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Information on SO_2 emissions and control technologies for Hope Cement Works. An initial Desktop study by CPI

Introduction

HCM are considering the impact of the recent (2013) BREF requirements upon the future operations of Hope Cement works. A major area of concern is the environmental and financial impact of complying with lower SO_2 emissions in the future including additional capital expenditure, additional electric power and maintenance operating costs, and the occurrence of a visible plume.

CPI were approached to provide HCM with an independent, professional opinion on the practicalities of implementing the options for SO2 emission control, as described in the BAT reference document for cement. This desktop study was prepared following relevant data collection and discussions between HCM and CPI personnel to exchange views on the potential impact of installing SO_2 reduction technology to both kiln systems with particular reference to operating costs, capital costs and SO_2 reduction efficiency.

The main objective of this study has been to provide HCM with a high level overview of the feasible options and associated costs of achieving SO_2 emission limits below 400 mg/Nm^3 dry gas @ 10% oxygen content before the 2017 deadline. The advantages and disadvantages of using either wet scrubbing (WS) or absorbent injection (AI) have been examined.

BREF 2013 requirements

Before examining the specific requirements for Hope Works, it is necessary to consider what the BREF document entitled "Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide" concludes as the BAT for SO_2 control.

Source from web:
http://eippcb.jrc.ec.europa.eu/reference/BREF/CLM_Published_def.pdf

It should be noted that BREF 2013 includes some capital and operating cost data. However, there is no reference to plant size and all capital/operating costs would need to be adjusted to suit the following conditions:-

- Plant size and number of units.
- Hope Works would require two separate SO_2 abatement systems for either Wet Scrubbing (WS) or Absorbent Injection (AI). Each unit would need to be sized for a capacity of 2,170 tpd clinker i.e. the present peak daily clinker output from each kiln system.
- The BREF cost comparison example is based upon 1,100 tpd clinker and so these costs are too low.
- Inflation to reflect current mid-2014 costs.

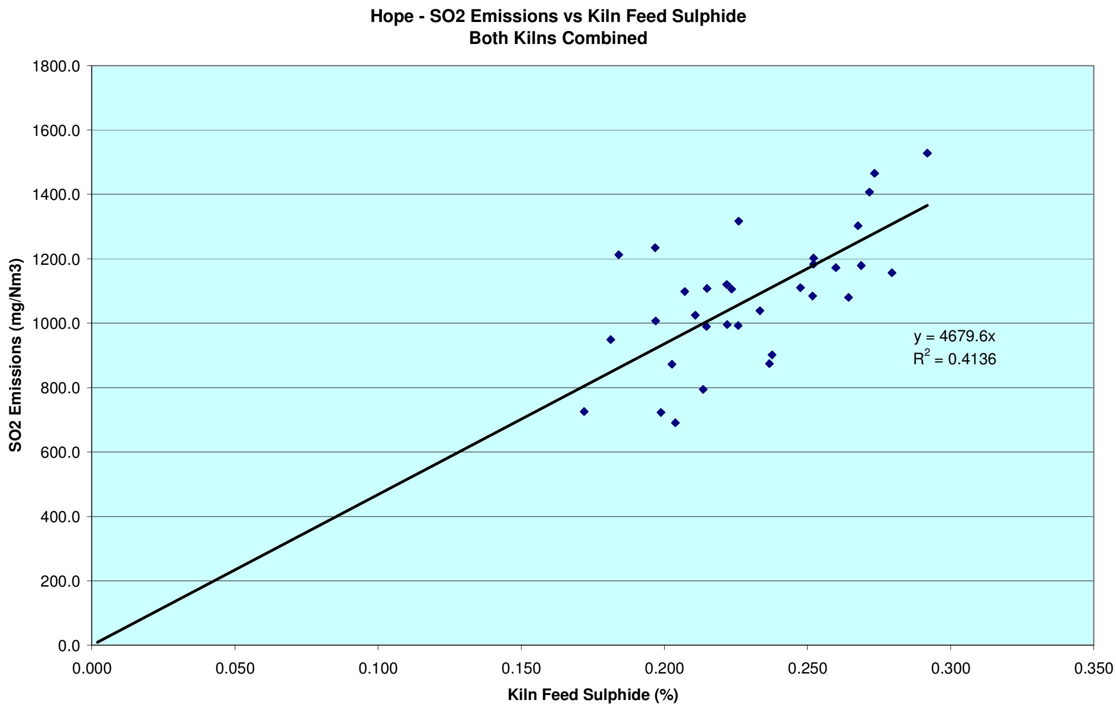
- Construction cost factors within UK.
- The most relevant information for the wet scrubber technology applications within the UK cement industry are the Ribblesdale and Dunbar works installations and further plant information is included below.
- The problem with using these published capital costs is that they are variable and it is not always clear what plant has been or has not been included in the capex figure. For example, the Dunbar reported capital cost is significantly higher than the equivalent Ribblesdale cost (i.e. after correction for plant size and inflation). Possible reasons for this discrepancy are discussed below.

Before considering these costs, the historical data for Hope Works SO_2 emissions should be considered.

Hope Works – SO_2 emissions and influencing factors

The following data was obtained from the Hope Works application under WID during 2005. Reference -Form IPPC/WID Part A(1) – WID/PPC variation existing co-incinerators.

The relationship between kiln feed sulphide and the stack SO_2 emissions was determined as follows:



CPI Comments – the graph above demonstrates that there is a clear relationship between the kiln feed sulphide content and the stack SO_2 emissions. Typically an increase of 0.1% kiln feed sulphide would be expected to increase the stack SO_2 by approximately 468 mg/Nm^3.

