



14 a 17 de Outubro 2002 - São Paulo - Brasil  
October 14-17, 2002

Os efeitos da queima de gases não condensáveis na  
composição da cal e das emissões de SO<sub>2</sub> do forno de cal

Effects of CNCG burning on lime composition and  
So<sub>2</sub> emissions from a lime kiln

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## **Effects of CNCG Burning on Lime Composition and SO<sub>2</sub> Emissions from a Lime Kiln**

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### **ABSTRACT**

A study was conducted at the VCP-Unidade, Luiz Antonio mill to examine the effect of CNCG burning on kiln operation, lime composition and gaseous emissions. The results show that while CNCG burning had no significant effect on kiln performance, it resulted in high SO<sub>2</sub> emissions from the kiln stack. Sulphur entered the kiln mainly with CNCG and methanol, and exited the kiln mainly with lime. Although lime can effectively remove SO<sub>2</sub>, the removal efficiency decreased markedly from 98% of the total sulphur input when CNCG was not burned, to 89% when CNCG was burned in the kiln. For the Luiz Antonio kiln, the critical sulphur input level above which excessive SO<sub>2</sub> emissions occur appears to be about 40 kg/hr.

**KEY WORDS : Lime Kiln, CNCG, NCG, HCLV, Emissions , Sulphur Emissions**

### **RESUMO**

O trabalho apresenta o estudo efetuado na VCP\_LA para avaliar o efeito da queima de gases não condensáveis na operação do Forno de Cal, composição da lama e emissões gasosas. Os resultados mostraram que enquanto a queima de gases não afeta de forma significativa a operação do forno, resulta em emissões altas de SO<sub>2</sub> nos gases de combustão. No sistema analisados a maioria do enxofre no forno entra com os GNCC, a lama de cal e o Metanol líquido utilizado como combustível complementar. Foi determinada a capacidade natural do sistema para capturar o enxofre e o comportamento da eficiência máxima de captura, acima da qual ocorrem emissões excessivas de SO<sub>2</sub>. Em paralelos é avaliados o enriquecimento na cal produzida, para o sódio e fósforo.

**PALAVRAS CHAVE : Forno de cal, GNC, GNCC, emissões, emissões de enxofre.**

### **BACKGROUND**

Malodorous non-condensable gases (NCG) produced in the kraft chemical recovery process contain large amounts of reduced sulphur compounds which must be treated before being vented to the atmosphere. NCG is typically burned in lime kilns, recovery boilers, bark boilers, or in dedicated incinerators, depending on its volume and concentration [1,2]. Although in recent years there has been a trend toward burning NCG in recovery boilers [3], lime kilns still remain the most common place for burning concentrated NCG.

Due to the high sulphur content, burning concentrated NCG (CNCG) is expected to have an effect on TRS and SO<sub>2</sub> emissions, as well as on the composition and quality of product lime. A study was conducted in March 2001 to examine such effects at Votorantim Celulose e Papel (VCP), Luiz Antonio mill. The study was possible due to the unique CNCG delivery system at this mill. The gas stream is normally burned in the recovery boiler; it can also be burned in the lime kiln in the event of boiler unavailability [4]. This feature made it possible to study the effect of CNCG burning on either recovery boiler operation, as previously reported [5], or on lime kiln operation, as in this study, by switching the CNCG stream back and forth between the boiler and the kiln. This paper discusses the study procedure, results, and practical implications of the results.

## STUDY PROCEDURE

The lime kiln at Luiz Antonio is a 1991 F.L. Smidth unit, capable of producing 240 metric tons of CaO per day. It is a 2.69m I.D. x 90m long kiln, equipped with product coolers and a lime mud flash drier that consists of a cyclone and an electrostatic precipitator (Figure 1). Dry mud and dust collected by the cyclone and the precipitator are returned directly to the kiln. No. 6 crude oil is usually burned in the kiln, along with methanol recovered from foul condensate strippers. Prior to 1996, CNCG was also burned in the kiln on a continuous basis. However, due to high SO<sub>2</sub> emissions from the kiln stack, difficulty in avoiding TRS excursions, and the need to maximize CO<sub>2</sub> in the flue gas for precipitated calcium carbonate production, CNCG has been burned mainly in the recovery boiler since that time.

The study was conducted on March 14, 2001. A total of seven sets of lime mud, dust and product lime samples were collected; three of these were collected prior to CNCG burning, at 08:40, 09:40 and 10:40. At 11:06, CNCG was introduced into the kiln at a flow rate of about 560 m<sup>3</sup>/h, through a concentric duct, parallel to the primary air of the oil burner (Figure 2). The CNCG burning continued for 9 hours and ended at 20:00. To account for the 4 to 5 hour retention time of the solids in the kiln, the first set of samples with CNCG burning was collected at 16:30, and three subsequent sets were collected at 17:30, 18:30 and 19:30. These 21 samples, along with samples of the crude oil and methanol, were subjected to chemical, thermal and morphological analyses.

