Complying with the kraft pulping process new source performance standard at five West Coast locations

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A review of the CEMS records from five lime kilns located at West Coast mills revealed improved adherence to new source performance standards.

The Environmental Protection Agency (EPA) kraft pulp mill new source performance standard (NSPS) lime kilns must satisfy is a total reduced sulfur (TRS) concentration in the emission of 8 ppm, standard dry conditions, corrected to 10% oxygen on a 12-h average basis (*1*). The limit is not related to kiln production or energy efficiency. Thus, efforts made to improve energy efficiency, which reduces gas volume emitted per unit of production, make the limit more restrictive. Periods of excess emissions must be reported semi-annually to the EPA. Some states require the submission of monthly summaries and prompt reporting of all periods of emissions in excess of the standard. Unlike the NSPS opacity and TRS limits for the recovery furnace, there is little guidance for interpreting the continuous emission monitoring system (CEMS) TRS record to help make a judgment on operation consistent with good air pollution control practices in the presence of excess emissions periods.

There are seven NSPS kilns in operation in the states of Oregon, Washington, and California. Selected CEMS TRS records were reviewed on the history of compliance with the NSPS. Where possible, causticizer or kiln operating conditions that were responsible for the excursions are presented. Modifications made to the systems and changes in operation that led to improvements in continuity of compliance with the limit will also be covered.

The quality assurance criteria TRS CEMS must satisfy will be discussed as well as the role of the causticizing system in producing a mud of low residual soluble sulfides to lessen the potential for kiln TRS excursions. At a number of locations, the kiln is depended upon for incineration of TRS in the digester and evaporator noncondensible gases. This practice increases the probability for the occurrence of excess emission periods, especially for energy efficient units. Justification for considering periods of excess emissions individually, reasons for the event, options for control, and time necessary to respond to an excursion before a judgment is made on whether the excursion should be considered a violation will be apparent.

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Monitoring system specifications

TRS monitoring systems on new sources must satisfy NSPS performance specification 5 (PS 5) before being placed in service (*2*). A day-to-day quality assurance check is part of PS 5. Appendix F of the NSPS presents the day-to-day specifications that reference methods CEMS quality assurance programs must satisfy (*3*).

TRS CEMS are considered performance monitors rather than reference method monitors. While the record generated by CEMS in the performance monitor category is satisfactory to make a judgment on source operation in a manner consistent with good air pollution control practices, these are not considered equivalent to compliance tests (*4*).

The elements of PS 5 are summarized in **Table I**. The instrument span for CEMS on kilns is 30 ppm(v). The system must be subjected to and satisfy a 7-consecutive day, 24-h calibration drift specification at two points: between 0% and 20% scale and between 50% and 80% scale. These drift checks cannot exceed 5% of span or 1.5 ppm(v) in six of the seven days. An on-stack relative accuracy comparison to the reference method must be conducted and be within 10% of span or 20% of the standard, whichever is greater (*2*). Once the system is on the stack, a minimum of one daily drift test must be conducted at between 50% and 80% of scale and an adjustment made to the instrument when drift exceeds twice that of PS 5 or 3.0 ppm(v).

Appendix F requires that quarterly audits be performed, three of which challenge the system with a Bureau of Standards traceable reference material. The fourth audit is a relative accuracy comparison to the reference method. Appendix F includes specifications for identification of a CEMS operating in an out-of-control manner. These are: (a) a 24-h challenge that is in excess of four times the calibration drift specification (6.0 ppm) and (b)

I. Performance Specification 5

Instrument span	
Recovery furnaces and kilns	30.0 ppm
Cross recovery furnaces	50.0 ppm
Seven-day calibration drift challenge at 24-h intervals	
Challenge points	
Downscale check	0–20% scale
Upscale check	50–80% scale
Specification	
Not to exceed 5% of scale in more than one of seven consecutive days	
Relative accuracy specification (whichever is greatest)	
±20% of the limit	
±10% of scale	
Daily calibration check	
At minimum 24-h intervals	
At between 50% and 80% of scale	
Instrument adjustment required if drift exceeds two times performance specification	

II. Pertinent process information

Source control	Mud washing system	Causticizing description	Monitor	Mud solids, %
A scrubber	New/ext.	New/ext.	DIL/PF	68–72
B scrubber	New	New	DIL/PF	68–72
C scrubber	New	New	DIL/CT	74–80
D ESP	New/ext.	New/ext.	GC/FPD	68–72
E ESP	New	New	DIL/PF	74–80

5-consecutive daily challenge drift responses that are more than twice that of PS 5 (3.0 ppm). Thus, the capability of a TRS CEMS for NSPS kilns is ±3.0 ppm.