The preheater gas sampling exercise carried out by Casella CRE indicated that the SO_2 derived from the pyritic sulphur in the raw materials was generated in the upper stages of the preheater.

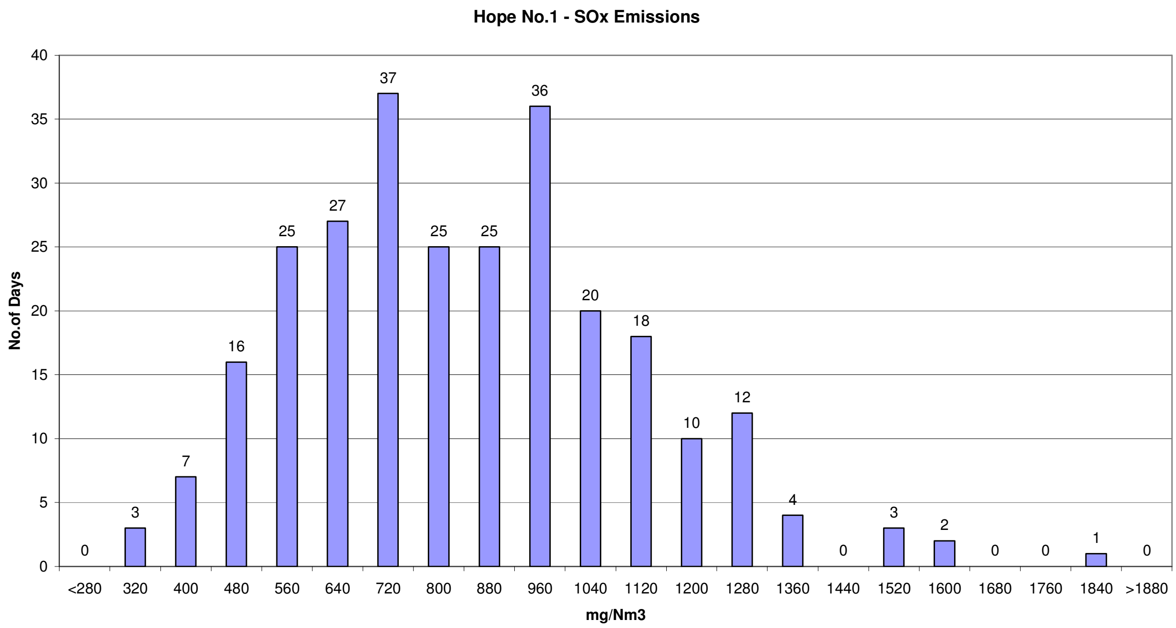
Sampling Point	Concentration $mgSO_2/m^3$, STP, dry, 10% O_2								
	Determination 1			Determination 2			Mean		
Kiln outlet (1)	<5	±	5	-	±	-	<5	±	5
Pre-heater Stage 4 inlet (2)	<5	±	5	<5	±	5	<5	±	5
Pre-heater Stage 3 inlet (3)	<5	±	5	<5	±	5	<5	±	5
Pre-heater Stage 2 inlet (4)	421	±	109	-	±	-	421	±	109
Pre-heater Stage 1 inlet (5)	473	±	123	-	±	-	473	±	123
Pre-heater Stage 1 outlet (6)	648	±	168	-	±	-	648	±	168
Kiln stack inlet (7)	542	±	136	559	±	137	551	±	138

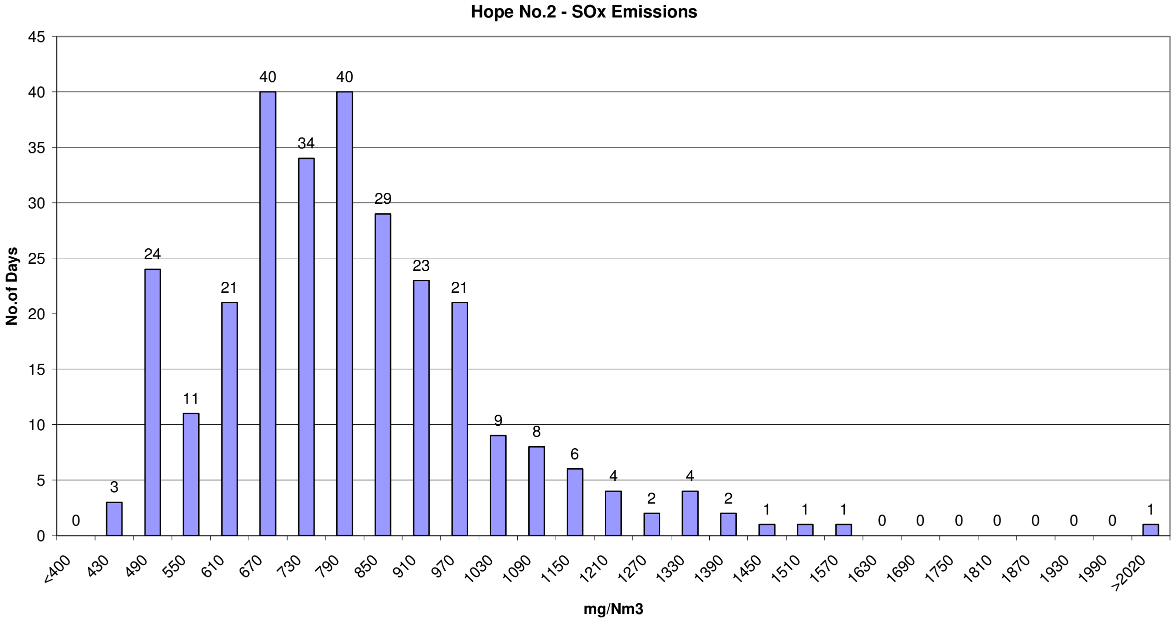
SO_2 from fuels burned in the process tend to be retained in the clinker and hence, do not tend to contribute to the stack exit SO_2.

