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A Driver for Environmental Performance in Industry”
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BAT process selection and split views

illustrated by examples from the
Cement and Lime and Chlor-Alkali BREFs

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1 BAT process selection

The Best Available Techniques Reference (BREF) documents are meant to be tools to drive environmental performance. Bearing this in mind the BREFs select BAT processes for the sectors when it is appropriate, instead of presenting BAT performance levels associated with each existing process technology. To change process technology is in many cases a very costly operation and not something you do every year or even every decade.

Within the Technical Working Groups (TWGs) this issue has been discussed at length. A commonly expressed view is:

- „We have to differ between new and existing plants, it is not possible for all existing installations to change process/implement BAT before 2007.“
- (2007 is when the IPPC Directive must be applied to existing plants)

Therefore, before I go to the examples of BAT process selection in the Cement and Lime and the Chlor-Alkali BREFs, I would like to take the opportunity to repeat some basic points, that have been repeated many times during the BREF work but, nevertheless, are worth repeating again.

- Implementing the IPPC Directive does not mean that every existing plant has to implement BAT before 2007.

To implement the IPPC Directive simply means that all installations should have a permit issued in accordance with the IPPC Directive by 2007.

- The BREF provides a general BAT on the sector level.

Which means that the presented BAT is considered to be appropriate for the sector as a whole, but not necessarily appropriate, nor even technically possible for immediate implementation at all individual sites.

- The IPPC Directive does not set a time limit for when BAT should be implemented at the individual plant.

Some BATs are easy to implement in the short term perspective, others, such as change of process, have to be considered in the long term investment planning. It is considered that existing installations could be expected, over time, to move towards the general BAT levels.

1.1 BAT process selection – Cement manufacturing

In the manufacture of cement there are alternative technologies for converting the raw materials into product cement clinker. The selected process has a major impact on the energy use and air emissions. The BAT conclusion regarding process technology is:

The first rotary kilns were long wet kilns where the whole heat consuming thermal process takes place in the kiln itself. Grate preheater technology, perhaps better known as the Lepol kiln, represented the first approach to letting part of the clinkering process take place in a stationary installation outside the kiln. This allowed the rotary kiln to become shorter and so reduced the heat losses and increased energy efficiency. The development towards more and more energy efficient kiln systems then continued with the suspension preheater technology, multi-stage cyclone preheaters and precalciners. With the precalcination technique the heat input is divided between two points. Up to 60% of the total fuel can be burnt in a special combustion chamber between the rotary kiln and the preheater, the raw meal is almost completely calcined when it enters the kiln and only the clinker forming stage takes place in the high temperature zone of the rotary kiln.

The theoretical energy use for the burning process (chemical reactions) is about 1700 to 1800 MJ/tonne clinker. The actual fuel energy use for different kiln systems is in the following ranges (MJ/tonne clinker):

- about 3000 for dry process, multi-stage cyclone preheater and precalciner kilns,
- 3100 – 4200 for dry process kilns equipped with cyclone preheaters, and
- 3300 – 4500 for semi-dry/semi-wet processes (Lepol-kilns),
- up to 5000 for dry process long kilns,
- 5000 – 6000 for wet process long kilns.

At present, about 78% of Europe's cement production is from dry process kilns, a further 16% of production is accounted for by semi-dry and semi-wet process kilns, with the remainder of European production, about 6%, coming from wet process kilns. The wet process kilns operating in Europe are generally expected to be converted to dry process kiln systems when renewed, as are semi-dry and semi-wet processes kiln systems. Plants using wet or semi-wet processes normally only have access to moist raw materials but the industry has moved towards the dry process preferentially even for these cases.

The shorter kilns and the precalciner technique enables less fuel to be burnt in the hot zone of the kiln which also results in lower emissions of nitrogen oxides (NO_x). The suspension preheater technology also facilitates the installation of Selective non-catalytic reduction (SNCR) for the further reduction of NO_x emissions.

In the cement sector it has thus been a development over time towards more energy efficient kiln systems with lower emissions to air, where the latest development is considered to be BAT.

