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NEWSLETTER

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CO₂ Capture and Storage – A future option for the cement industry?

High costs and low societal acceptance are important impediments for implementation

The production of cement clinker is an important source of CO₂ emissions worldwide. For decades - and still today - the main objectives of the cement industry to reduce its CO₂ emission were the optimization of the energy efficiency of its production facilities, the increased use of waste fuels and the production of cement with a lower clinker content. Nowadays, CO₂ capture technologies are discussed for the energy sector being the biggest and most important CO₂ source worldwide. From a technical point of view these technologies could also be used for the cement industry. But today there are a lot of unsolved technical questions and the costs are significantly too high. Last but not least, the question whether long term CO₂ storage is acceptable to the societies has to be discussed and solved.

Whereas storage technologies are the same for all industry sectors, CO_2 capture technologies must be adapted to the different industrial processes and to the process gas conditions. For example the CO_2 concentration in the waste gas of a cement kiln is higher compared to the one in power plants. Therefore certain technologies could work with a higher efficiency in cement kiln plants compared to power plants.

Pre-combustion technologies

CO, capture technologies can be divided into so-called pre-combustion and post-combustion technologies. Pre-combustion means that the fuel used will be pretreated or the process itself will be adapted in a way that the process gas either is CO₂-free or very CO₂-rich. The pre-combustion technology which is mostly discussed for power plants today is the oxyfuel technique. In this process the combustion air will be enriched with oxygen or pure oxygen will be used for the oxidation of the fuel. The objective of this technology is to produce a process gas which is very high in CO, and which then can be cleaned by a post-combustion technology. As the process temperatures would increase significantly, waste gas of the kiln has to be recycled to the kiln firing.

The oxyfuel technology is already used in certain industrial sectors like the glass industry. Therefore pure oxygen has to be produced for example by air-fractionation which is one important reason for the high costs. A theoretical and simplified process scheme for the use of the oxyfuel technology in the clinker burning process is shown in **Fig. 1**. The kiln plant itself would have to be adapted to this process because the kiln atmosphere and the temperature profile in the kiln will be changed significantly.

Another option is the production of a carbon-free fuel like hydrogen by a conventional reforming process. This means that fuel like natural gas or coal is treated and partially oxydized in a thermal process. The product gas of this process has then to be separated into hydrogen and CO/CO₂. The hydrogen can be used in any thermal process like the clinker burning process.

But again, the clinker burning process has to be adapted to this fuel. Being highly explosive, hydrogen cannot be used in a pure form as a fuel for clinker burning. But in principle this problem could be solved by waste gas recirculation and mixing with the hydrogen. Nevertheless a number of unsolved questions remain concerning the use of hydrogen for clinker burning.

Post-combustion technologies

Post-combustion technologies mean the capture of CO_2 from the process waste gas by different physical or chemical mechanisms. Some of the technologies discussed are already used today for example in the chemical industry but no experiences are available for the huge gas volumes from a power plant or even a cement kiln.

Chemical absorption in liquid solvents is an industrially proven technique by which high pureness of the product gas CO_2 can be achieved. But regeneration and degradation of the solvent lead to very high costs. Another option is the physical adsorbtion of CO_2 with porous materials like ceolites or activated carbon. While regeneration costs are lower, very large quantities of these materials are required. Other materials or techniques like the use of gas separation membranes are far from commercialization.

Energy penalty

All technologies discussed today need significantly more energy. Air fractionation for oxyfuel technique or the regeneration of absorbent or



Fig. 1: Use of the oxyfuel technology in a cement kiln plant

adsorbent materials require a high energy consumption. Therefore an important aspect of research is to develop and to determine the so-called energy penalties of the technologies discussed. Therefore an important aspect of CCS technologies is the fact that the energy resources worldwide will be exhausted significantly earlier when CCS is used in a huge scale. Concerning coal fire power plants for example an energy penalty of 30 to 40 % is discussed for the implementation of the oxyfuel technology combined with a post-combustion CO, capture.

Transport and storage

The implementation of CO₂ capture technologies for the cement industry provides for the existence of transport systems like pipelines to the storage areas. Such a system will only make sense if common systems are used for the relevant industry sectors. The storage of CO, is discussed in exploited oil or gas fields for example in the North Sea or on-shore in porous mineral materials underground. Important technical, political and societal questions have to be solved before CO₂ storage can be implemented. The main technical question is for which period of time the storage can be guaranteed. An important political question is who

will be responsible for the future storage areas and for the risk assessment. For the whole society mainly the acceptability of such techniques will be decisive (**Fig. 2**).