The above relationships have been found with other UK cement kilns although the relationship differs from plant to plant. It is expected that the raw milling circuit will tend to absorb typically 50% to 55% of the SO_2 generated during normal operation.

SO_2 emission reduction measures

- A key issue to reduce the overall plant SO_2 emissions is to maximise the raw mill run time to match the kiln run time and thereby reduce the higher emissions levels experienced during "Direct" operation.
- Eliminating periods of "peak" SO_2 emissions –the concern with the data above is the wide range of SO_2 emissions for the reported kiln feed sulphide level. The degree to which these peaks may be reduced by tighter control over the raw mix composition is an issue which only HCM can assess.
- The frequency distribution data for both Kilns shown in the WID application shows the following relationship.





- Control techniques – the main control techniques considered within BREF 2013 tend to be based upon Wet Scrubber and Absorbent Injection techniques.
- Activated Charcoal is reviewed in BREF but has very limited application (ref Siggenthal, Switzerland) and so cannot be considered as an industry wide BAT option. The Polysius "Polvitec" system for SO_2 reduction is understood to require higher capital costs than wet scrubbing although this system can also help to reduce NOx and HM levels.
- Similarly, systems such as the Lurgi CFB (Circulating Fluidised Bed) system used at Untervac Works have not been universally applied to the cement industry as capital costs are higher than Wet Scrubber/Absorbent Injection systems.
- A variation of lime injection to the preheater process is the DeSOx system used at two FLS plants in USA. In this process some of the gases are ducted from the calciner to the upper stage of the preheater to allow some lime rich raw meal to react in the upper cyclone stages. This method can reduce SO_2 emissions but has a fuel consumption penalty and is only really suitable for a precalciner process where the raw meal has around 92% decarbonation level. The dust in the gases leaving the Hope Kiln enlarged riser ducts has a lower decarbonation level (the quoted figure for Hope kilns is around 60% decarbonation).
- The Cement kiln flue-gas treatment with dry sodium bicarbonate and chemical re-use method is mentioned in BREF 2013 but is also not a common proven method.
- Hence the Wet Scrubber and Absorbent Injection methods are considered as the two most viable options under BREF guidelines. See Section 1.4.5.2 of the document for further details.
- Before comparing capital and operating costs for both these systems, it is worthwhile considering the advantages and disadvantages of both these systems.

Advantages and Disadvantages of Wet Scrubbing and Absorbent Injection systems for SO_2 control and potential impacts upon existing plant operations

- To simplify this comparison, from this point forward in this file note, the abbreviation AI refers to Absorbent Injection and WS refers to Wet Scrubbing technology for SO_2 control.
- These notes are intended to be read in conjunction with the BREF 2013 notes contained in Appendix 1.
- The BREF assessment is considered to be reasonable although some of the capital and operating costs may be misleading. Hence **CPI** has added some additional comments upon these parameters within these notes.
- Capital costs – AI systems can be significantly cheaper to install than WS systems. The BREF comparison for a 1,100 tpd clinker line quotes a Euro 200,000 for AI and Euro 5,500,000 for WS. These figures are questioned as the WS cost appears too low when scaled up for quoted installed equipment costs for the reference plants. See estimates shown below.
- SO_2 removal efficiency – The BREF example in Section 1.4.8.3 quotes efficiencies of AI = 60% and WS = 75%. However, from earlier studies and literature reviews, the WS efficiency has been claimed to be around 90% for the Ribblesdale and Slite Work's units. Similarly, figures of 50% to 80% efficiency have been claimed for some AI systems with lime injection rates above the stoichiometric rate.
- It is difficult to accurately quantify and directly compare different SO_2 abatement systems in terms of efficiency values alone due to the following reason;
    - The removal efficiency of any SO_2 scrubbing system will depend upon the ratio of the input SO_2 emissions (note this varies with raw mill on/off operating scenarios and typical values may be 2,000 mg/Nm^3 or more) plus the required outlet ELV for SO_2 at the main stack.
- WS process provides a source of synthetic FGD Gypsum replacing imported gypsum. However, the liquid effluent will require treatment before disposal.
- A major concern with respect to the application of WS at Hope Works would be the visible stack plume. This was a factor which was given very careful consideration when the plant was uprated in the late 1990's with the new baghouses and downcomer sonic water sprays.
- Hence an area requiring particular attention will be the stack exit temperature and its impact upon ground level concentrations of the main pollutants plus the potential for plume grounding.
- With WS, the scrubbed gases will require re-heating to provide sufficient buoyancy for the stack. This will involve additional capital expenditure to route the cooler exhaust gases to the WS exhaust gases. The low raw material moisture levels at Hope Works mean that these cooler exhaust gases are not needed for raw material drying. Hence, in theory, there should be no additional fuel penalty for raw material drying.
- **CPI's** understanding is that the cooler exhaust system was not substantially modernised during the late 1990's uprating. The existing ESP units were retained after optimising gas distribution etc.
- If a WS system were to be installed than this cannot be considered in isolation and its impact upon the existing gas circuit design has to be considered.
- Furthermore, whilst the WS process provides a source of FGD gypsum it uses raw meal which has a negative impact upon the plant's raw milling capacity to support the required clinker output.