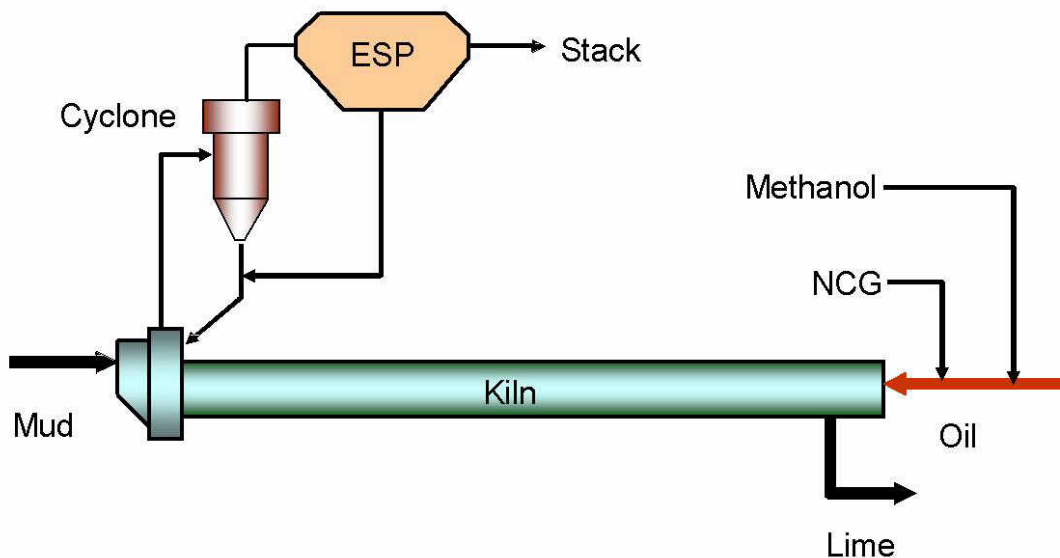
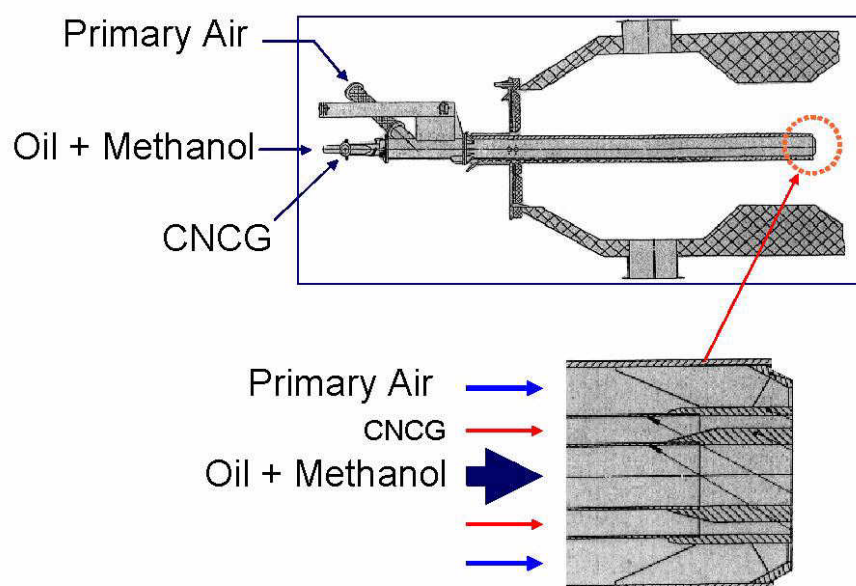


Figure 1. Lime Kiln at VCP-Luiz Antonio Mill





**Figure 2.** Burner Configuration

## RESULTS AND DISCUSSION

### CHEMICAL ANALYSIS

Table 1 summarizes the chemical composition of all lime mud, dust and product lime samples collected. The crude oil sample collected during the study was found to contain 1.06 wt% S. This sulphur content is at the low end of the typical range of 1 to 4 wt% S for the crude oil used at Luiz Antonio. There was little Na in methanol, about 3.5 ppm.

