ABSTRACT: A study was conducted at a Brazilian mill to examine the effects of CNCG burning on kiln operation, lime composition, and gaseous emissions. While CNCG burning had no significant effect on kiln performance, it caused high SO$_2$ emissions from the kiln stack. Sulfur entered the kiln mainly with CNCG and methanol and exited the kiln mainly with lime. Although lime can effectively remove SO$_2$, the removal efficiency decreased from 98% of the total sulfur input when CNCG was not burned to 89% when CNCG was burned in the kiln. For this kiln, the critical sulfur input level, above which excessive SO$_2$ emissions occur, was about 40 kg/h.

Application: Burning CNCG has little or no effect on kiln performance, but it can lead to high SO$_2$ emissions.

BACKGROUND
Malodorous noncondensable gases (NCG) produced in the Kraft chemical recovery process contain large amounts of reduced sulfur compounds that must be treated before being vented to the atmosphere. Noncondensable gases are burned in lime kilns, recovery boilers, bark boilers, or dedicated incinerators, depending on volume and concentration [1, 2]. Although in recent years there has been a trend toward burning NG in recovery boilers [3], the lime kiln is still the unit most commonly used.

Concentrated NCG (CNCG) has a high sulfur content. Consequently, burning CNCG is expected to have an effect on TRS and SO$_2$ emissions, as well as on the composition and quality of product lime.

In March 2001, we conducted a study to examine such effects at Votorantim Celulose e Papel (VCP), Luiz Antonio mill, Sao Paulo, Brazil. This mill has a unique CNCG delivery system. The gas stream is normally burned in the recovery boiler, but it can also be burned in the lime kiln in the event the boiler is unavailable [4]. This feature made it possible for us to study the effect of CNCG burning on either the recovery boiler operation, as previously reported [5], or on lime kiln operation by switching the CNCG stream back and forth between the boiler and the kiln. Here, we discuss the study procedure, the results, and the practical implications of the results.

STUDY PROCEDURE
The lime kiln at this mill is a 1991 F.L. Smidth unit, capable of producing 240 metric tons of CaO per day. The kiln is 2.69 m in internal diameter by 90 m long. It is equipped with product coolers and a lime mud flash drier that consists of a cyclone and an electrostatic precipitator (Fig. 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. Since then, however, CNCG has been burned mainly in the recovery boiler because of high SO$_2$ emissions from the kiln stack, difficulty in avoiding Total Reduced Sulphur gases (TRS) excursions, and the need to maximize CO$_2$ in the flue gas for precipitated calcium carbonate production.

We collected a total of seven sets of lime mud, dust, and product lime samples, for a total of 21 samples. Three of these sets 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$^3$/h, through a concentric duct, parallel to the primary air of the oil burner (Fig. 2). The CNCG burning continued for 9 h and ended at 20:00. To account for the 4–5 h retention time of the solids in the kiln, we collected the first set of samples with CNCG burning at 16:30 and collected three other sets at 17:30, 18:30, and 19:30.

RESULTS AND DISCUSSION
Chemical analysis
The 21 samples, along with samples of the crude oil and methanol, were subjected to chemical, thermal, and morphological analyses. Table 1 summarizes the chemical compositions for all lime mud, dust, and product lime samples collected, presenting the mean values for sets sampled prior to CNCG burning and for sets sampled during CNCG burning.

The crude oil sample collected during the study was found to contain 1.06 wt% S. This sulfur content is at the low end of the usual range of 1–4 wt% S for the crude oil used at the mill. There was little Na in methanol—about 3.5 ppm.

Although attempts were made to maintain kiln operating conditions as constant as possible, the average mud flow rate and mud solids when CNCG
was on (from 11:06 am to 8:00 pm) were respectively 1.1% and 2.4% higher when CNCG was off, whereas the oil flow rate was 5% higher (Table II). This disproportional increase in the 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. However, additional heat input from CNCG burning may also have been a contributing factor.

The lime availability and residual CaCO₃ content were estimated based on the lime compositions for the 21 samples for mud, dust, and product lime. The availability was 90.3% during the period when CNCG was switched off and 88.6% when CNCG was being burned. The decrease was primarily due to the increased sulfur content of the lime as a result of calcium sulfate (CaSO₄) formation. The residual CaCO₃ content was slightly higher, at 4.3%, with CNCG burning, compared to 3.6% when CNCG was off. The increase was insignificant since it was within the normal range of the residual carbonate.

Effect on gaseous emissions
As shown in Table II. TRS, CO, and CO₂ emissions from the kiln were not affected by CNCG burning. The SO₂ concentration in the stack gas increased from 25 ppm to over 500 ppm during the CNCG burning period. The effect is clearly shown in Fig. 3.

Effect on solids composition
As expected, the sulfur content in the dust and the product lime was much higher when CNCG was burned than when it was not, as shown by the SO₃ measurements in Table I. All other components were not affected significantly by CNCG burning.

Sulfur. Figure 4 shows the enrichment factor, EF, for sulfur in dust and product lime, with and without CNCG burning. The 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 sulfur is defined as the ratio of the amount of sulfur in the sample, to the equivalent amount in the mud. Thus, a component is considered to be enriched if its EF is equal to 1, and depleted if its EF is less than 1.