- From discussions held with HCM, **CPI** understands that HCM has carried out lime injection tests in the raw mill. Whilst this reduced HCL emissions there were concerns that its efficiency would not be sufficiently high to ensure that the new SO_2 limits could be achieved under all operating scenarios. Obviously, any form of SO_2 abatement control must cope with the worst case scenario i.e. highest levels of pyritic sulphur in raw materials, no PFA available etc.
- The main conclusions from BREF are shown in Appendix 1 and BREF considers AI and WS to be suitable technologies. From BREF and other SO_2 reduction studies, a simplified summary of the advantages and disadvantages of AI and WS would be as follows:
    - **Absorbent Injection** – proven technology, simple to install and lower capital cost than Wet Scrubbing systems. Suitable for modest reduction in SO_2 and may not suit cases where a large reduction in SO_2 is required. Efficiency lower than WS although the use of micro-fine lime may warrant further investigation. Operating costs have been quoted as typically 0.1 to 0.4 Euros/tonne clinker using slaked lime injection. However, these costs are irrelevant without any detailed reference to the reduction in SO_2 achieved and a higher reduction ratio obviously increases the lime injection costs.
    - **Wet Scrubber** - this technology has been around for many years and is well established in the power industry etc. Several different WS system designs have been applied to cement kilns and it would be difficult to say which system is the optimum in terms of efficiency, capital and operating costs. The WS system would be considered to be the best option for plants with high SO_2 emissions and this has a penalty in terms of investment costs (see below for estimated capex to suit Hope Works). In the context of Hope Works it would be necessary to use reheating of the stack gasses to increase their buoyancy and aid dispersion. A major concern would be the visible plume. Operating costs are variable and are design dependent –see table and data below.

Before considering the operating and capital costs for a Hope Works wet scrubber system, some background notes on recent WS systems follow.

Dunbar Works –Wet Scrubber installation

The capital cost of this unit has been generally quoted as around £20m. However, a higher figure of £22m was quoted in the Dunbar Works Exhibition article available on the web at:

http://www.lafargeukconsultations.co.uk/downloads/dunbar_exhibition_panels.pdf

The date of installation is quoted as 2007 and it is not clear if the £22m reflects current costs or final costs after completion of the installation plus settlement of any claims, optimisation modifications etc.

The typical SO_2 emissions prior to 2007 were around 1.94 to 2.15 kg SO_2/tonne cement equivalent PCE. Since 2007 the SO_2 emission has reduced to 0.58 kg SO_2/tonne cement equivalent PCE during 2010.

The capital cost appears to be high in comparison with Ribblesdale/Slite but this may be due to the fact that other projects were carried out in conjunction with the wet scrubber project. Without detailed cost breakdown data it is not possible to determine the standalone wet scrubber installed cost.

There is a very visible plume from the stack as shown in the photo available on the Cement Kilns UK website reference:
http://www.cementkilns.co.uk/cement_kiln_dunbar.html

Heidelberg data for Ribblesdale and Slite Wet Scubber Installations

There are several published references to these plants including:

- World Cement August 1999 – Reducing Emissions at Slite.
- The Chemical Engineer 20 November 1997 – Air with Graces. A description of the Ribblesdale process. This reference claimed a reduction from 2,300 to 50 mg/Nm^3 in SO_2 after installing the wet scrubber.
- Heidelberg has published a comparison of Ribblesdale and Slite plants in cement journals but the actual reference is lost. However, data from this article has been used to draw up the table below using various sources and both plants were visited by **CPI** personnel during the late 1990's.

A direct comparison is shown below:

Heidelberg SO_2 Scrubber Comparison using Limestone/Raw Meal slurry as a reagent-producing gypsum			
		Plant	
	Units	Ribblesdale	Slite
Make of Scrubber		MONSANTO DYNAWAVE	SMS/LURGI
Result		-90% of SO_2 and 50% Ammonia	
Clinker tpd		2,500	5,400
Waste Gas Quantity	m^3/h	308,000	700,000
Waste Gas Quantity	m^3/kg clinker	2.957	3.111
SO_2 inlet -up to	mg/m^3	2,300	2,700
SO_2 outlet-below	mg/m^3	200	200
SO_2 Reduction %	%	91.3%	92.6%
SO_2 inlet -typical	mg/m^3	800	
SO_2 outlet-typical	mg/m^3	70	
SO_2 Reduction %	%	91.3%	
Power Consumption	Kwh/t clinker	13	8
Water consumption	m^3/h	16	28.5
Water consumption	m^3/tonne clinker	0.154	0.127
Waste Gas Reheated?		Yes	No
Gas temp. ex scrubber	°C	55	N/A
Reheat by		Cooler Exhaust gases	N/A
Temp. of reheat gases	°C	250	N/A
Volume of reheat gases	m^3/h	240,000	N/A
Stack exit temp	°C	120	N/A
Date		1996-97	1997-98
Investment Cost	Million Euros	8.0	9.5
Escalation Factor assumed		1.674	1.630
Current Investment Cost	Million Euros	13.4	15.5
Current Investment Cost	Million £'s	10.7	12.4
Investment	£/tonne clinker	4,282	2,293
Investment Cost- Alternative Data	Million £'s	5.0	
Current Alternative Data Investment Cost	Million £'s	8.4	
Current Alternative Data Investment	£/tonne clinker	3,347	

In the table above the Heidelberg figure for Ribblesdale of 8m Euro is assumed to be the more accurate value. Similarly the 9.5m Euro capex quoted by Heidelberg is assumed for the Slite cost. Appendix 2 shows the principle of the DYNAWAVE WS system.