**Table 1.** Chemical composition of lime mud, dust and product lime samples collected during the March 14, 2001 study.

No.	Time Collected	Sample Type	CaO %	SO <sub>3</sub> %	Na <sub>2</sub> O %	P <sub>2</sub> O <sub>5</sub> %	MgO %	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	K <sub>2</sub> O %	MnO %	TiO <sub>2</sub> %	CO <sub>2</sub> %*	Total %
<b>CNCG-OFF</b>															
1	8:40	Mud	54.5	0.08	0.87	1.54	0.74	0.22	0.05	0.10	0.02	0.03	0.01	41.6	99.7
2	8:40	Dust	54.4	0.60	1.11	2.64	0.66	0.30	0.04	0.11	0.08	0.03	0.02	39.7	99.7
3	8:40	Lime	90.3	1.30	1.37	2.65	1.19	0.38	0.09	0.19	0.07	0.06	0.03	2.1	99.7
4	9:40	Mud	54.7	0.13	0.85	1.60	0.73	0.23	0.04	0.09	0.03	0.03	0.01	41.4	99.8
5	9:40	Dust	54.7	1.00	1.17	2.60	0.67	0.29	0.04	0.11	0.08	0.03	0.01	39.5	100.2
6	9:40	Lime	90.3	1.40	1.34	2.65	1.23	0.36	0.07	0.19	0.09	0.05	0.02	2.0	99.7
7	10:40	Mud	54.6	0.10	0.82	1.72	0.71	0.22	0.04	0.09	0.02	0.03	0.01	41.4	99.8
8	10:40	Dust	54.3	1.45	1.31	2.67	0.69	0.32	0.04	0.10	0.07	0.04	0.02	39.1	100.2
9	10:40	Lime	90.2	1.53	1.18	2.64	1.21	0.37	0.09	0.18	0.07	0.05	0.02	2.0	99.6
<b>CNCG-ON</b>															
10	16:30	Mud	54.6	0.10	0.87	1.61	0.73	0.23	0.05	0.09	0.02	0.04	0.02	41.4	99.7
11	16:30	Dust	54.6	1.73	1.57	2.36	0.66	0.40	0.05	0.10	0.05	0.03	0.02	39.2	100.8
12	16:30	Lime	88.9	3.33	1.43	2.63	1.17	0.36	0.07	0.18	0.08	0.06	0.02	1.9	100.2
13	17:30	Mud	54.7	0.13	0.84	1.62	0.74	0.24	0.05	0.11	0.03	0.04	0.01	41.4	99.8
14	17:30	Dust	54.9	1.70	1.03	2.40	0.67	0.43	0.06	0.12	0.06	0.03	0.02	39.1	100.5
15	17:30	Lime	88.4	3.40	1.27	2.61	1.17	0.37	0.08	0.18	0.05	0.04	0.03	2.6	100.2
16	18:30	Mud	54.7	0.10	0.81	1.61	0.74	0.23	0.05	0.09	<0.01	0.04	0.01	41.3	99.8

17	18:30	Dust	54.8	1.75	1.09	2.41	0.69	0.32	0.05	0.11	0.06	0.03	0.01	38.9	100.2
18	18:30	Lime	89.6	3.83	1.24	2.60	1.18	0.37	0.08	0.18	0.05	0.05	0.03	1.6	100.7
19	19:30	Mud	54.7	0.13	0.85	1.62	0.73	0.23	0.05	0.09	0.02	0.02	0.01	41.3	99.7
20	19:30	Dust	54.7	1.58	1.05	2.48	0.67	0.32	0.05	0.11	0.05	0.03	0.01	39.0	100.1
21	19:30	Lime	87.4	3.50	1.35	2.57	1.21	0.38	0.08	0.17	0.08	0.05	0.03	3.7	100.6

Note: The CO<sub>2</sub> content was based on Loss on Ignition

#### EFFECT ON KILN PERFORMANCE

During the study, although attempts were made to maintain kiln operating conditions as constant as possible, the average mud flow rate and mud solids during the period when CNCG was on (from 11:06am to 8:00pm) were respectively 1.1% and 2.4% higher than when CNCG was off, while the oil flow rate was 5% higher (Table 2). This disproportional increase in oil flow rate was probably the main reason for the higher flue gas temperatures at the kiln feed end, the flash drier inlet, and the precipitator inlet when CNCG was burned, although additional heat input from CNCG burning may have been a contributing factor.

The lime availability and residual CaCO<sub>3</sub> content were estimated based on the lime compositions shown in Table 1. The availability was 90.3% during the period when CNCG was off, and 88.6% during the time when CNCG was burned. The decrease was primarily due to the increased sulphur content of the lime as a result of calcium sulphate (CaSO<sub>4</sub>) formation. The residual CaCO<sub>3</sub> content was slightly higher (4.3%) with CNCG burning, compared to when CNCG was off (3.6%). The increase was insignificant since it was within the normal range of the residual carbonate.

