 3 HeidelbergCement clinker kilns, are considered (2 cement plants and 1 clinker plant). For each of the 3 cement or clinker plants, several samples of each of the classical clinker raw meal components were taken and analyzed too.

Based on all these chemical data, for each clinker plant 2 clinker raw meal compound compositions were calculated by means of a HeidelbergCement in-house developed simulation program. For each plant, next to a raw meal that represents the average standard raw meal composition, an alternative mixture was prepared that aimed at maximizing the content of one of the FC products in it. The mixtures all had to meet specific chemical requirements in view of obtaining suitable clinker quality (mineralogy) and to assure smooth kiln operation. With respect to the latter, special attention was given to the sulphur, chloride and alkalis contents. Indeed, due to the presence of sulphate-based setting regulator in the cement used for producing the FC, in most cases, and especially for air-cured FC, the FC waste's sulphate content is higher than that of the common clinker raw meal. Further, quite some difference exists between the sulphur content of the limestone or marl used in the respective clinker plants. Therefore it was mainly the consideration of the sulphate that determined which type of FC product was the most suited for application in a given clinker plant. But, for all clinker plants, also the other 3 products could have been used as alternative raw meal component, albeit at somewhat lower dosage.

So far, the study revealed that compared to a situation where pure limestone is used in the cold clinker meal, an inorganic CO_2 emission reduction as well as a decarbonation energy gain is possible. Furthermore, the study demonstrated that the chemistry and mineralogy of the final clinkers were not influenced significantly by the use of the FC materials. Because of its compositional constancy, and by that its chemical stability, FC production waste or FC demolition waste can be considered as valid clinker raw materials. In some cases, a selective way of FC collection could have some clear advantages and a triage according to the criterion of hardening principle, i.e. air-cured or autoclaved could already be sufficient. Another way of organisation could aim at assuring to always have a mixture of the different FC products on the market in more or less constant mutual ratios.

But, like the VDZ study, also this study indicates that for industrial application, the FC waste should be inserted at a hot point in the process, e.g. a pre-calciner in order to ensure the full thermal degradation of the organic fibres for physical and chemical reasons, such as the avoidance of clogging the filter system and exceeding the organic volatile emissions levels. The possible energy gain by use of FC versus limestone, coming from the exothermal degradation of organic compounds as well as from the lowered decarbonation energy, were quantified. Together with the estimated energy consumption needed for the liberation of chemically bound H_2O, it was shown that using air-cured as well as autoclaved FC, as raw material for clinker production lowers the total energy requirement compared to the use of classic raw materials, without compromising either physical, chemical or mineralogical clinker properties.

THE POTENTIAL OF NEAR INFRARED SPECTROSCOPY FOR THE RELIABLE DISTINGUISHMENT BETWEEN ASBESTOS CEMENT AND FIBRE CEMENT

The use of FC waste requires that it is clearly recognized as asbestos-free material. In part this can be done by means of appropriate identification systems such as design and construction documents about the construction that has to be demolished, or specific stamps on the products which state its asbestos-free nature. (Michatz, 2009).

In the past decade, at Redco, some studies were done to develop systems that allow positive marking of the FC products during their production process and in a way that the marker is quasi homogeneously present throughout the product mass, down till the scale of a few mm. Indeed, recycling applications exist which after crushing, allow identification at the level of an individual fragment (of say, few cm). In such cases, features that just are present in places, such as stamps or safety strips (introduced in European corrugated sheets practically exclusively after the ban of asbestos) will not be sufficient. But, so far, and for several reasons, a bulk marking of FC has not been actively applied by Etex FC works.

Own experience and information gathered from the construction and recycling market indicates that, especially with respect to FC construction and demolition waste, the reliable experimental confirmation of the absence of any asbestos in it, is and is believed to remain, an absolute prerequisite for its acceptance by any recycler. In some cases, the need for such experimentally obtained evidence even exists for FC production waste. It is obvious that, in order to be practically applicable, the experimental investigation asks for a simple, mobile and not too expensive analysis tool. Some years ago, Redco identified equipment that already fulfils the first two of these requirements. This is a hand-held apparatus, named "Phazir^{TM}", which makes use of near infrared identification technology and which is commercialized by the French company Fondis Electronic (www.fondiselectronic.com).

In 2010, Redco commissioned a study by the Bauhaus-Universität Weimar, in order to evaluate the reliability and user-friendliness of this identification tool. Hereafter we briefly summarize the setup and the major findings of that study about which some publications have already appeared (Müller, 2011a, 2011b).

The study considered the analysis of 20 asbestos cement samples and 30 FC samples, which were all measured 5 times (5 positions, shifted each time a few mm away from the preceding measurement position) and for 7 different sample preparation treatments. Additionally, in situ measurements on roofing and façade materials were done with and without pre-treatment, in order to check whether the tool is practically usable on site indeed. Also some measurements of asbestos cement and FC products enwrapped in polyethylene foil were done.