Operating costs for Wet Scrubber systems

- Note that the electric power consumption required for the WS system is very dependent upon the actual WS design selected. Heidelberg quoted between 13 kwh/tonne (Ribblesdale) and 8 kwh/tonne (Slite). However, the Slite plant did not have a system to reheat the exhaust gases using cooler exhaust gases. Hence the Ribblesdale power consumption figure of 13 kwh/tonne clinker may be more suitable.
- HCM has made significant progress in reducing electric power consumption in recent years. The additional 13 kwh/tonne clinker required for a WS system is an area of concern as this represents an increase of around plus 10% on the plant total electric power consumption (plus associated CO_2 emissions derived from electric power generation).
- There may be some additional power consumption costs to add to this as it is not clear whether Heidelberg has included all the power consumed for raw meal preparation etc.
- The power consumption for drying and grinding the raw meal or limestone used in the scrubber must also be considered.
- In 1998 the operating cost was quoted as £750,000 per annum and this would be equivalent to around £1.09m in May 2014 allowing for inflation. This is equivalent to around £1.5/tonne clinker.
- However, without a detailed breakdown it is not possible to say whether or not this includes all of the costs for additional raw meal, power consumption, maintenance etc.
- The BREF operating cost figures (with a reference date of 2008) are shown in the table below. Updating these costs to current May 2014 give the following cost/tonne clinker.

BREF 2013 Opex for WS	Min	Max	Average
Quoted Euro/tonne clinker	1	2	1.5
Date	2008	2008	2008
Current Euro/tonne May 2014	1.22	2.45	1.84
£/tonne clinker in 2014	£0.98	£1.96	£1.47

- BREF also quotes an Austrian WS plant which may be the Retznei 500,000 tpd cement plant. However the operating cost of Euro 140,000 per annum appears to be too low even after escalation for inflation. This figure is not consistent with or in the range of operating costs that other plants have published and should not be considered as a reliable data point in any analysis.
- This points out a weakness in the BREF information in that the data is incomplete and it is not clear if all costs are included. The actual operating costs will obviously depend upon the required reduction in SO_2 and this will vary for each plant considered.
- From a review of the BREF data plus other information found for WS systems in USA, the typical updated operating costs were estimated as follows:-
    - Minimum opex = £1.40/tonne clinker.
    - Maximum opex = £2.90/tonne clinker.
    - Average opex = £2.15/tonne clinker.

  - It should be noted that care has to be exercised when comparing operating costs from international operations as labour and materials costs can vary significantly.
  - It is not clear, from any of the published data, whether or not all the operating costs are included such as raw meal preparation (materials, power, maintenance), water treatment costs etc.
  - A further factor which has to be considered is the range of input SO_2 plus the outlet ELV required from the WS system. This directly affects the costs for raw meal injection, power etc.
- Whilst the above BREF opex figures do not appear unreasonable, HCM may wish to consider the higher opex figures quoted above which are derived from a larger data set.
- For the Hope Works study an initial figure of between £1.50 and £2.90 per tonne clinker would seem to be reasonable. It would not be possible to improve upon this figure without a detailed scheme prepared after competitive tendering.

Scaling of Wet Scrubber capital costs to suit Hope Work's installation

The very wide range of capital costs quoted for Ribblesdale, Slite and Dunbar presents a problem when attempting to arrive at a realistic capital cost for Hope Kilns 1 and 2 wet scrubbing systems. The following approach has been taken:

- It is assumed that it would not be practical to install a single large wet scrubber to handle gases from both kilns.
- A large single unit may cause problems with balancing the exhaust gas flows and would result in lower gas velocities when one kiln is shut down. There is the further potential problem of ensuring gas tight isolation of ducting from the kiln which is shut down.
- Site visits to Slite and Dunbar show a very visible plume and this is an area of concern for Hope. The use of cooler exhaust gases to reheat the stack gases would be necessary.
- Scaling up of wet scrubber costs to suit the Hope Works required size is assumed to follow a 0.74 power law factor.
- A current exchange rate of 1.2506 Euros per £ is assumed.
- No attempt has been made to include currency exchange rate changes between 1996-1998 to 2014 as there are no details of the currency splits and rates used during construction of these projects. Similarly the split between local and imported equipment is not specified and this will also influence current capital cost estimates.
- Any wet scrubber installation at Hope Works is assumed to be sized upon the clinker output of 2,170 tpd per kiln.
- The wet scrubber capital cost data obtained from the web plus BREF is summarised in the table below.
- It should be noted that:-
  - The very high cost for Dunbar is difficult to explain. The Dunbar costs may include costs for refurbishing existing plant and without detailed cost data it is not possible to establish the standalone WS plant capex.
  - An expenditure of £22m for Dunbar in 2007 would be nearer to £28m in 2014 after adding 7 years inflation.

- The Slite cost scaled to suit Hope Works would be slightly low as it does not include cooler exhaust heat recovery to boost the stack exit gases which would be essential for Hope Works.
- The BREF examples for a 1,100 tpd WS plant, when scaled up to 2,170 tpd size are considered to give too low a capital cost when compared with a larger data set of published information and so these have not been considered as representative of the necessary installed capex costs.
- The capital costs for seven different installations are listed below, including the Dunbar unit.
- The average capital cost is estimated after taking into account inflation, currency exchange rates and plant size. This gives an average cost of £10.08 m per kiln for a WS system.
- Allowing for two WS systems plus 10% contingencies, the total capex is = 2 x £10.08 x 1.1 = £22.18m for Hope Works.

