

NOTE	
Date:	19/03/10
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Subject:	Solution to extend Hope quarry life: Scrubber
Distribution:	HOPE, ETC, LCUK
Classification:	INTERNAL

1. EXECUTIVE SUMMARY :

Hope shale quarry life is limited by its sulphur level. This sulphur, that is 90% pyritic, has two impacts:

- One fraction of the pyritic sulphur (20-37%) is effectively emitted at the stack as SO₂. The current plant limitation is 1600mg/Nm³@10%O₂ but may be reduced in the future to 400mg/Nm³@10%O₂.
- The remaining fraction is trapped in the clinker. The SO₃ in clinker can be limited by the quality and by the volatilisation and build up in the kiln.

In order to extend the shale quarry life, two options have been studied, the installation of a gas wet scrubber to be able to use high sulphur shale, and a partial to total substitution of shale.

This report concludes that even with a wet scrubber, the high sulphur shale remaining in the quarry cannot be used. If the shale is not substituted, the sulphur fraction that would be trapped into the kiln would not be manageable from a process and quality point of view. At the opposite, shale substitution is a good solution.

2. INTRODUCTION

Hope shale quarry life is limited by its sulphur level. This sulphur is 90% pyritic.

This pyritic sulphur has two impacts:

- One part of the pyritic sulphur (20-37%) is effectively emitted at the stack as SO₂. The current plant limitation is 1600mg/Nm³@10%O₂ but may be reduced in the future to 400mg/Nm³@10%O₂. As the raw mill is trapping some SO₂, the emission raw mill off is significantly higher than raw mill on.
- The remaining fraction is trapped in the clinker. The SO₃ in clinker can be limited by the quality and by the volatilisation and build up in the kiln.

The objective of this report is to study the installation of a wet scrubber to increase the plant raw material reserve. The impact on the SO₂ stack emission and the impact on the sulphur in the clinker is the object of the study.

3. SHALE AND LIMESTONE RESERVE

In case of wet scrubber: due to the fact that the shale would be used at 16% of the raw mix, the shale content will be 9% SO₃ for the first layer and 11% SO₃ for the second one.

In the last phase of the limestone quarry, the average limestone SO₃ will be 0.7%.

As no low sulphur material will be available to compensate the increase of the limestone SO₃ in the last phase, the calculation for the wet scrubber scenario will be made with this basis.

4. WET SCRUBBER

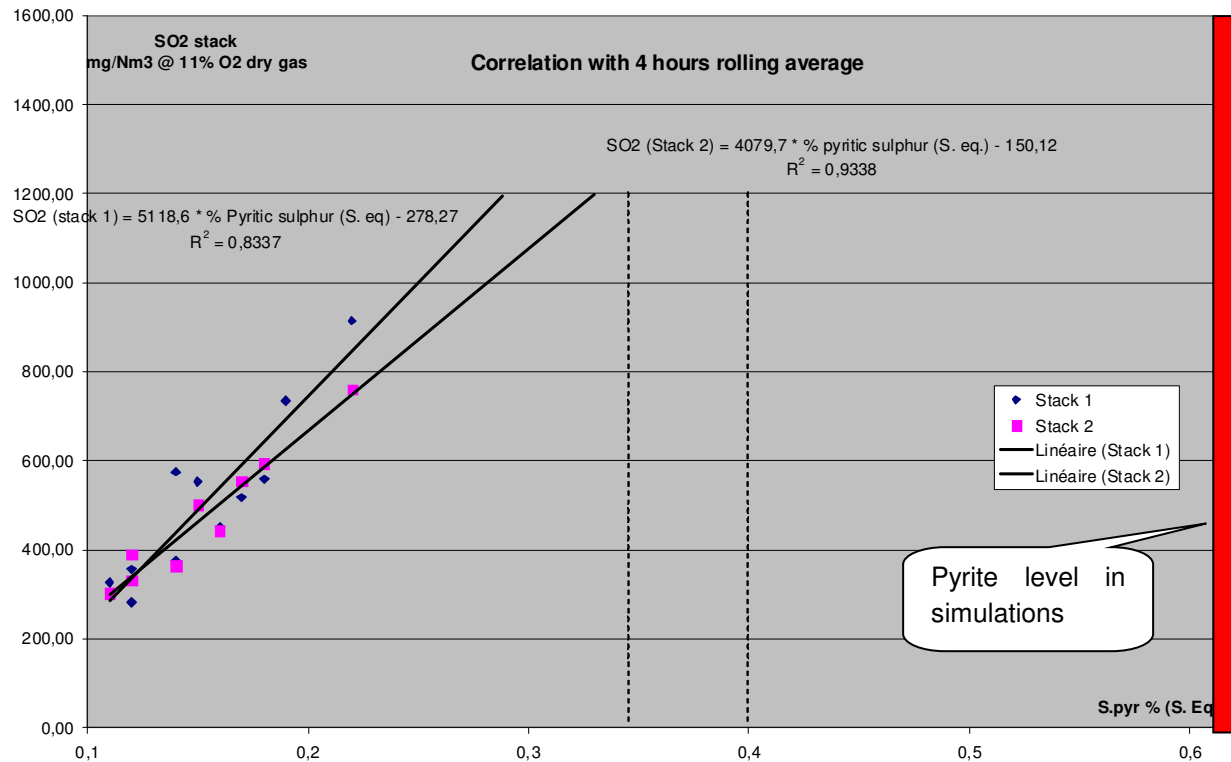
In this scenario, the installation of a gas wet scrubber is considered together with the use of the high sulphur shale (9% SO₃). A model has been developed to simulate this scenario.

