Imagination included – New HPLC system LC-20A *prominence*

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TOC in the cem

The Portland cement plant in Rohrdorf

The Rohrdorf cement plant is situated in southern Bavaria, Germany, some 50 km south-east of Munich. Due to its proximity to the Alps this region also plays an important role in the tourist industry. For this reason, environmental protection and sustainable development have been shaping business politics for decades.

The cement production process

During cement manufacture, the required raw materials are transported from stone quarries in the vicinity and from further surroundings, mostly by railway. The raw materials are stored in a gravel bed hall and are subsequently ground to raw meal in a ball mill. Calcined pyrites and mill scale are used as modification materials. Since several months, fly ash from a caloric power plant is being added as a secondary raw material. During burning the cement clinker is formed via chemical conversion from the raw cement meal. A 4-trap heat exchanger is positioned immediately preceding the rotary kiln with a diameter of 5.2 m and a length of 85 m. For cooling, 10 satellites with 2.2 m diameter and 20 m length are used. The main burn unit is a ROTAFLAM burner (Pillard) with 4 burn channels. The nominal clinker capacity of the rotary kiln plant is 3,000 tonnes per day.

In the cement meal conveyor pipelines to the lowest cyclone stage of the preheating cyclone tower, foundry sand and 'special limestone' enter one section and shredded waste tyres and paper scavenger materials are added to the other section. The primary fuels, bituminous coal and 'heavy fuel oil' as well as BPG secondary fuels, i.e. fuels from product-specific industrial wastes, are supplied via the main burner of the burn unit. In addition, a plant for liquid secondary fuels is being taken into operation.

The use of secondary fuels is limited to a total of 90 % of the total furnace thermal capacity, whereby a maximum of 65 % BPG, 20 % waste tyres and 15 % liquid secondary fuels may be deployed.