Plant	Units	Ribblesdale	Slite	Austria	Web	Web	Web	Dunbar	Average
Data Source		Heidelberg	Heidelberg	BREF/Other	Data 1	Data 2	Data 3	L/T	
Efficiency SO_2 removal	%	90%							
Clinker output	tpd	2,500	5,400	1,260	1,714	3,427	2,722	3,300	
Annual Clinker @ 87% runtime	Tonnes	793,875	1,714,770	400,000	544,200	1,088,400	864,244	1,047,915	
Date		1996-97	1997-98	1998	2002	2002	2010	2007	
Original Investment Cost	m Euro	8.0	9.5	5.8					
Escalation Factor assumed		1.674	1.630	1.590	1.459	1.459	1.161	1.278	
Current Investment Cost	m Euro	13.4	15.5	9.2					
Current Investment Cost	£m	10.7	12.4	7.4				28.1	
Investment	£/tpd clinker	4,282	2,293	5,855	2,950	2,018	3,009	8,518	
Investment Cost - other data/original	£m	£5.0			5.06	6.92	8.19	22.0	
Investment Cost – other current	£m	8.37			7.37	10.09	9.51	28.11	
Investment	£/tpd clinker	3,347						8,518	
Average estimate (Mid 2014)	£m	9.54	12.38	7.38	7.37	10.09	9.51	28.11	
Scale to Hope	£m	8.59	6.31	11.03	8.78	7.19	8.04	20.61	10.08
Clinker tpd peak per kiln	tpd	2,170	2,170	2,170	2,170	2,170	2,170	2,170	2,170
Investment	£/tpd clinker	3,958	2,906	5,083	4,047	3,315	3,706	9,498	4,645
						Two units for Hope Works - Millions			£20.16
						Plus 10% contingencies - Millions			£22.18

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Conclusions

- The preferred process route would be to install a wet scrubber system rather than an absorbent injection system since this technology is well established in the cement industry with two plants operating in UK (Ribblesdale and Dunbar). The WS system can handle high SO_2 inputs and achieve low outlet emissions. For example, Ribblesdale is quoted as 2,300 to 2,500 mg/m^3 input and the permit application for firing SRF quotes an outlet below 200 mg/Nm^3 dry gas @10% oxygen.
- The option to use absorbent injection (AI) has not been ruled out but there are concerns over the ability for an AI system to handle periodic high SO_2 inputs. The use of microfine lime injection could be considered although operating costs are still significant especially when treating high SO_2 inputs.
- The concern over the use of AI is that it may not provide a 100% guarantee of complying with the required SO_2 emission limit under all plant operating conditions especially if there are periods of high pyritic sulphur input.
- Hence, although the use of AI may have advantages of lower investment costs, it cannot be considered to be the optimum solution as there are concerns over its efficiency being lower than that of the WS system.
- It would not be possible to guarantee that the lower SO_2 ELV value required could be achieved upon all operating conditions. Hence the recommended approach is to use a proven WS system for SO_2 reduction at Hope Works.
- Although the required SO_2 ELV is around 400 mg/Nm^3 dry gas @10% oxygen, published emission data from Ribblesdale in 2005 showed that values around 60 mg/Nm^3 dry gas @10% oxygen were being achieved.
- If Hope Works were required to install wet scrubbing it has been estimated that the capital cost would be around £22.18m to install two units. This sum includes 10% contingencies.
- Operating costs for a WS system are expected to be in the range of £1.50 to £2.90/tonne clinker. These costs will depend to some extent upon the design of the WS system selected and more accurate costs will only be established during a competitive tendering process.
- Power consumption for the wet scrubber system is estimated to be around 13 kwh/tonne clinker based upon the Ribblesdale information. However, it is not clear what this includes as kwh/tonne need to be allowed for raw meal preparation. This is an area of concern as the use of a WS system would result in a net increase of around plus 10% higher electric power consumption for Hope Works.
- Whilst the raw meal used can be converted to synthetic gypsum, the loss of raw milling capacity raises some concerns as this would have a negative impact upon the potential clinker out from the plant.
- The visual impact of the plume leaving the wet scrubber is another cause for concern.
- The estimated cost figures cannot be considered to have an accuracy greater than +/- 15% for capital costs and +/- 25% for operating costs.
- The only way in which these costs can be improved would be by competitive tendering and technical evaluation of the proposals for different WS systems.

Appendix 1 –BREF 2013

The most relevant sections of the BREF papers are as follows:

- Section 1.4.5.2 – Reduction of SO_2 emissions.
  - 1.4.5.2.1 Absorbent addition.
  - 1.4.5.2.2 Wet scrubber.
  - 1.4.5.2.3 Activated carbon
- Section 1.4.8.3 – Example cost data for SOX reduction technique.
- Section 4.2.6.2 - Conclusions SO_2 emissions.

The main conclusions made in the BREF 2013 document concerning AI and WS system are as follows :-

1.4.5.2 Reduction of SO_2 emissions

The first step with respect to SO_2 control is to consider primary process optimisation techniques, such as optimising the clinker burning process including the smoothing of kiln operation, uniform distribution of the hot meal in the kiln riser and prevention of reducing conditions in the burning process as well as the choice of raw materials and fuels. Moreover, the oxygen concentration in the kiln inlet area is crucial to SO_2 capture in the kiln charge. Increasing the oxygen content in long kilns decreases the SO_2 level and increases the NOx level. However, to achieve the specified product quality, the clinker burning process requires an excess of oxygen.
Accordingly, there is always a sufficient supply of oxygen to ensure the formation of sulphates in the bottom section of the cyclone preheater or the hot gas chamber of the grate preheater, which are discharged from the kiln system via the clinker. A balance for protecting the environment should be sought by optimising NOx/SO_2/CO by adjusting the back-end oxygen content. In those cases where these techniques are not enough, additional end-of-pipe techniques can be applied. Table 1.36 and Table 1.37 give an overview of techniques that have a positive effect on, i.e. reduce, the emissions of SO_2 arising from the manufacture of cement, mainly from the preheater and the bypass process. Table 1.36 is a summary of operational data which are available within the text of this section and should be read in conjunction with the corresponding paragraphs in following sections (see Sections 1.4.5.2.1–1.4.5.2.3). In this context, it has to be noted that, when co-incinerating waste, the requirements of Chapter IV of and Annex VI to the Directive 2010/75/EU have to be met.
No semi-wet and dry scrubbers are used in the European cement industry. The principle of these techniques is the neutralisation of SO_2 from the exhaust gas by the injection of chemical or physical sorption agents. The reaction products are dissolved or dry salts, following the techniques. In Untervaz, Switzerland in 2003, the only plant in Europe to have installed a circulating fluidised bed dry scrubber was shut down due to economic and, to a lesser extent, technical reasons.