The Measurement Principle

Near infrared spectroscopy (NIR) is a quick, non-destructive and non-invasive spectroscopic analysis technique which makes use of near infrared light (wavelengths between 800 and 2500 nm). In fact, NIR is based on the absorption of near infrared light by molecules which make them oscillate. The molecular composition of the sample can be deduced from the reflected radiation, which is analysed by a spectrometer. Until today NIR analysis technique has been mainly focussed on agriculture, the food and chemical industries, and pharmacy, although the technique can also be used to detect minerals that contain OH groups in their structure, on the basis of their characteristic spectra. In the Phazir^{TM} analysis tool, the diffuse reflected light is analysed in the wavelength range between 1321.1 and 1448.9 nm. The detected spectrum is compared with that of 6 asbestos minerals: chrysotile, amosite, crocidolite, tremolite, actinolite and anthophylite. From the moment that one of these minerals is identified, it is indicated on the apparatus' display. The use of this equipment does not require any specific mineralogical knowledge.

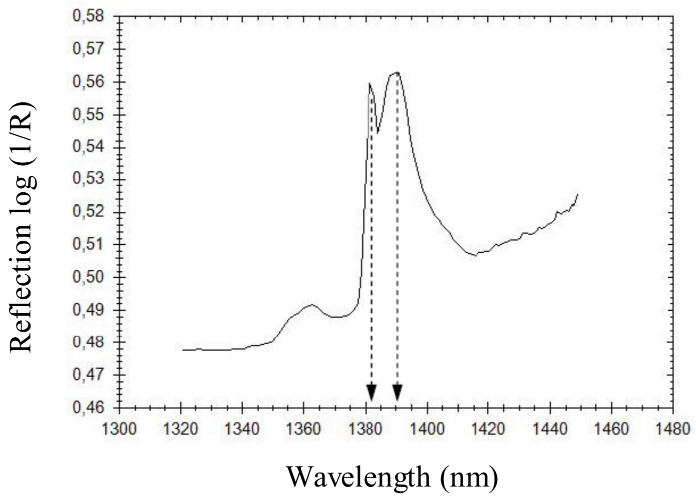


Figure 8 - NIR-Spectrum of a tissue containing > 40 % of chrysotile asbestos

Figure 9 – The microPHAZIR analyser

Application to Building Materials

This detection technique requires that the incident light can reach the asbestos cement or FC surface. Therefore when surface coating and/or contamination is present, these have to be eliminated at the position of analysis. The study has shown that a simple mechanical scratching off of the paint or contamination, is sufficient to assure a sufficiently intense reflection. Also a too high humidity content of the sample may hinder the measurement, but not that much because of modifications of the spectra, but rather because of the darkening of the surface by which the intensity of the reflected light decreases. This is also the case for dark products. The study showed however that this problem can be overcome by increasing the number of analyses per object. Additionally, the application of diluted sulphuric acid proved to be very effective to brighten the surface to increase the intensity of the reflected light. It is worth mentioning that the analysis of 1 sample, including surface pre-treatment, and based on 5 individual measurements, only takes about 15 minutes and that all results are automatically registered and can be transferred to other databank via USB.

Figure 10 – Examples of in situ use of the NIR – based analysis tool

Reliability

It is obvious that, in order to be reliable, the analysis method should always detect asbestos when it is present. Further it is preferable that the method does not, or only very exceptionally, give faulty asbestos detections. Such incorrect proof of asbestos in asbestos-free products may be caused by silicate and also carbonate minerals which have similar spectra to asbestos such as talc.

Though the study concluded that, out of 200 measurements on asbestos cement samples, that were obtained by analysing 20 different samples, after elimination of the coating and/or superficial contamination, and for each sample executing 5 measurements in dry condition and 5 measurements in wet condition, only 2 measurements did fail to indicate the presence of asbestos (identification error 1 %). So since for each sample 2 series of 5 measurements were done, all 20 samples were recognized as containing asbestos yet.

From a total of 305 measurements on FC products, only 3 measurements erratically indicated the presence of asbestos (again identification error 1 %). So also in this respect, the result is very satisfying.

The study also showed that the analysis method can be reliably applied to material that is packed in polyethylene foil. The increased identification error that may occur in that case, can be set off by increasing the number of measurements.

CONCLUSION

In the coming decades, the amount of FC demolition waste will gradually increase. As Etex wants to contribute to an ever more sustainable construction industry, several studies were undertaken (and others are still going on) which aim at the development and promotion of viable and valuable recycling applications for this waste. Up till now, these studies have been done with FC production waste only.

It has been shown that FC waste can effectively be used in road basement layers, an application that may be expected to have the capacity for absorbing large volumes of this waste.

Furthermore, it has been proved by industrial evidence as well as by fundamental studies, that FC waste can be used as a valuable component of Portland clinker raw meal.

Studies aiming at still other potential valuable FC recycling routes are still ongoing but it is clear that in order to maximize the recycling ratio of the FC demolition waste that will come free, a sufficiently diverse portfolio of recycling routes should be available, in order to always enable the selection of a logistically, economically and technically feasible FC recycling solution.

It is believed that the reliable experimental confirmation of the absence of any asbestos in FC waste, is an absolute prerequisite for its acceptance by any recycler. Practical evaluation of a NIR-based mobile analysis tool indicated that technique might be the solution to the problem of reliably distinguishing between asbestos cement and FC products.

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