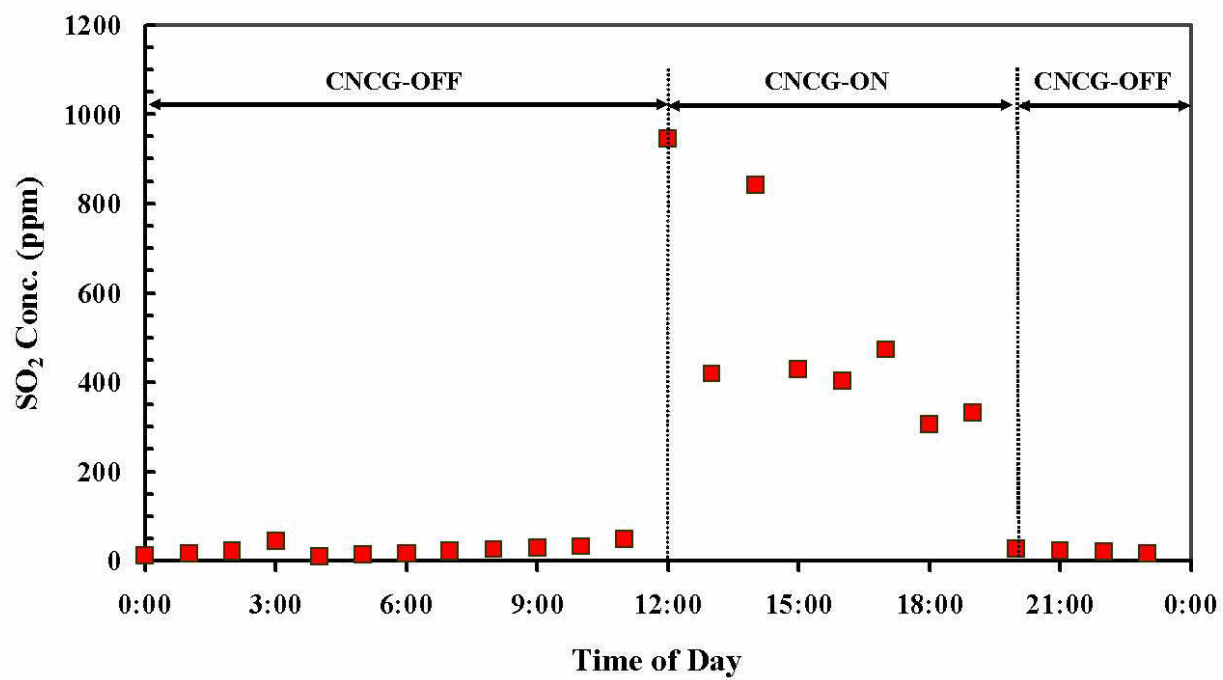
#### EFFECT ON GASEOUS EMISSIONS

As shown in Table 2, TRS, CO and CO<sub>2</sub> emissions from the kiln were not affected by CNCG burning. The SO<sub>2</sub> concentration in the stack gas increased significantly from 25 ppm to over 500 ppm during the CNCG burning period. The effect is clearly shown in Figure 2.

**Table 2.** Kiln Operating Variables (average) during the Study

VARIABLES	CNCG	
	OFF	ON
Mud flow rate (dry) t/h	15.75	15.93
Mud solids, %	80.8	83.4
Lime flow rate, t/h*	9.51	9.93
Oil flow, m <sup>3</sup> /h	1.14	1.21
Oil temperature, °C	241	239
Oil pressure, kg/cm <sup>2</sup>	8.35	8.11
Methanol flow rate, L/h	698	681
CNCG flow rate, Nm <sup>3</sup> /hr	0	560
Primary air flow, m <sup>3</sup> /h	2,390	2,390
Back end gas temperature, °C	657	672
Flash drier inlet gas temp., °C	317	368
ESP inlet gas temperature, °C	259	272
O <sub>2</sub> conc. at cyclone outlet, %	6.2	6.5
CO conc. at cyclone outlet, %	0	0
CO <sub>2</sub> conc. in kiln stack, %	22.7	22.4
TRS conc. in kiln stack, ppm	3.7	3.8
SO <sub>2</sub> conc. in kiln stack, ppm	25	519
Lime availability, %*	90.3	88.6
Residual carbonate content, %*	3.6	4.3

\* Calculated based on chemical composition



**Figure 3.** *Effect of CNCG Burning on SO<sub>2</sub> Emissions During March 14, 2001 Study.*

## EFFECT ON SOLIDS COMPOSITION

As expected, the sulphur content in the dust and the product lime was much higher when CNCG was burned than when it was not, as shown by the % SO<sub>3</sub> measurements in Table 1. All other components were not affected significantly by CNCG burning.

### Sulphur

Figure 4 shows the enrichment factor (EF) for sulphur in dust and product lime, with and without CNCG burning. EF for a component is defined as the ratio of the amount of that component, normalized for the CaO content in the sample, to the equivalent amount in the mud. For example, the enrichment factor for sulphur is defined as follows:

$$EF_s = \frac{\left( \frac{C_{S\text{-sample}}}{C_{CaO\text{-sample}}} \right)}{\left( \frac{C_{S\text{-mud}}}{C_{CaO\text{-mud}}} \right)}$$

Where  $C_{S\text{-sample}}$  and  $C_{S\text{-mud}}$  are respectively the sulphur contents in the sample and the mud, and  $C_{CaO\text{-sample}}$  and  $C_{CaO\text{-mud}}$  are respectively the CaO contents in the sample and the mud. Thus, a component is considered to be “enriched” if its EF is greater than 1, “not enriched” if EF is equal to 1, and “depleted” if  $EF < 1$ .

When CNCG was off, the  $EF_s$  for both dust and product lime was about 9, indicating that the sulphur content in the dust and product lime was 9 times higher than that in lime mud. This increase in sulphur enrichment was due to the capture of SO<sub>2</sub> from the combustion of fuel oil and/or methanol by dust and lime particles. When CNCG was on, the enrichment factor was much higher, about 15 for dust and 20 for lime. These results confirmed that dust and product lime can absorb a significant amount of sulphur from fuel oil, methanol and CNCG.