Factors influencing kiln TRS emissions

Factors that influence kiln TRS emissions have been identified as:

- Residual soluble sulfides in the mud charged to the kiln
- Use of a solution that contains soluble sulfides at wet particulate capture systems
- Incomplete destruction of noncondensible gases if the kiln is used for this purpose
- Combustion conditions (*5*).

Quality specifications that the mud must satisfy to assure compliance with the TRS NSPS, other than essentially nondetectable soluble sulfides, have not been established.

Role of the kiln scrubber in TRS control

The potential for the use of caustic at wet particulate capture devices to elevate pH of the scrubbing solution and increase its capacity in the capture and retention of sulfides has been advanced as a strategy for control of TRS (*6*). However, this practice is not without potential for a negative effect on the ability to filter mud. Keep in mind that these scrubbers were designed for particulate capture rather than gas absorption. This is a practice that was used intermittently at two of the locations from which TRS CEMS records were reviewed. The importance of using a water supply free from soluble sulfides for make-up at the kiln scrubber is clear.

Potential for TRS loss at the kiln

Kilns that fire noncondensible gases accept a TRS load at the hot end of 0.5–1.5 lb of sulfur/ton of product (*7*). The soluble sulfide load at the mud dewatering system that is introduced to the cold end has been calculated and measured at about 6 lb/ton of lime for systems representative of current design practices (*6*).

A heat efficient kiln at the time the NSPS was developed had a minimum Btu consumption of about 8.0 million Btu/ton of product. Improvements in design for energy conservation have reduced this value to about 5.0 million Btu/ton of product, a 35% reduction in gas volume discharged per unit of production. The volume of gas emitted from the calcining of one ton of product for an oil fired kiln at a Btu input of 5.0 million is about 80,000 ft^3 at standard dry conditions corrected to 10% oxygen. At the regulatory limit of 8.0 ppm(v), this is equivalent to a TRS emission rate of less than 0.06 lb of sulfur/ton of lime. In effect, this requires complete destruction of the TRS in the noncondensible gases, if fired in the kiln, and either the washing or oxidation of at least 99% of the soluble sulfides in the mud at the precoat filter.

Control of soluble sulfides in lime mud

Residual soluble sulfides in the mud charged to the kiln are the most difficult to control and require the longest time for a process change to result in a lowering of TRS emissions. This requires careful control of the entire process from lime addition and operation of the causticizers, to design and operation of the mud washing system, to assure a product of high porosity at the dewatering device as well as a mud that is effectively washed and gravity thickened to maintain a minimum sulfide and soda load to the filter. This is necessary to assure ideal conditions for oxidation and washing of residual sulfides in the mud at the dewatering device. All systems examined in this exercise used precoat filters for mud dewatering.

Surrogate indicators of an effective causticizer and washer operation are: (a) a cake charged to the kiln at 75% solids and higher and (b) a fresh water addition rate on the filter sufficient to displace the moisture in the mud charged to the kiln. Experience has shown centrifuges to be ineffective unless complemented with a mud oxidation system.

Control of combustion conditions

Some energy efficient kilns are operated at excess oxygen contents in the exit gas, as measured in the kiln proper,

III. Summary of TRS CEMS records from five mills

Source and year	Time kiln operated, %	Time monitor operated, %	No. of TRS excursions
A 1986	63-100	91-100	0-4
A 1987	78-100	76-100	0-3
A 1988	18-100	95-100	0-3
B 1986	63-100	94-100	0-3
B 1987	77-100	93-100	0-1
B 1988	67-100	87-100	0-3
C 1986	81-100	92-100	None
C 1987	85-100	100	None
C 1988	55-100	70-100	None
D 1986	84-100	92-100	0-10
D 1987	66-100	76-100	0-5
D 1988	77-100	94-100	0-1
E 1986	89-100	6-100	0-5
E 1987	60-100	78-100	0-1
E 1988	60-100	77-100	0-12

IV. Magnitude of three highest annual excursions, ppm

Source and year	First highest	Second highest	Third highest	Total
A 1986	23	9.5	9.0	12
A 1987	9.5	8.7	8.6	5
A 1988	9.5	9.0	8.9	6
B 1986	16	13	12	13
B 1987	11	10	9	6
B 1988	40	16	13	10
D 1986	13	12	12	41
D 1987	12	11	10	15
D 1988	9	9	9	3
E 1986	15	14	10	19
E 1987	20	11	10	5
E 1988	37	36	24	16

of about 2%. Firing a kiln that is also used for incineration of noncondensible gases at these conditions can result in the escape of TRS due to normal changes in the quality of noncondensible gases. There is a need for quick responses to changes in combustion conditions to assure destruction of TRS in the kiln combustion zone. Associated TRS excursions can be corrected quickly by adjustment of combustion conditions. These conditions can be sensed and corrected by the measurement of both oxygen and carbon monoxide in the exit gas. A TRS increase associated with an elevation in carbon monoxide concentration may be corrected by adjusting combustion air. These two measurements give the operator the tool necessary to determine if the excursion may be associated with firing conditions or for some other reason.