4.1.1 Data :

This study is based on previous study made by TCEO in 2002. The data from this report will be used in the different simulations.

4.1.2 Stack SO2 emissions vs kiln feed pyritic sulphur:

The stack SO2 emission is predicted from the experiments that were done in 2002:



This relation Stack emission vs kiln feed pyritic sulphur content was used in the past because it is easier to determine. But in reality, this correlation is the results from combinations of:

- The percentage of pyritic sulphur that is really emitted at the preheater exit. This factor will be important to determine what would be the SO2 emission RM off if there is no scrubber.
- The percentage of SO2 that is effectively trapped into the raw mills

It is very important to notice that, as no experiment has ever been done with such high level of pyritic sulphur (0.62%Seq), we have to extrapolate the curve very far. This is bringing some uncertainty to the result of this simulation.

4.1.3 SO2 trapping in the raw mills

During the 2002 trial, it was calculated that **30% of the SO2 emitted at the stack was scrubbed into the raw mills**. Nevertheless, some trials were done in the past

in order to increase the trapping into the mills. Those trials gave some undesired results by reducing the trapping in the mills.

4.1.4 Fraction of pyritic sulphur that is really emitted as SO₂ at the preheater exit

As the pyritic sulphur relation was obtained when the Raw mills trapping was 30%, the stack SO₂ correlation with kiln feed pyritic sulphur is corrected by a factor 0,7.

The relation between kiln feed Pyritic sulphur and preheater SO₂ becomes:

$$\text{Preheater SO}_2 \text{ (mg/Nm}^3 \text{ @11\%O}_2\text{)} = 6570 \times \text{KF Pyr S (S equ)} - 306$$

The emission calculated by this formula is close from the results of other plant with high pyritic sulphur level.

	Hope	Dunbar	Retznei	CKHC
Ratio % SO ₂ at preheater/ Potential SO ₂	42%	57 %	50 %	66 %
Ratio % SO ₂ <u>trapped in raw mill</u> circuit / SO ₂ entering raw mill circuit	30%	47 %	75 %	n.i.
Ratio % SO ₂ at stack/ Potential SO ₂	35 %	37 %	20 %	n.i.

Benchmarking of SO₂ generation and trapping efficiencies

4.1.5 Raw meal vs kiln feed chemistry

All the SO₂ prediction formulas are based on the kiln feed. It is logical, as the SO₂ emission will definitively depend of the chemistry of the kiln feed going into the preheater. Nevertheless, the “real” input of the system is the raw mix coming from the quarry. The difference between the raw mix and the kiln feed is the following:

- The recirculation load of preheater dust. As mentioned in the 2002 report, the dust composition is close to the kiln feed composition. This is the reason why, for simplification of the model, the impact of dust is neglected.
- The SO₂ trapping in the raw mills that is then “converted as SO₃”. This is the reason why the total SO₃ in the kiln feed is higher than the raw mix, but also why the percentage of pyritic sulphur in the kiln feed is lower than in the raw mix.

The model back calculates the relation between raw meal and kiln feed based on the trapping.

4.1.6 Raw mix composition:

In this scenario with a wet scrubber, the shale available would content 9% of SO₃, in which 90% is pyritic. It is also very important to notice that the limestone SO₃ (0.7%SO₃) is a very big contributor to the sulphur input.

Raw mix composition	% in RM	% of pyr S	RM S tot SO ₃ equ	S Pyr SO ₃ equ
Shale	16%	90%	9.00%	8.1%
Limestone	84%	90%	0.70%	0.6%
PFA	0%	0%	1.80%	0.0%
RM calculation			2.003%	1.80%

In a second phase, the use of shale at 11% SO₃ (last layer) is also simulated.

4.1.7 Results of the simulations

The simulation gave the following results:

	Shale SO ₃	Limestone SO ₃	Clinker SO ₃	SAR	Na ₂ O eq	BeforeStak em. @10% O ₂	Preheat em. @10% O ₂	R%SO ₂ pheat/Pot SO ₂	Trap RM	Overall trap
Baseline	2.10%	0.20%	1.05%	1.18	0.69%	521	744	42%	30%	70%
Scrubber 1	9.00%	0.70%	2.73%	3.35	0.63%	2 502	3 574	42%	30%	70%
Scrubber 2	11.00%	0.70%	3.09%	3.58	0.67%	2 874	4 105	42%	30%	71%

4.2 Scrubber scenario: Impact of the on the stack emission

As a scrubber is installed, we consider that the plant will be able to meet is current and future SO₂ limits at the stack.