When CNCG was off, the EF, for both dust and product lime was about 9, indicating that the sulfur content in the dust and product lime was 9 times higher than that in lime mud. At 25 ppm to over 500 ppm during the CNCG burning period. This increase in sulfur enrichment was caused by dust and lime particles capturing the SO₂ from the combustion of fuel oil or methanol. 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 sulfur from fuel oil, methanol, and CNCG.

Sodium. The enrichment factor for sodium in the mud, dust, and product lime did not vary significantly as a result of CNCG burning (Fig. 5). This outcome was expected since there was little or no sodium in the CNCG. There was, however, a significant enrichment of Na in the dust (EFₙₐ = 1.2 to 1.7), regardless of CNCG burning. Such enrichment was likely a result of the vaporization-condensation cycle 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.

The Na enrichment factor in the lime was 1 or slightly lower. This value means that the total Na content in the lime was about the same as, or slightly less than, the Na content in the mud when normalized for the amount of CaO in the sample. As shown in Fig. 6, however, the normalized water-soluble sodium content in the lime was 1.2–1.5 wt% Na₂O, 3–4 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 CaCO₃ 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, because of 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 outcome was probably caused by the greater degree of sulfation of sodium compounds when CNCG was being burned. The resulting Na₂SO₄ is more thermally stable than other sodium compounds (mostly Na₂CO₃), thus, more remains in the lime.

**Mass Balance**

Using the chemical analysis results and the kiln operating data, we performed a mass balance around the kiln to examine how CNCG burning may affect sodium and sulfur flows. The results are summarized in Table III.

Sodium entered the kiln with lime mud and exited the kiln mainly with lime. The input amount was not significantly affected by CNCG burning. Sulfur, 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 sulfur input increased by a factor of almost three, from 54 kg/h to 157 kg/h, while CNCG was being burned.

**Phosphorus.** There was a significant enrichment of phosphorus in all dust samples collected both with and without CNCG burning (Fig. 7). This finding is difficult to explain, because unlike sodium compounds that may vaporize at high temperatures, phosphorus in lime mud is supposedly in the form of calcium phosphate, which is thermally stable. However, the data in Table I show that the P₂O₅/Na₂O molar ratio was similar (between 0.8 and 1.0) in the mud, dust, and lime samples, while the P₂O₅/CaO molar ratio in dust samples was about 1.5 times higher than that in mud and lime samples. This outcome 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.
EMISSIONS MONITORING

III. Sodium and sulfur mass balances with CNCG burning switched on or off.

### IMPPLICATIONS

The results of this study confirm that the sulfur in fuel oil, methanol, and CNCG can be effectively captured as CaSO₄ in the product lime solids. The sulfur removal efficiency, however, decreased markedly, from 98% to 89% of the total sulfur input, as a result of CNCG burning.

There is an explanation for this decrease in sulfur removal efficiency with an increase in sulfur input, despite the presence of a large amount of CaO in the kiln. Since this is a gas-solid reaction, the CaSO₄ layer formed on the surface of lime particles serves as a barrier through which SO₂ must pass in order to react further with CaO. As illustrated in Fig. 8, as the reaction proceeds, the lime particle becomes covered with an increasingly thicker and denser CaSO₄ layer, making it difficult to capture more sulfur.

As the sulfur input to the kiln reaches a critical level, the sulfur removal efficiency decreases drastically, resulting in an abrupt increase in SO₂ emissions. The critical sulfur input level may be different from kiln to kiln, depending on many factors. Such factors include the retention times of the flue gas and solids in the kiln, the temperature of the flue gas, the O₂ 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 sulfur removal efficiency and SO₂ concentration in the kiln gas as a function of sulfur input in this study. Although the data were insufficient to determine the precise breakthrough point, the critical sulfur input level for this kiln appears to be about 40 kg/h.

### SUMMARY

We conducted a systematic study to examine the effect of CNCG burning on lime kiln operation, product lime composition, and gaseous emissions at the Luiz Antonio mill. From the results, we derived several insights.

While CNCG burning had no significant effect on kiln performance, it resulted in high SO₂ emissions from the kiln stack. Sulfur entered the kiln mainly with CNCG and methanol and exited the kiln mainly with lime.

Although lime can effectively remove SO₂, the removal efficiency depends strongly on the total sulfur input to the kiln. Removal efficiency decreased from 98% of the total sulfur input when CNCG was not burned to 89% when CNCG was burned.

There appears to be a critical sulfur input level, above which significant SO₂ emissions result. For the kiln in this study, the critical sulfur input level was about 40 kg/h.

Finally, the water-soluble sodium content in lime was about three times higher than that in mud.

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INSIGHTS FROM THE AUTHORS

To assess the effects of burning CNCG, we needed to be able to compare results obtained while burning CNCG with results obtained while not burning CNCG. Most lime kilns are not equipped with a CNCG delivery system that can send the CNCG elsewhere when the gases are not burned. The delivery system at the Luiz Antonio mill makes it possible to switch the CNCG stream back and forth between the lime kiln and the recovery boiler. This unique feature is probably the main reason why no study of this kind has been carried out before.

Three results were particularly interesting. First, the sulfur absorption in the lime kiln was relatively low, despite the large quantity of lime mud the kiln processed. Second, there was a sharp increase in SO₂ emissions from the lime kiln when the sulfur input reached a critical level. Third, phosphorus was enriched in the kiln dust.

Mill personnel should bear in mind that CNCG burning has no significant effect on kiln performance. However, the sulfur input in the kiln must be monitored to keep it below the critical level, or the SO₂ emissions from the kiln stack will rise sharply.

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