For cement grinding, four ball mills are available. The cement

Rotary kiln

ent manufacturing process

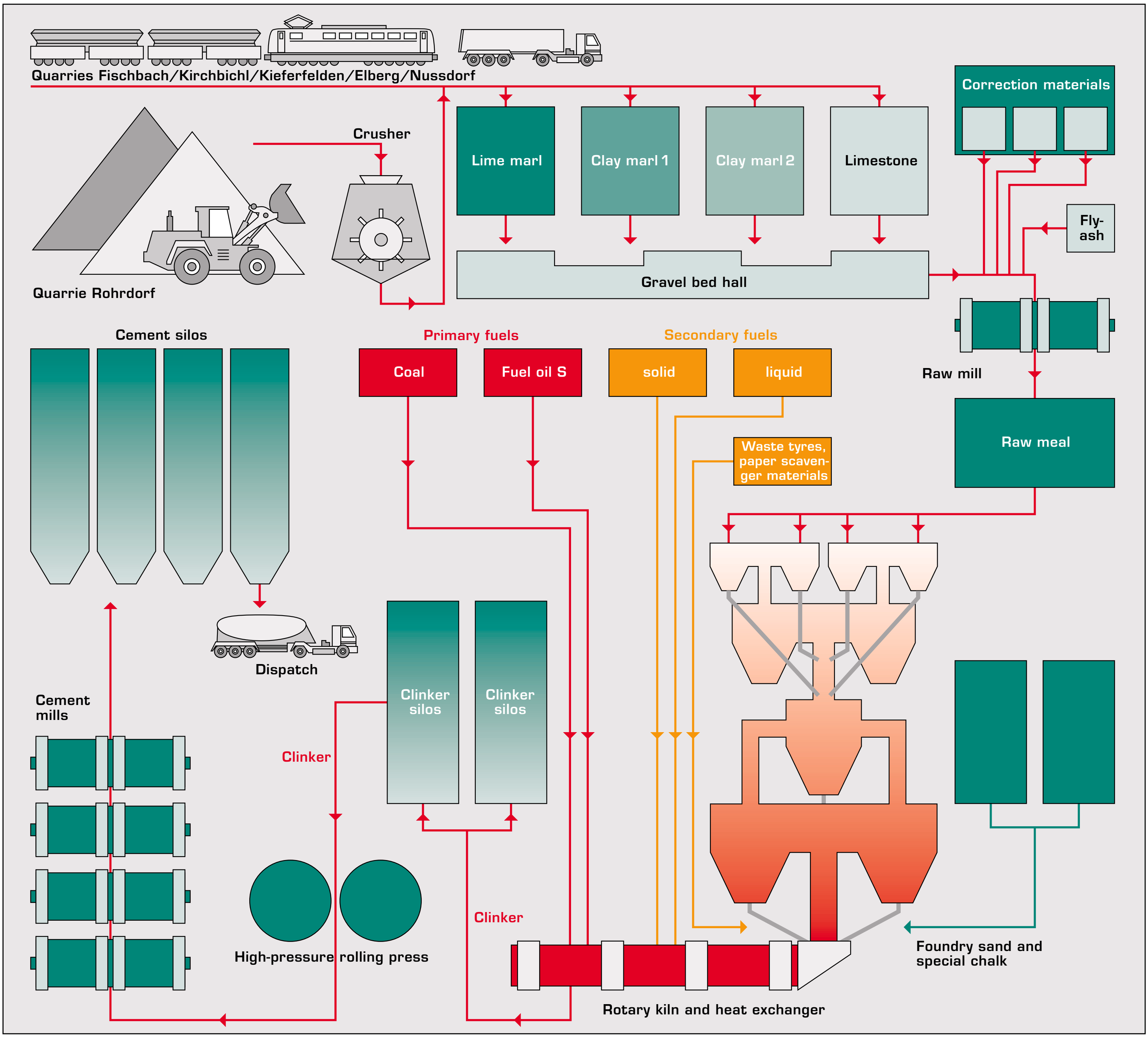

Figure 1: The cement production process

clinkers are pre-crushed in a high-pressure rolling press. Together with a mill in Austria supplied with clinker from the Rohrdorf cement plant, the cement dispatch amounts to approximately 1 million tonnes per year (Figure 1).

The burn process

10 years ago, the burn process in the main burner was begun with approximately 4 cm² chopped-up polyethylene foils obtained from Tetra-Pak recycling. In order to maintain a high quality standard, the high caloric value fraction from municipal wastes or similar materials is excluded from the process. Only synthetic wastes, textile wastes as well as plastic coated paper wastes originating from well-defined production processes are being used. In the Rohrdorf cement plant approximately 60,000 tonnes of synthetic waste materials are deployed annually. This corresponds to the ratio of approximately 60 % of the total furnace capacity. ➧

The product 'clinker'

Waste tyres are being added in shredded form – the maximum length is approximately 30 cm – together with paper scavenger materials through a 3-valve lock system in the ascending shaft of the heat-exchange tower.

Some paper manufacturers process waste paper in order to recover fibres that can be used in the production of cardboard. In the course of the production process in which synthetic materials and other interfering materials are removed, so-called paper scavenger materials also accumulate in the paper mills. These consist essentially of fibres that are too short and cannot be used for cardboard production. The water content is, at times, higher than 50 weight % and consequently the heat capacity varies from approximately 2.5 - 8.0 MJ/kg.

Based on their chemical composition, paper scavengers are used as secondary raw materials in many cement plants. In general, the paper scavenger materials are added via the entry shaft of the planetary cooler. However, as this is not possible in the Rohrdorf cement plant due to the use of a satellite cooler, the paper scavenger materials are added together with the shredded waste tyres in the ascending shaft of the heat exchanger.

The use of secondary fuels requires a fully functioning quality control system, as variations in the fuels can have a profound effect on the burn process and consequently on the characteristics of the clinkers. A well-organised quality control system and a corresponding instrumental configuration in the plant laboratory are essential for quality control.

A suitable parameter for the evaluation of the burn process is the TOC value. Sources for organic carbon in the rotary kiln plant are, in addition to the secondary raw- and combustion fuels, also the natural raw materials that contain, in part, considerable amounts of organic compounds. These organic compounds must be completely combusted in the rotary kiln in order to capture their total energy content. Through the solid- and gas flows in the heat exchanger, the burn process does not occur stationarily. TOC measurement at different locations in the production line enables monitoring of the combustion of the organic components of the added raw- and burn materials as well as their transport through the system.

a: Suspension method

Sample		TOC (mass %)	Injections (n)	RSD (%)
Raw meal	Suspension 1	0.157	4	0.6
	Suspension 2	0.151	4	1.7
Cement kiln dust	Suspension 1	0.204	4	1.0
	Suspension 2	0.203	4	1.1

b: Solid sample method

Sample	TOC (mass %)	Measurements (n)
Raw meal	0.155 ± 0.009	2
Cement kiln dust	0.210 ± 0.006	2