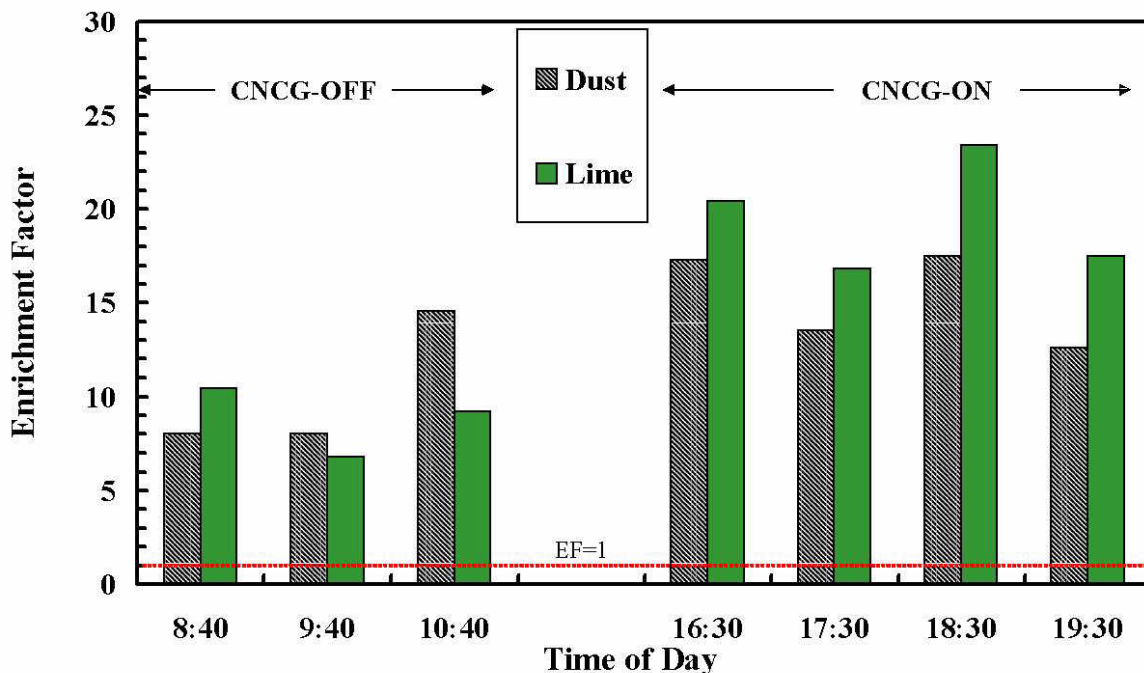


Figure 4. Sulphur Enrichment in Dust and Lime



## Sodium

The enrichment factor for sodium in the mud, dust and product lime did not vary significantly as a result of CNCG burning (Figure 5). This was expected since there was no or little sodium in the CNCG. There was, however, a significant enrichment of Na in the dust ( $EF_{Na} = 1.2$  to  $1.7$ ), regardless of CNCG burning. Such enrichment was likely a result of vaporization-condensation of sodium compounds in the kiln. Sodium compounds tend to vaporize from the solids at the burner end of the kiln, flow with the flue gas, condense as fume particles, and eventually become part of the dust stream at the feed end of the kiln.

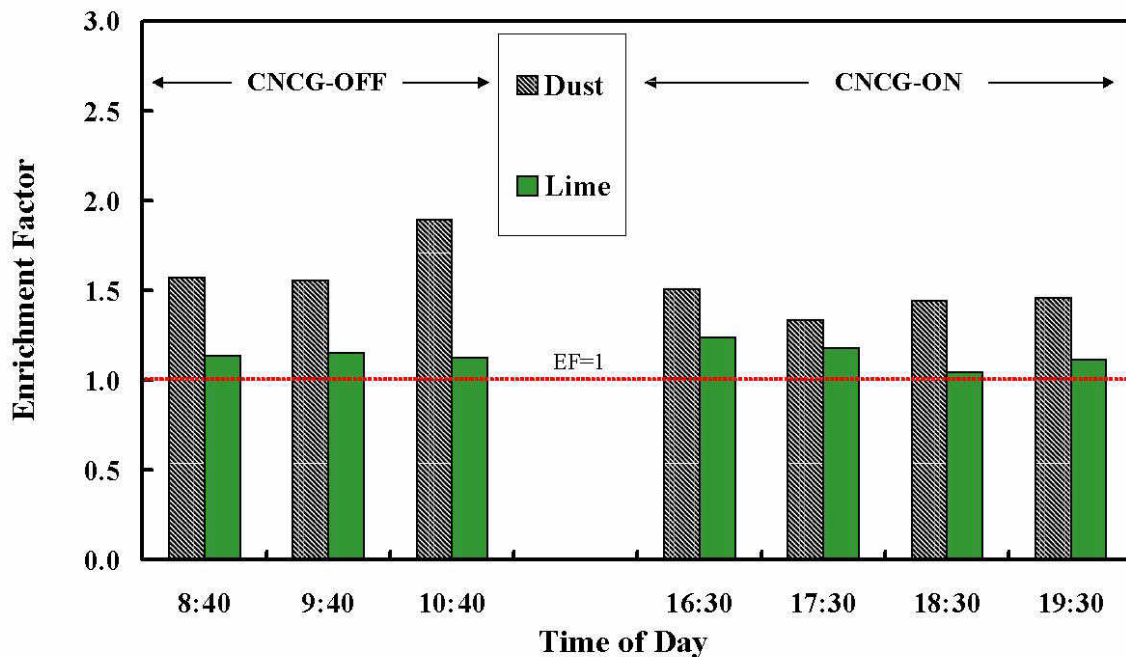


Figure 5. Sodium Enrichment in Dust and Lime

The Na enrichment factor in the lime was 1 or slightly lower. This means that the total Na content in the lime was about the same as, or slightly less than, that in the mud when normalized for the amount of CaO in the respective sample. As shown in Figure 6, however, the normalized water-soluble sodium content in the lime was 1.2 to 1.5 Na<sub>2</sub>O wt%, 3 to 4 times higher than that found in the mud. The low water-soluble Na content in the mud was due to the presence of “guarded Na”, a type of sodium compound that is locked within the lattice structure of CaCO<sub>3</sub>, and consequently is not soluble in water at low temperatures [6]. Since lime is essentially mud that has been heat treated, it should have a higher water-soluble Na content than mud, due to the release of guarded Na at high temperatures in the kiln.