Pertinent process information

Permanent causticizing, mud washing system, and CEMS information at the five sites where CEMS records were reviewed is presented in **Table II**. These were all similar and representative of current design parameters associated with new generation systems. Of the kilns from which TRS CEMS records were obtained for review, the units identified as D and E were equipped with electrostatic precipitators (ESP) for particulate control, while the other three used scrubbers. The two ESP equipped kilns were not used for incineration of noncondensible gases; those equipped with scrubbers were. The lime mud washing and causticizing systems serving kilns A and D were a combination of new construction and existing facilities.

All but two of the kilns dried and calcined a mud at from 74% to 80% solids content. Two of the kilns processed lime mud in the solids range of 68% to 72%. The solids content of the mud from these two systems was not related to differences in sizing of the washers, causticizers, or mud dewatering devices. The mud solids differences may have been due to the method of pumping, source of make-up chemical, or subtle impurities in the mud. A notable difference in particle size distribution between the products dewatered at locations D and C was measured (*8*).

One unit was equipped with a reference method 16 CEMS. The four remaining systems diluted the gas stream prior to detection of the TRS components in the sample gas as SO_2 after combustion. Three of these CEMS detected SO_2 by pulsed fluorescence (PF), and one used the coulometric titration (CT) principle.

Performance

The five kilns selected for TRS record review had CEMS that had satisfied PS 5 and had been in operation for three years. This length of record was necessary to identify trends as well as changes made in the process that reduced the number of excess emissions periods experienced. A summary of TRS monitor uptime is presented in **Table III**. The range of excess emission periods reported on a monthly basis is also summarized.

Monitor on-line time

During 1986, the CEMS on source E was on-line as low as 6% of the time on a monthly basis. This was due to the unit obtaining its sample ahead of the particulate control system. The monitor was located here because the mill was using two stacks at the exit of the device, one serving for each compartment of the ESP. The state regulatory agency, based on successful experience in operation of a CEMS on gas ahead of a particulate capture device at another site, insisted the sample be obtained from this point or that the mill install a CEMS on each stack on the clean gas side. Once these unsolvable difficulties were sufficiently documented and the cost of a second monitor considered, permission was granted to locate the probe on one of the stacks following the particulate control device. The reference source on which successful experience had been obtained chose to make the same change to reduce CEMS downtime and maintenance expense. Once this change was made, monitors for all sources on a monthly basis were always on-line more than 75% of the time, with the exception of the CEMS at site C for one month in 1988.

At site C, the monitor was on-line 100% of the time the kiln was in operation during 1987. On an annual average basis, these units would have satisfied a 90% on-line criteria.

Periods of excess emissions recorded

During the three-year interval reviewed, the kiln at site C recorded no 12-h periods in excess of the NSPS TRS limit. This record was not duplicated at either of the other four sites. This kiln was processing mud with a solids content of 75–80% and fired noncondensible gases via an independent nozzle. At this site, both kraft and sulfite pulp is manufactured. Causticizer dregs and kiln particulate control scrubber water are used for effluent neutralization. Lime make-up to the causticizing system is reported at 35 lb/ton of pulp.

Before proceeding further with analysis of the TRS monitoring records obtained, the magnitude of the three highest events in individual years for the four sources with excess emissions were compiled. This information is summarized in **Table IV**. When the CEMS measured excess emission values were compared to the 24-h challenge recovery specification of 3.0 ppm(v), most of the periods reported would be questioned and considered minor.

Three periods stand out by reviewing the records in this manner:

1. The 23-ppm value measured at site A in 1986
2. The 40-ppm excursion at site B in 1988
3. The three high values reported in 1988 at site E as well as the number of excursions recorded in 1988 as compared to 1987.

When considering the potential for the release of soluble sulfides remaining in the dewatered mud at the cold end of the kiln and control of combustion conditions, there is some question whether any of the excess emissions reported were outside of what could be expected from prudent operation of a system this complex.

The mud solids content to the kiln at site E was similar to that at site C. The number of TRS events at site E was as high as 12 in an individual month during 1988. These 12 periods were traced to an accumulation of inert solids in the mud washing system that reduced the solids content of the kiln feed to less than 70%. This was judged responsible for the carryover of soluble sulfides to the kiln and for the TRS excursions reported. It took better than one week for the system to flush itself once the difficulty was noticed and corrective action taken. To avoid repetition of this abnormal operation, the source increased frequency of mud testing. Excluding that period from the record would have lowered the maximum number of monthly excursions to three during 1988.