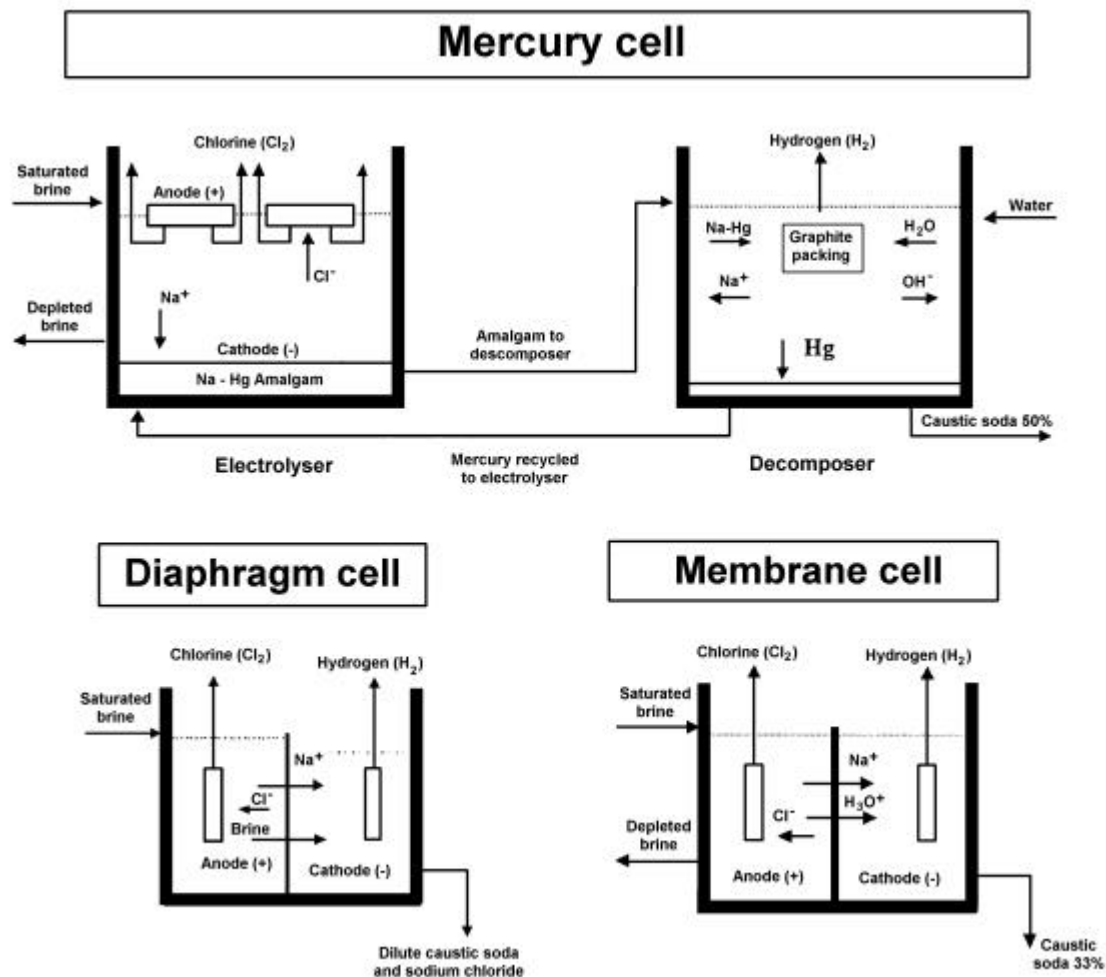
1.2 BAT process selection – Chlor-Alkali manufacturing

Again, in the case of the chlor-alkali process there are true alternative technologies for the electrolysis of salt solution to produce sodium (or potassium) hydroxide and chlorine. The selected process technology has a major impact on the energy use and emissions from the manufacture of chlor-alkali. The draft BAT conclusion regarding process technology is:

- Best available techniques for the production of chlor-alkali is considered to be membrane technology. Non-asbestos diaphragm technology can also be considered as BAT when there is a need for weak caustic. The total energy use associated with BAT for producing chlorine gas and 50% caustic soda is less than 3000 kWh (AC) per tonne of chlorine, liquefaction excluded.

There are three basic process technologies for the electrolytic production of chlorine and caustic solution (NaOH or KOH). These three processes are the diaphragm cell process, the mercury cell process, and the membrane cell process. Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode. Figure 3 shows a simplified scheme of chlorine electrolysis cells.

Figure 3: Simplified scheme of chlorine electrolysis cells



The diaphragm and mercury cell technologies were both developed in the late 1800s whereas the membrane cell technology was first used in industrial production in the 1970s.

The diaphragm in the diaphragm cell process is usually made of asbestos. The cathode in the mercury cell process is liquid mercury. Both asbestos and mercury are substances that have been declared unwanted in the technosphere by society at large. They are both high priorities on a number of environmental and health hazard action lists world wide.

Diaphragm cells produce a 12% caustic solution with impurity levels that make it unsuitable for some applications. Mercury cells produce 50% caustic solution with low salt levels but contaminated with mercury.

Membrane cell technology does not have the disadvantage of using hazardous substances in the production process and it produces 33% caustic solution with low salt levels (<50 ppm NaCl). Membrane cells require higher brine purity than diaphragm and mercury cells as impurities affect the membrane performance.