Figure 6 also shows that the water-soluble sodium content in lime was somewhat higher when CNCG was burned than when it was not. This was probably due to the greater degree of sulphation of sodium compounds during the period when CNCG was burned. The resulting Na<sub>2</sub>SO<sub>4</sub> is more thermally stable than other sodium compounds (mostly Na<sub>2</sub>CO<sub>3</sub>) and thus more remains in the lime.



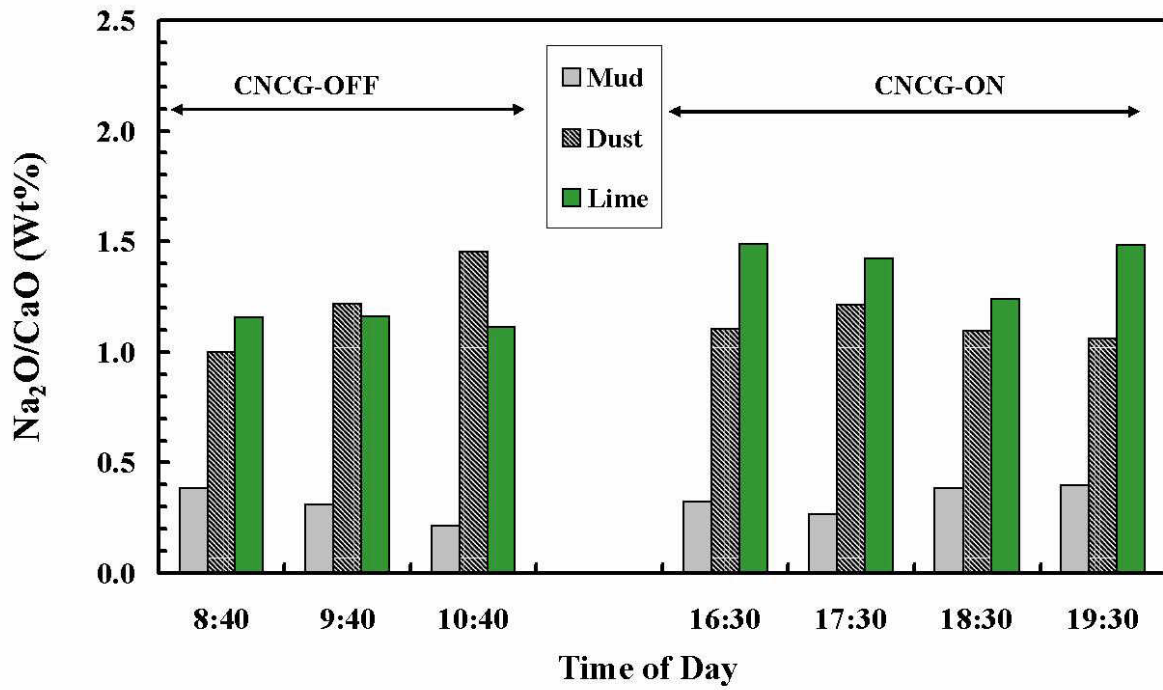


Figure 6. Normalized Water-soluble Sodium Content in Mud, Dust and Lime.