Most of the 19 events at site E during 1986 were associated with operation of the precoat filter. There seemed to be a correlation between TRS excess emissions and solids in the mud from the filter. By increasing the frequency of precoat replacement, this problem was solved and its effectiveness documented in 1987 and 1988.

The 23-ppm excursion in 1986 at site A was related to an identified design condition that permitted precoat filter filtrate to enter the scrubber solution recirculation well. Plumbing changes solved that problem.

All other excess emission periods reported for site A during 1986 were close to the compliance value. At this location, caustic may be added at the scrubber; this is done when an excess emission period is anticipated. The addition rate is about 3 lb/ton of kiln product. Excess scrubbing solution is routed to dilute the mud washer underflow to the precoat filter, returning the soda added to the process at this point. This kiln calcined a mud of 68–72% solids content and, as expected, operated close to the regulatory limit.

The changes made to the kiln to improve combustion efficiency reduced energy consumption by about 30% and settling of the mud in the clarifiers was reported to have improved significantly. Mill personnel believe this is also responsible for a change in particle characteristics and improved mud filtering, which has resulted in an increase in the solids content of the mud charged to the kiln by four percentage points. Periods of caustic addition at the scrubber have been reduced (*8*). Only one excess emission period was recorded following this modification. Most of the other excursions reported at site A were judged to be associated with either (a) a lime mud of low solids content or (b) a kiln operated with low residual oxygen in the exit gas.

The 40-ppm excursion in 1988 at site B was believed to be associated with the piping of a high-sulfide stream directly to the scrubber for a short period of time. Maintenance had been in progress at the scrubber prior to the excursion, and an effort was made to keep the system in operation during the repair. The short response time to correct the excursion as well as a verification of combustion conditions at the time revealed the temporary use of a high-sulfide stream at the scrubber as responsible for the excursion. The actual piping changes made during the repair could not be verified.

There was a notable reduction in the number of excess emissions periods recorded at site D from 1986 to 1988. This change corresponded to:

- An increase in the use of fresh water at the precoat filter showers
- Better control of kiln firing conditions
- The option to add peroxide at the precoat filter to aid in oxidation of residual sulfides in the cake during periods when a TRS excursion was anticipated (*9*).

Peroxide bleaching is practiced at this mill. An ESP is used for particulate control at this site, and the option for TRS capture at this point is not available. Noncondensible gases are not burned in the kiln. Due to the high moisture content of the mud charged to this kiln, the TRS record indicated this unit to be operating closer to the limit than the other four. The reason for the low solids content of the mud charged to the kiln was judged to be related to particle size distribution in the mud washing system. The particle size distribution of the mud at site D was substantially less than at site C (*10*). Conditions responsible for this difference are not known.

The records did not indicate a significant difference in TRS excursions between kilns equipped with scrubbers and ESPs. While wet systems offer the opportunity for elevation of solution pH for capture and retention of some TRS gases, control of combustion conditions and the calcination of a mud of low residual sulfides at the two sites equipped with ESPs produced similar compliance records.

From a review of conditions responsible for the TRS excess emission periods at these five sites, it appears that the kiln NSPS TRS limit for the complex system should not be interpreted on a "shall not exceed basis." The need to consider conditions responsible for individual excursions is indicated prior to making a decision on compliance.

Summary

The CEMS TRS record for five NSPS kilns on the West Coast were reviewed for the three-year period from 1986 through 1988. An improvement in operation within the NSPS limit was noticed at all sites.

Excess emissions were traced to:

- High soluble sulfides in the particulate control scrubber solution
- Low fresh water application rate at the precoat filter
- Changes in combustion conditions due to the firing of noncondensible gases in the kiln.

TRS excursion frequency at units equipped with scrubbers and ESP were similar.

The records indicated that unexplainable excursions were recorded and that excess emissions in this category were close to the NSPS limit. Frequency of unexplained excursions was less than 2% of the total number of monitoring periods on an annual basis. Since some of the factors that must be satisfied for washing and oxidation of residual soluble sulfides in the mud at the dewatering device are not totally understood, some TRS excursions associated with the carryover of soluble sulfides to the cold end of the kiln cannot be explained. Hence, these periods should be considered as within the norms of good operation for these complex systems.

Where the kiln is used for the incineration of noncondensible gases, essentially complete destruction of the sulfides is necessary to attain compliance with the limit. This requires timely sensing of and response to combustion conditions, especially for energy efficient kilns.□

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