1.4.5.2.1 Absorbent addition

Description and achieved environmental benefits

Secondary emissions control techniques employed in the cement industry are hydrate-of-lime addition using the so-called 'dry additive process' (sorbent addition to raw material) or the 'dry sorption process' (sorbent injection into the gas stream). Hydrate-of-lime addition offers the additional advantage that the calcium-bearing additive forms reaction products that can be directly incorporated into the clinker burning process.
The optimum temperature ranges for hydrate-of-lime addition are 350 to 400°C and below 150°C if the gas is enriched with water. Suitable locations for hydrate-of-lime addition in cement rotary kiln systems are the upper cyclone stages or the raw gas duct.

Alternatively, hydrate-of-lime can be charged into the raw mill together with the raw material constituents or directly added to the kiln feed. Hydrate or slaked lime ($Ca(OH)_2$), quicklime (CaO) or activated fly ash with a high CaO content, is injected into the exhaust gas path at temperatures close to the water dew point, which results in more favourable conditions for SO_2 capture. In cement kiln systems, this temperature range is available in the area between the raw mill and the dust collector. The hydrate-of-lime reacts with the SO_2 in the upper cyclone stages and is carried out of the system as raw gas dust (dust collector) which is returned to the downstream grinding-drying unit with the raw gas. Factors limiting the reduction efficiency of this process are the short gas retention times in the upper cyclone stages (minimum two seconds) and the high exhaust gas CO_2 levels of over 30%.

Cross-media effects
Intensive lime injection impacts on raw meal quality.

Operational data
The SO_2 reduction potential of hydrate-of-lime addition is determined by the initial SO_2 level and the exhaust gas conditions versus the concentration level of the sulphur cycles forming in the respective plant. SO_2 reductions of 60 to 80% can be achieved by absorbent injection in suspension preheater kiln systems. With initial levels not higher than 400 mg/Nm^3, it is theoretically possible to achieve around 100 mg/Nm^3. For initial SO_2 levels of up to 1200 mg/Nm^3, it is possible to achieve a reduction to 400 mg/Nm^3. Higher initial SO_2 levels above 1200 mg/Nm^3 require significant amounts of absorbent which might not be cost effective.
Moreover, a higher initial concentration of the sulphur cycles leads to process upsets due to the formation of deposits in the calcining area. Therefore, there might be a risk of higher sulphur recirculation and kiln instability as higher levels of sulphur are returned to the kiln when this technique is applied.

Applicability
Absorbent addition is, in principle, applicable to all kiln systems, although it is mostly used in suspension preheaters. There is at least one long wet cement kiln injecting dry $NaHCO_3$ to the exhaust gas before the ESP is used to reduce peak emissions of SO_2.
Lime addition to the kiln feed reduces the quality of the granules/nodules and causes flow problems in Lepol kilns.
The dry sorption process (absorbent injection into the gas stream) can be applied in a dry or a wet form. For preheater kilns it has been found that direct injection of slaked lime into the exhaust gas is less efficient than adding slaked lime to the kiln feed. The SO_2 will react with the lime to form $CaSO_3$ and $CaSO_4$, which then enters the kiln together with the raw material and is incorporated into the clinker. This technique is suitable for cleaning gas streams with moderate SO_2 concentrations and can be applied at an air temperature of more than 400°C. The highest reduction rates can be achieved at temperatures exceeding 600 ºC. It is recommended that a $Ca(OH)_2$ based absorbent with a high specific surface area and high porosity should be used.
Slaked lime does not have a high reactivity, therefore $Ca(OH)_2/SO_2$ molar ratios of between 3 and 6 have to be applied. Gas streams with high SO_2 concentrations require 6–7 times the stoichiometric amount of absorbent, implying high operational costs.

Economics
Absorbent addition is in use at several plants to ensure that the limits are not exceeded in peak situations. This means that, in general, it is not in continuous operation, but only when required by specific circumstances. With an initial SO_2 concentration of up to 3000

mg/Nm^3, a reduction of up to 65% and a slaked lime cost of EUR 85 per tonne, the investment costs for a 3000 tonne clinker/day preheater kiln are about EUR 0.2 million–0.3 million and the operating costs are about EUR 0.1–0.4 per tonne clinker.
See also Table 1.36 and Section 1.4.8.3 where example cost data are shown.

Driving force for implementation
Legal requirements.
Local conditions.

Example plants and reference literature
Cement plants in the EU-27.
[8, CEMBUREAU, 2001], [9, CEMBUREAU, 1997 November], [12, Netherlands, 1997], [30, Marchal, 2001], [76, Germany, 2006], [97, CEMBUREAU, 2007], [101,France/ADEME/MEDD, 2002], [168, TWG CLM, 2007].