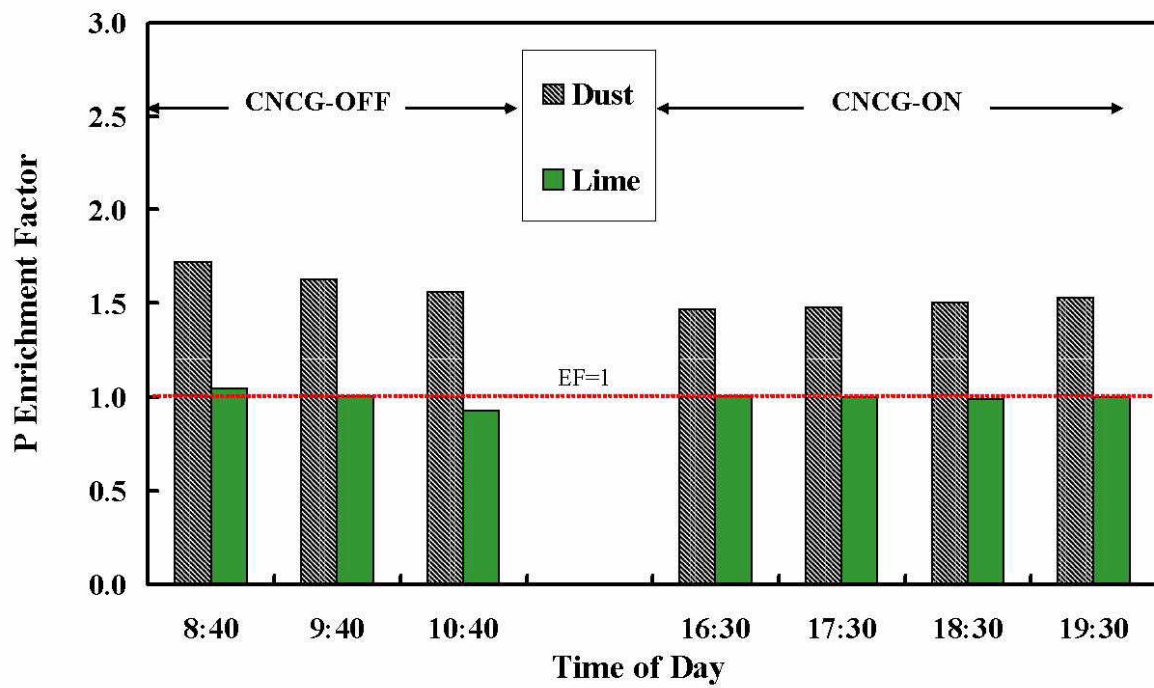


Figure 7. Phosphorous Enrichment Factor in Dust and Lime

## Phosphorus

There was a significant enrichment of phosphorus in all dust samples collected during both periods with and without CNCG and burning (Figure 7). This finding is difficult to explain, because unlike sodium compounds which may vaporize at high temperatures, phosphorus in lime mud is supposedly in the form of calcium phosphate, which is thermally stable. However, examination of the data in Table 1 shows that the  $P_2O_5/Na_2O$  molar ratio was similar (between 0.8 and 1.0) in all mud, dust and lime samples, while the  $P_2O_5/CaO$  molar ratio in dust samples was about 1.5 times higher than that in mud and lime samples. This means that phosphorus is more related to sodium than to calcium, and that phosphorus may be present as sodium phosphate in the lime mud, rather than as calcium phosphate.

## MASS BALANCE

Using the chemical analysis results in Table 1 and kiln operating data in Table 2, a mass balance was performed around the kiln to examine how CNCG burning may affect sodium and sulphur flows. The results are summarized in Table 3.

Sodium entered the kiln with lime mud and exited the kiln mainly with lime. The input amount was not significantly affected by CNCG burning. Sulphur, on the other hand, entered the kiln mainly with CNCG, methanol and fuel oil, and exited the kiln mainly with lime and flue gas. The sulphur input increased by a factor of almost three, from 54 kg/hr to 157 kg/h, during the time when CNCG was burned.

**Table 3.** Sodium and Sulphur Mass Balance

INPUT (kg/h)				
	Sodium		Sulphur	
	OFF	ON	OFF	ON
CNCG	OFF	ON	OFF	ON
Mud	98.9	99.6	7.1	7.2
Fuel oil	0	0	12.4	10.4
Methanol	0	0	34.7	33.9
CNCG	0	0	0	105.7
Total	98.9	99.6	54.2	157.2
OUTPUT (kg/h)				
	Sodium		Sulphur	
	OFF	ON	OFF	ON
CNCG	OFF	ON	OFF	ON
Lime	91.5	97.3	53.3	139.5
Flue gas	7.3	2.3	0.9	17.7
Total	98.9	99.6	54.2	157.2
S removal efficiency (%)			98.2	88.7

## IMPLICATIONS

The results of this study confirm that the sulphur in fuel oil, methanol and CNCG can be effectively captured as  $CaSO_4$  in the product lime solids. The sulphur removal efficiency, however, decreased markedly, from 98% to 89% of the total sulphur input, as a result of CNCG burning. This decrease in sulphur removal efficiency with an increase in sulphur input, despite the presence of a large amount of  $CaO$  in the kiln, is explainable. Since this is a gas-solid reaction, the  $CaSO_4$  layer formed on the surface of lime particles serves as a barrier through which  $SO_2$  must pass in order to react further with  $CaO$ . As illustrated in Figure 8, as the reaction proceeds, the lime particle becomes covered with an increasingly thicker and denser  $CaSO_4$  layer, making it difficult to capture more sulphur.

As the sulphur input to the kiln reaches a critical level, the sulphur removal efficiency decreases drastically, resulting in an abrupt increase in  $SO_2$  emissions. The critical sulphur input level may be different from kiln to kiln, depending on many factors. These includes the retention times of the flue gas and solids in the kiln, the temperature and  $O_2$  concentration in the flue gas, the size and hardness of the lime pellets, the dusting condition in the kiln, and the amount of fresh lime used.

Figure 9 shows the sulphur removal efficiency and SO<sub>2</sub> concentration in the kiln gas as a function of sulphur input in this study. Although the data was insufficient to determine the precise breakthrough point, it appears that for the Luiz Antonio kiln, the critical sulphur input level may be on the order of about 40 kg/hr.