Finally the question whether CO₂ capture and storage will become an option for the cement industry depends on several political and technological uncertainties. In the short term the relevance for the cement industry sector is very low due to the extremely high costs, non-existant technical availability and other favorable abatement options. In the medium or long term it may become

an option when other technical options are exhausted, worldwide comparable CO_2 additional costs for cement and construction material production are introduced, notably less clinker is produced in large to very large plants and if CCS potentials in the energy sector are largely exhausted.

Anyway, significantly more research and development into CO_2 capture and storage technologies is required. Today major research projects are aiming exclusively at the energy sector.



Fig. 2: Criteria for the application of CCS

Latest Developments in Clinker Cooling Technology

Modern coolers provide for energy savings, cost reduction and product quality maintenance

Recuperation of heat from the burnt cement clinker has a decisive influence on the total energy consumption of the clinker burning process. The progress in clinker cooling technology in the last years has led to a substantial improvement in the thermal efficiency and availability of the kiln plants. The composition and properties of the clinker are crucially affected by cooling conditions.

The most important criteria in evaluating clinker coolers are their availability and their degree of recuperation, both of which have a crucial effect on the economic efficiency of kiln operation. In the last years, the clinker coolers in many European cement works were replaced in the wake of modernisation and new construction measures.

Operating experience with clinker coolers

Regardless of cooler type and manufacturer, initial problems in cooler operation regarding the refractory lining in the area of the secondary and tertiary air outlet, the service life of the grate plates, clinker and air distribution and too high temperatures of the cooled clinker occurred in some cases.

The cooler-specific and constructive modifications carried out in the meantime have made it possible to remedy most of the above problems. As a consequence, current experience with clinker coolers and their availability is thoroughly favourable. Depending on the respective problem, some of the following measures have been implemented to increase the availability of existing clinker coolers, to facilitate their control and to set optimum clinker cooling conditions:

1. The service life of the grate plates was markedly increased by installing high quality plates.

2. Owing to high wear and tear, dynamic pre-grates were replaced by static ones.

3. Clinker distribution was homogenised by constructive changes (e.g. bottlenecking of the cooler inlet), by changes in air distribution and by individual adjustment of the specific air requirement (between 1.5 and 1.9 m³/kg clinker).

4. Ventilation of the first two grates was partially shifted from direct ventilation to chamber ventilation.

5. Installation of a slide in the tertiary air duct proved to be effective for better regulation of the tertiary air volume flow. In this way, damage to the refractory lining in the area of the tertiary air outlet was reduced substantially.

6. The clinker particle size that is optimal for clinker distribution should be controlled via adjustment of the kiln feed composition.

7. Furthermore, hot spots should be prevented as far as possible by the mode of kiln operation and bypass operation.

8. Insertion of stopper elements in the clinker cooler to prevent "red rivers" turned out to be another adequate measure.

Effects on product properties

Exceeding the before mentioned process operational aspects of clinker coolers, also the cooling rate is known to impact the clinker reactivity extensively. Accordingly, the resulting cementitious product properties depend to a high degree on the cooling conditions. During the cooling process, the aluminous and ferrous phases start crystallising from the partial melt between the solid silicate phases. At the same time an exchange of ions between the liquid and the solid phases takes place. As an example, the formation of C₃A is connected with a demand of excess calcium, which is supplied by the adjacent alite crystals. This resorption leads to the formation of secondary belites covering the alite surfaces (Fig. 1). If the cooling rate is low, the secondary belites start to recrystallise.

On the other hand, the oxides of aluminium and iron can migrate from the interstitial phases into the silicates. The degree of mass transport is enhanced by a slow cooling rate as well as by a high alumina ratio or a high C_3A content, respectively. As a result, the progressive uptake of Al and Fe by the alite can lead to a decrease of its reactivity and furthermore to a loss in cement compressive strength. Thus, a rapid cooling process is advantageous, particularly for clinkers with a high C_3A content.

Furthermore, the setting behaviour of cement can be affected by the cooling conditions. C_3A is known



Inside view of a clinker cooler



Fig. 1: Formation of clinker phases during cooling process

to be the dominating clinker phase regarding the initial hydration reactions. As a rule, the C_3A reactivity rises with decreasing cooling rate. The setting behaviour of cement can be adjusted by optimising the dosage of calcium sulphates, as the solubility of hemihydrate, formed by partial dehydration of gypsum during cement grinding, is higher than the solubility of anhydrite. This means that the increased need of available sulphate caused by slow clinker cooling can be met, if a gypsum-rich sulphate mix is added during cement grinding.

Cooler-Seminar in December

The seminar on December 6th and 7th this year will give an overview of modern clinker cooling systems. Also operation experiences with the latest developments will be presented. Finally the participants will have the opportunity to visit the Siggenthal cement plant.



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