4.3 Scrubber scenario: Impact of the sulphur on the burning line process.

From the simulation, the impact of the pyritic sulphur on burning line process is very critical: The clinker SO₃ at 2.73% and the Sulphur over alkali molar ratio (SAR) will not be manageable for Hope plant. From a process point of view, the sulphur load would imply huge build-up, rings and cyclones blockages. From a quality point of view, it would also not be manageable (cf annex 1: What is the acceptable process level of SO₃ and SAR in Hope clinker?)

4.4 Conclusion:

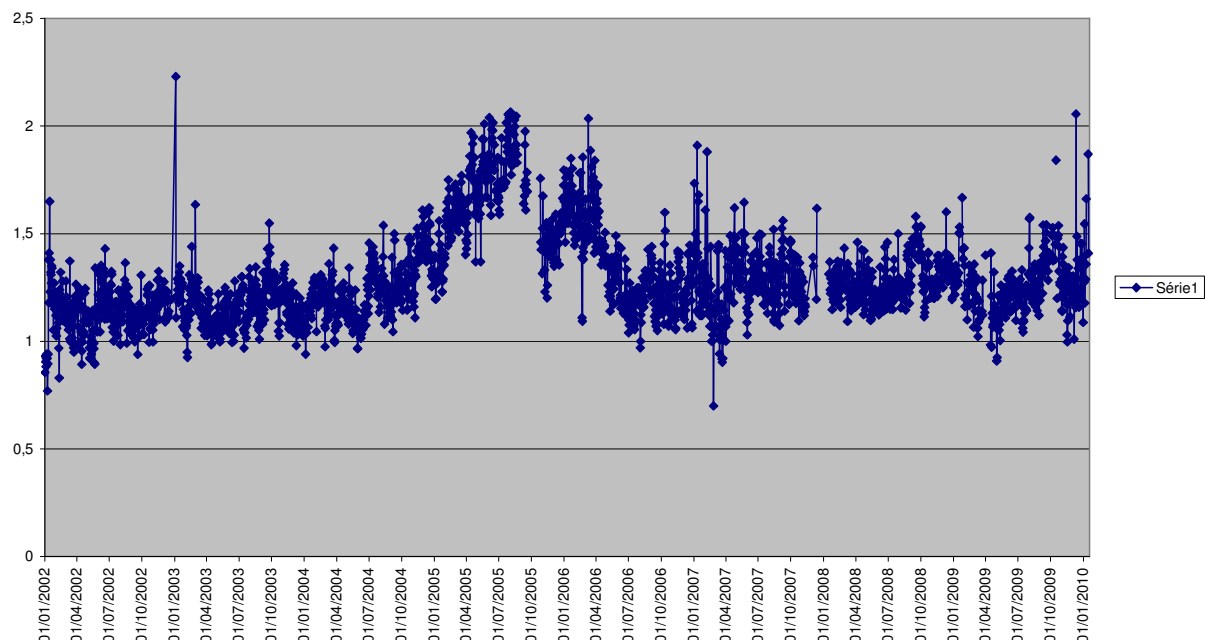
The wet scrubber installation is not a solution to increase the shale quarry life. Indeed, the high sulphur shale utilisation will be limited by the impact of sulphur that will be trapped into the preheater and the raw mill.

5. GENERAL CONCLUSION

In order to extend the Hope shale quarry life, the only option is the substitution of shale. Even with a wet scrubber, the high sulphur shale remaining in the quarry cannot be used. The sulphur input would be so high that the kiln will not be able to cope with the sulphur trapped in the clinker.

6. ANNEX 1: WHAT IS THE ACCEPTABLE PROCESS LEVEL OF SO₃ AND SAR IN HOPE CLINKER?

6.1 From the historical data:



When Hope plant was burning 60% petroleum coke the clinker SO₃ has reach up to 1.8-2%. Unfortunately, figures are not available to check the process failure rate at that time.

6.2 From benchmark:

	HOP 8%SO ₃ shale	LAF C	DNB	DNB Max
Burnability	35-43	56-92	176	176
KK SO ₃	2,73	2,3	1,8	2,2
SAR	3,35	4,2	3,3	4,0

From TCEA database the only 2 preheater kilns that are running with very high sulphur over alkali ratio are Le Teil grey kiln and Dunbar kiln.

The columns DNB max is the well-known situation of the maximum achievable by DNB. In this configuration, the plant has experienced very severe ring formation.

For assessing the maximum sulphur achievable in Hope, we also have to take into consideration that Hope burnability is one of the poorest of the TCEA database.

6.3 Conclusion in the SO₃ in clinker:

From the historical data and the benchmark, we can conclude that any configuration where Hope kiln would have to face a clinker SO₃ over 2.1% and a sulphur alkali ratio greater than 3 would be very very challenging, with a strong impact on the process failure rate of the kiln.