Table 1: TOC* in raw meal and cement kiln dust (*measured as NPOC)

TOC analysis

For adequate TOC measurements of the relevant materials used during cement manufacture, the quantitative separation of the

Figure 2: Sample preparation procedure

a: Suspension method

Sample		TOC (mass %)	Injections (n)	RSD (%)
Portland cement	Suspension 1	0.054	4	5.6
	Suspension 2	0.043	4	5.8
Limestone	Suspension 1	0.038	4	2.9
	Suspension 2	0.041	4	8.7

b: Solid sample method

Sample	TOC (mass %)	Measurements (n)
Portland cement	0.031 ± 0.001	2
Limestone	0.054 ± 0.002	2

Table 2: TOC* in Portland cement and limestone (*measured as NPOC)

Sample	TOC (mass %) (Suspension)	RSD (%) (Suspension)	TOC mass (%) (Comparison value from solid method)
Oil shale	7.95	3.2	8.42
Dry sludge	24.5	2.6	26.4
Fly ash	5.22	2.4	2.98
Paper scavengers	17.4	2.8	16.8

Table 3: TOC* in secondary fuels (*measured as NPOC)

inorganic carbon from the organic carbon compounds is an essential requirement. Limestone consists of more than 90 %, and raw meal of approximately 75 % of calcium carbonate. This requires a special sample preparation procedure, especially when taking into account the commonly low TOC content in the parts per thousand range and even lower.

Consequently, the TOC (**T**otal **O**rganic **C**arbon) can only be determined via the NPOC (**N**on **P**urgeable **O**rganic **C**arbon) method or using a comparative solid sample preparation procedure. The IC (**I**norganic **C**arbon) compounds can be quantitatively removed using acid. Volatile organic components can, in this case, be neglected. The following simplification can therefore be used: NPOC = TOC.

The very fine pulverised and homogenised material is subjected to a complex and time-consuming procedure for the solid sample addition method according to DIN EN 13639. The sample is first suspended, acidified, heated and dried. If necessary, an additional homogenisation step is needed before the TOC measurement of the resulting solid can be carried out via catalytic combustion.

The application of the 'suspension method' offers an alternative, highly effective sample preparation procedure with a significantly lower complexity.

The set-up shown in Figure 2 symbolises the total sample

The TOC analyser TOC-V_{CPN} with ASI-V autosampler

preparation procedure for raw meal. The homogenised sample is suspended under stirring with a suitable concentrated hydrochloric acid solution. The sample material can be weighed directly into the autosampler vial. Subsequently, the TOC value (or NPOC) of the suspension is carried out and calculated with respect to the solid sample according to DIN EN 1484.

The TOC measurements of the suspensions were carried out using a Shimadzu TOC-V_{CPN} system (principle: catalytic combustion) including an ASI-V autosampler. Due to an optimised sample dispensing technique using the ISP module (**I**ntegrated **S**ample **P**retreatment) the suspensions can be ideally quantified using this instrument.

For the production of clinker, the TOC values for the raw meal and cement kiln dust materials are especially significant. The raw meal is a natural TOC source into the rotary kiln. The TOC in cement kiln dust is a function of the production process, which is influenced by the primary and secondary fuels. The results for raw meal and cement kiln dust are summarised in table 1.

In the end product, Portland cement, the TOC value is very low. However, the TOC determination can be useful when for instance concrete building materials come into contact with drinking water. As expected, TOC values were very low here. The TOC values for limestone raw material are also very low. Table 2 shows the results of these two materials.

The relative inaccuracy at low TOC concentrations can be attributed to the typical inhomogeneity of this sample material. Measurements from a sample series show comparably small deviations (see table 2 a).

The suspension method can also be used, in part, for the secondary fuels. Table 3 presents the comparative measurements of a few materials. Dry sludge and oil shale, however, are not relevant for the Rohrdorf plant.

The results above, as well as the corresponding RSD values, are mean values from four separately prepared suspensions. A maximum of five injections were evaluated for each suspension.

For fly ash only, there is a significantly large difference between the individual analysis methods. This fact has not yet been explained and further research and analyses are necessary.

Conclusions

TOC analysis in cement manufacture provides a good indication that the majority of the solid materials under investigation can be substituted by suspensions. The likelihood is high that this finding can be extended to additional TOC applications for solid materials. This will result in a significantly less complex sample preparation process, which goes hand in hand with a high degree of automation during the analytical procedure.

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