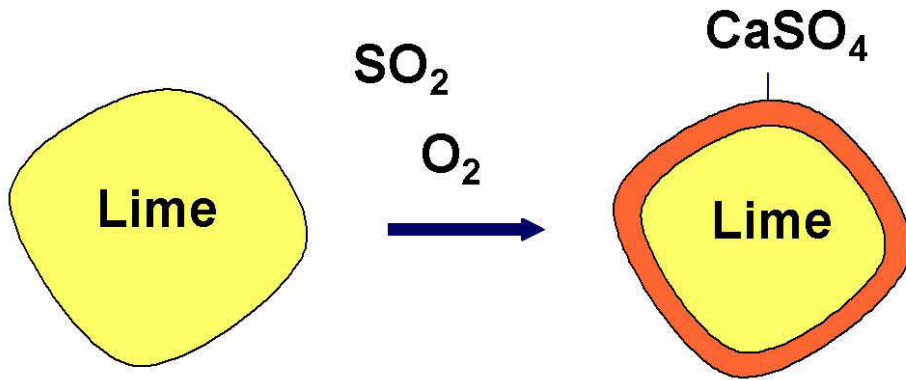


Figure 8. Formation of CaSO<sub>4</sub> on the Lime Particle Surface

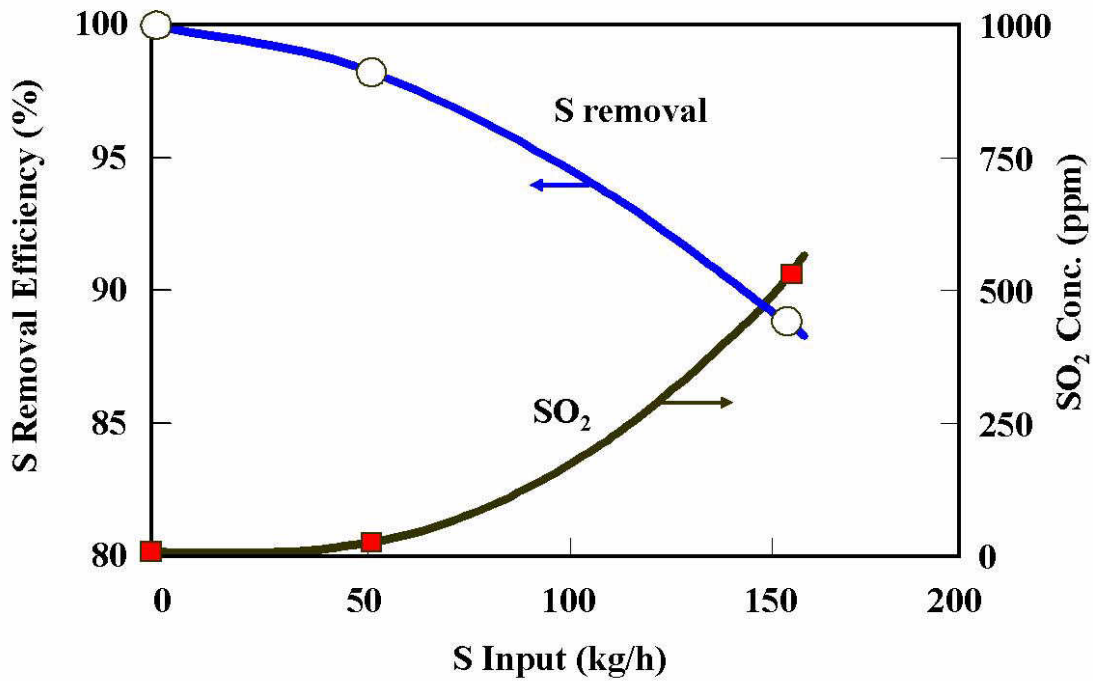


Figure 9. Effect of Sulphur Input on Removal Efficiency and SO<sub>2</sub> Emissions.

## SUMMARY

A systematic study was conducted to examine the effect of CNCG burning on lime kiln operation, product lime composition and gaseous emissions at the VCP Luiz Antonio mill. The results show that:

- While CNCG burning had no significant effect on kiln performance, it resulted in high SO<sub>2</sub> emissions from the kiln stack.
- Sulphur entered the kiln mainly with CNCG and methanol, and exited the kiln mainly with lime.
- Although lime can effectively remove SO<sub>2</sub>, the removal efficiency depends strongly on the total sulphur input to the kiln. Removal efficiency decreased from 98% of the total sulphur input when CNCG was not burned to 89% when CNCG was burned.
- There appears to be a critical sulphur input level, above which significant SO<sub>2</sub> emissions result. For the VCP-Luiz Antonio kiln, the critical sulphur input level was about 40 kg/hr.
- The water-soluble sodium content in lime was about 3 times higher than that in mud.

## ACKNOWLEDGEMENTS

This work is part of the research program, "Increasing Throughput and Reliability of Recovery Boilers and Lime Kilns", supported by Alstom Power Inc., Andritz, Aracruz Celulose S.A., Babcock & Wilcox Company, Boise Cascade Corporation, Bowater Canada Inc., Clyde-Bergemann Inc., Daishowa-Marubeni International Ltd., Domtar Inc., Georgia Pacific Corporation, International Paper Company, Irving Pulp & Paper Limited, Kvaerner Pulping Technologies, Stora Enso Research AB, Votorantim Celulose e Papel, MeadWestvaco Corporation, and Weyerhaeuser Paper Company.

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