The membrane cell process is more energy efficient than diaphragm and mercury cell processes, also when steam requirements for concentration of caustic (if higher concentration than 33% is required) and brine purification are included.

Membrane cell technology thus produces high quality caustic, pollutes less and uses less energy than diaphragm or mercury cell processes. All things considered, the conclusion that membrane cell technology is BAT in the chlor-alkali sector can not come as a surprise to anyone.

2 Split views

In the cement and lime BREF work the TWG had to agree to disagree about the BAT emission level for NO_x from cement kilns. Although everyone agreed that the technical information on NO_x abatement techniques is correct, the evaluation of the information differed and, despite long discussions, we had a split view.

2.1 BAT conclusion regarding NO_x abatement for cement kilns

Best available techniques for reducing NO_x emissions are primary measures combined with staged combustion or selective non-catalytic reduction (SNCR). Therefore, based on the combination of these techniques and the performance of each component of the combination, the emission level associated with the use of BAT is 200-500 mg NO_x/m³ (as NO₂, expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas).

Whilst there was support for the above concluded BAT to control NO_x emissions, there was an opposing view within the TWG that the BAT emission level associated

with the use of these techniques is 500-800 mg NO_x/m³ (as NO₂). There was also a view that selective catalytic reduction (SCR) is BAT with an associated emission level of 100-200 mg NO_x/m³ (as NO₂).

2.2 Techniques for controlling NO_x emissions

The current reported NO_x emission range in the cement industry is from less than 200 up to 3000 mg NO_x/m³. Techniques for controlling NO_x emissions that are discussed in the BREF are primary measures, staged combustion, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR).

2.2.1 Primary measures and staged combustion

Some modern well-optimised suspension preheater kiln systems and suspension preheater/precalciner kiln systems are achieving NO_x emission levels of less than 500 mg/m³ with either primary measures only or combined with staged combustion. Raw material quality and kiln system design may be reasons for not achieving this emission level. On a sector level the majority of kilns in the European Union is said to be able to achieve less than 1200 mg/m³ with primary measures.

2.2.2 Selective non-catalytic reduction (SNCR)

With SNCR the achieved NO_x emission levels in the best cases are less than 200 mg/m³ with initial levels between 750-1350 mg/m³ (80-85% reduction) without significant NH₃ slip, although the majority of SNCR installations are today operated to achieve an emission level of 500-800 mg/m³ (10-50% reduction).

The TWG experts agree that a reduction with SNCR of 60-65% is achievable without significant NH₃ slippage problems. On a sector level the majority of kilns in the European Union is said to be able to achieve less than 1200 mg/m³ with primary measures. By applying SNCR at moderate reduction efficiencies of about 60% this could reduce the NO_x emission level to less than 500 mg/m³.

To fit SNCR, an appropriate temperature window has to be accessible. The right temperature window is easy to obtain in suspension preheater kiln systems, in suspension preheater/precalciner kiln systems and possibly in some Lepol kiln systems. At the moment no full scale installation of SNCR in Lepol kilns exists, but promising results from pilot plants have been reported. In long wet and dry process kilns it might be very difficult, or impossible, to obtain the right temperature and retention time needed. At present, about 78% of Europe's cement production is from dry process kilns and an overwhelming majority of these kilns are suspension preheater kiln systems or suspension preheater/precalciner kiln systems.

2.2.3 Selective catalytic reduction (SCR)

Large NO_x emission reductions are potentially achievable by SCR high dust systems (85-95%). Pilot plant trials on small portions (3%) of the exhaust gas in Austria,

Germany, Italy and Sweden have shown promising results. The NO_x emission levels were approximately 100-200 mg/m³ with no loss of catalyst activity, except for one recent trial in Austria that has reported considerable abrasion of the catalyst after a working period of about 5000 hours which shortened the lifetime of this type of catalyst to less than one year. Full-scale production runs will have to be carried out in order to remove the technical and economic uncertainties related to upscaling of the SCR technique. The main uncertainties are related to the high dust concentration in the gases (up to 500 g/Nm³), the catalyst dust removal techniques, lifetime of catalysts and total investment costs.

Up to now SCR is only tested on preheater and semi-dry (Lepol) kiln systems, but it might be applicable to other kiln systems as well.

As the catalysts remove hydrocarbons as well, SCR will in general also reduce volatile organic compounds (VOCs) and polychlorinated dibenzodioxins and furans (PCDD/Fs). According to one supplier, new pilot projects for NO_x reduction are being developed in which specific catalysts are applied for the additional reduction of VOCs and carbon monoxide (CO).