1.4.5.2.2 Wet scrubber
Description and achieved environmental benefits
The wet scrubber is the most commonly used technique for flue-gas desulphurisation in coalfired power plants. For cement manufacturing processes, the wet process for reducing SO_2 emissions is an established technique. Wet scrubbing is based on the following chemical reaction:

$$SO_2 + \frac{1}{2} O_2 + 2 H_2O + CaCO_3 \longleftrightarrow CaSO_4 \bullet 2 H_2O + CO_2$$

The SOx is absorbed by a liquid/slurry which is sprayed in a spray tower. The absorbent is calcium carbonate. Wet scrubbing systems provide the highest removal efficiencies for soluble acid gases of all flue-gas desulphurisation (FGD) methods with the lowest excess stoichiometric factors and the lowest solid waste production rate. However, wet scrubbers also significantly reduce the HCl, residual dust and, to a lesser extent, metal and NH_3 emissions. The basic principle of the working system of a wet scrubber is shown in Figure 1.69.
Source: [91, CEMBUREAU, 2006]

Figure 1.69: Basic operational features of a wet scrubber

There are seven wet scrubbers currently in use in 2008 and one is planned to be used in the European cement industry, all of them spray towers. The slurry is sprayed in counter currently to the exhaust gas and collected in a recycle tank at the bottom of the scrubber where the formed sulphite is oxidised with air to sulphate and forms calcium sulphate dihydrate. The dihydrate is separated and depending upon the physico-chemical properties of gypsum this material can be used in cement milling and the water is returned to the scrubber.
In comparison to the dry scrubber, the potential to generate cement kiln dust (CKD) in a wet process is much lower and natural gypsum resources are saved. In Untervaz, Switzerland, the only installed circulating fluidised bed dry scrubber in Europe was retired in 2003, due to economic–and to a lesser extent–technical reasons. Normally, during the cement manufacturing process or from gas scrubbing applications, the aim is not to generate waste dust.
In wet desulphurisation processes, $CaSO_4 \bullet 2 H_2O$ is formed–which is used as a natural gypsum replacement and in the follow-up integrated as a modulating agent in the cement. In a dry/semidry desulphurisation process, a large quantity of the product $CaSO_3 \bullet \frac{1}{2} H_2O$ is formed, the latter of which is harmful for the cement quality and

integration possibilities in the cement are limited. The majority of the dry scrubber product would therefore have to be taken either back to the kiln or would need to be disposed of.

Cross-media effects
Increased energy consumption.
Increased waste production from flue-gas desulphurisation (FGD), and when maintenance is carried out, additional waste may occur.
Increased CO_2 emissions (see the chemical reaction above where it is shown how CO_2 is derived from the wet scrubber process)
Increased water consumption.
Emissions to water and increased risk of water contamination.
Increased operational cost.
Replacement of natural gypsum by artificial gypsum.

Operational data
The SO_2 reduction achieved can be more than 95%. Cementa AB in Sweden operates a 5800tonne clinker/day preheater kiln and has an initial SO_2 concentration in the flue-gas of 800–1000 mg/Nm^3, resulting in levels of <10 mg/Nm^3. Castle Cement in the UK operates a 2500 tonne clinker/day preheater kiln and has an initial SO_2 concentration in the flue-gas of about 800–1400 mg/Nm^3 as a daily average with peak values of more than 2000 mg/Nm^3 at times. Furthermore, SO_2 emissions of 207 mg/Nm^3 as a yearly average over the years between 2002 and 2006 have been reported and the maximum daily averages have varied from 248 to 296 mg/Nm^3 due to the high sulphur content in the raw material.

Applicability
A wet scrubber can be fitted to all cement kiln types with appropriate (sufficient) SO_2 levels in order to manufacture the gypsum.

Economics
In 2008, capital expenditure costs for a wet scrubber of Ribblesdale works, Castle Cement in the UK, were estimated by the supplier to be around EUR 23 million, when considering inflation. In 2000, the investment costs for the scrubber of Castle Cement (including plant modifications) were reported to be EUR 7 million and the operating costs were about EUR 0.9 per tonne clinker. In 1998 for Cementa AB in Sweden, the investment costs were about EUR 10 million and the operating costs were about EUR 0.5 per tonne clinker. With an initial SO_2 concentration of up to 3000 mg/Nm^3 and a kiln capacity of 3000 tonne clinker/day, the investment costs in the late 1990's were EUR 6 million–10 million and the operating costs EUR 0.5–1 per tonne clinker. Furthermore in 1998 at an Austrian cement plant, the investment costs for a wet scrubber (SO_2 emissions reduction to less than 200 mg/Nm^3) were EUR 5.8 million and until 2008, the yearly operational costs were EUR 140,000. In 2008, the European cement industry reported investment costs of between EUR 6 million and 30 million and operational costs of between EUR 1–2 per tonne clinker.
Example costs data along with a set of different data calculated for a reference plant with a capacity of 1100 t/d can be found in Table 1.41 in Section 1.4.8.3.

Driving force for implementation
Legal requirements.
Local conditions.

Example plants and reference literature

Cementa AB (Sweden), Castle Cement (UK), Retznei plant (Lafarge, Austria), Dunbar (UK), Trebovlje (Slovenia), Untervaz (Switzerland).

[8, CEMBUREAU, 2001], [9, CEMBUREAU, 1997 November], [10, Cementa AB/Hagström, 1994], [11, Coulburn, 2001], [24, Junker, 2001], [81, Castle Cement UK, 2006], [86, EURITS, 2006], [92, Austria, 2006], [103, CEMBUREAU, 2006], [114, Sweden, 2006], [132, CEMBUREAU/Federhen, 2007], [168, TWG CLM, 2007], [175, Lafarge, 2007], [182, TWG CLM, 2008], [183, Szednyj/Schindler, 2005].

Appendix 2– DynaWave SO2 Wet Scrubber

Picture from web site

http://www.mecsglobal.com/howthe-dynawave-wet-gas-scrubber-works.aspx