Considering the high reduction potential, the successful pilot tests and the fact that SCR is state-of-the-art technology for comparable installations; SCR is an interesting technique for the cement industry. There are at least three suppliers in Europe that offers full scale SCR to the cement industry with performance levels of 100-200 mg/m³. However, results from the first full scale SCR installation in the cement industry is not yet available.

3 References

- [1] European Commission, Joint Research Centre, IPTS, European IPPC Bureau. Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries, March 2000.
- [2] European Commission, Joint Research Centre, IPTS, European IPPC Bureau. Draft Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry, Draft dated January 2000.

The BREF documents are available in pdf-format on the European IPPC Bureau (EIPPCB) web site at <http://eippcb.jrc.es> (Activities – select TWG (industry sector) – Documents and reports).

Figure 1 and 2 are from a presentation by M. Schneider, G. Hirth and P. Magel (VDZ, Germany) copied from the Proceedings of the International Workshop on Economic Aspects of BAT held in Brussels 10-11 February 2000.

Figure 3 is from the draft chlor-alkali BREF dated January 2000.

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BAT process selection - Chlor-Alkali

Three basic process technologies for the electrolytic production of chlorine and caustic solution:

- **the diaphragm cell**
- **the mercury cell**
- **the membrane cell**

BAT process selection - Chlor-Alkali

The diaphragm and mercury cell processes were both developed in the late 1800s

- Diaphragm cells ® Asbestos**
- Mercury cells ® Mercury**

Both asbestos and mercury are high priorities on a number of environmental and health hazard action lists world wide

BAT process selection - Chlor-Alkali

The membrane cell technology was first used in industrial production in the 1970s

Membrane cells:

- are more energy efficient than diaphragm or mercury cell technologies**
- produce high quality products**
- do not use hazardous substances in the production process**

BAT process selection - Chlor-Alkali

Best available technique for the production of chlor-alkali is considered to be membrane technology. Non-asbestos diaphragm technology can also be considered as BAT.

BAT process selection - Cement

The clinker burning is the most important part of the process in terms of the key environmental issues:

- energy use, and
- emissions to air of nitrogen oxides (NO_x), sulphur dioxide (SO_x) and dust

BAT process selection - Cement

ENERGY USE
MJ / tonne clinker

wet or dry long kiln system

up to 6000

semi-wet or semi-dry grate
preheater (Lepol) kiln system

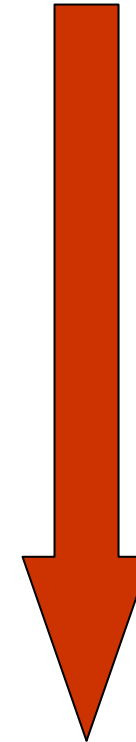
3300-4500

dry cyclone preheater kiln
system

3100-4200

dry cyclone preheater and
precalciner kiln system

about 3000



BAT process selection - Cement

- The shorter kilns and the precalciner technique enables less fuel to be burnt in the hot zone of the kiln which also results in lower emissions of nitrogen oxides (NO_x)
- The suspension preheater technology also facilitates the installation of selective non-catalytic reduction (SNCR) for further reduction of NO_x emissions

BAT process selection - Cement

® Development over time towards more energy efficient kiln systems with lower emissions to air

Best available technique for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination. The associated BAT heat balance value is 3000 MJ/tonne clinker

Split view

Split view in the cement and lime TWG about the BAT emission level for nitrogen oxides (NO_x) from cement kilns

Even though there was agreement on the technical information given in the BREF about NO_x abatement techniques

Split view

The TWG agreed that:

- **a few kilns are achieving less than 500 mg NO_x/m³ with primary measures only or combined with staged combustion**
- **the majority of kilns in the EU can achieve less than 1200 mg NO_x/m³ with primary measures**

Split view

- selective non-catalytic reduction (SNCR) could be applied at 60-65% reduction efficiency without significant problems
- 60% reduction of 1200 is 480 mg NO_x/m³
- the best performing plants are applying SNCR at 80-85% reduction to achieve less than 200 mg NO_x/m³

Split view

Best available techniques for reducing NO_x emissions are primary measures combined with staged combustion or selective non-catalytic reduction (SNCR).

The emission level associated with the use of BAT is 200-500 mg NO_x/m³.

Split view

Whilst there was support for the above concluded BAT to control NO_x emissions, there was an opposing view within the TWG that the BAT emission level associated with the use of these techniques is 500-800 mg NO_x/m³.

Split view

There was also a view that selective catalytic reduction (SCR) is BAT with an associated emission level of 100-200 mg NO_x/m³.

Split view

Conclusion:

The split view is not because of technical disagreements but rather of different interpretations of ‘available’