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Formation and Techniques for Control of Sulfur Dioxide and Other Sulfur Compounds in Portland Cement Kiln Systems

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KEYWORDS

Portland cement, kiln, sulfur, sulfur dioxide, sulfur oxides, SO₂, formation, control, technology

ABSTRACT

This report presents the chemical and physical factors governing the generation of sulfur dioxide (SO₂), its transformation into other sulfur compounds, and the removal of sulfur oxides within the cement kiln system. Sulfur in cement kilns is derived from both kiln feed and from the kiln fuel. The form of the sulfur dictates the location in the kiln where the SO₂ generation takes place. Sulfur in the fuel is oxidized in the burning zone or calciner, and is easily removed by reactive lime present in the kiln. Kiln feed sulfur may be in the form of elemental sulfur, organic sulfur compounds, sulfides (either simple sulfides or polysulfides, such as pyrites), or sulfates. When present in the form of sulfate, it usually does not form SO₂ but rather leaves the kiln system with the clinker. When present in any of the other forms, it may be oxidized to SO₂. Several control techniques were evaluated including: inherent SO₂ removal in rotary kilns, inherent SO₂ removal by in-line raw mills, process alterations, dry reagent injection, hot meal injection, spray dryer absorber, and wet SO₂ scrubber.

REFERENCE

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EXECUTIVE SUMMARY

This report presents the chemical and physical factors governing the generation of sulfur dioxide (SO₂), its transformation into other sulfur compounds, and the removal of sulfur oxides within the portland cement kiln system. Sulfur in cement kilns is derived from both kiln feed and kiln fuel. The form of the sulfur dictates the location in the kiln where the SO₂ generation takes place. Sulfur in the fuel is oxidized in the burning zone or calciner, and is easily removed by reactive lime present in the kiln. Kiln feed sulfur may be in the form of elemental sulfur, organic sulfur compounds, sulfides (either simple sulfides or polysulfides, such as pyrites), or sulfates. When present in the sulfate form, it usually does not form SO₂ but rather leaves the kiln system with the clinker. When present in any of the other forms, it is oxidized to SO₂, generally in the temperature range of 300-600°C [570-1,110°F]. Sulfur compounds undergo transformation as the zones of the kiln change:

- In the burning zone, SO₂ and alkali sulfates are the most stable forms; the alkali sulfates usually remain with the clinker.
- In the upper transition zone, sulfates become relatively more stable.
- The calcining zone has optimum conditions for the capture of SO₂.
- In the preheat and drying zones, SO₂ capture is slower.
- In-line raw mills, despite their low operating temperature, are often highly efficient SO₂ scrubbers, due in part to the abundance of freshly generated limestone surfaces from grinding.
- There usually also will be some SO₂ removal by the kiln dust collector, with the remainder being emitted into the atmosphere.

Although the capture of SO₂ by lime becomes increasingly favorable as the temperature decreases, the rate of the capture reaction actually diminishes. It is the resultant of these two opposing factors that dictates how much of the SO₂ is in fact captured within the process. Also important for the capture reaction is the nature of the scrubbing material—lime is far more efficient than limestone.

Data from the literature reveal that preheater and calciner kilns generally emit less SO₂ than do long kilns due to the far more intimate interaction between feed and flue gas in the more energy-efficient kilns—those having suspension preheaters. Another important factor is the excess oxygen (O₂). Low amounts of excess O₂ are often correlated with high SO₂ emissions. Also discussed is the effect of alkali/sulfur ratio on sulfur circulation, and hence, on emissions, and burnability (or the ease of formation of tricalcium silicate) of kiln feed. These parameters have important roles, as an easier-burning mix will result in lower sulfur volatility from the clinker. Chlorine chemically combines with alkali that could otherwise reduce sulfur circulation.

Many of the conclusions presented in the report were formulated or strengthened by visits to six operating cement manufacturing plants presently managing SO₂ emission issues. Control techniques for SO₂ emissions from kiln systems fall into three broad categories: inherent removal by the process, process alterations, and SO₂ scrubbing technologies. Raw material grinding and drying systems that use all or a portion of kiln gases for drying may accomplish substantial SO₂ removal because of the nature of the process. *Process alterations* reduce the amount of SO₂ generated while *scrubber technologies* capture SO₂ after it has been generated.

Due to the interaction of raw materials and kiln gases, rotary kiln systems have inherent SO₂ removal efficiencies ranging between 40-99% of the sulfur input to the system. The literature suggests that 50-70% of the remaining SO₂ will be removed from exhaust gases when passed through an in-line raw mill system.

Some kiln systems can potentially reduce the amount of SO₂ generated through the use of process alterations, such as equipment changes, alterations to operating procedures, and/or raw material or fuel changes. Equipment changes that may reduce SO₂ emission for some kiln systems include the installation of a burner system that provides for improved efficiency of combustion of the fuel and/or avoidance of flame impingement on the raw materials. An additional equipment change that may reduce SO₂ emissions for some kilns with a dual-string multistage preheater tower is the adjustment of the kiln feed distribution in the riser duct which more nearly equalizes the material flow rates and gas temperatures between the two bottom-stage cyclones. Operating alterations that may reduce SO₂ emissions include an appropriate arrangement of the burner system to provide the necessary O₂ for efficient combustion and flame orientation. It must be noted that oxidizing conditions in the burning zone that limit SO₂ emissions are favorable for the generation of nitrogen oxides (NO_x) in the rotary kiln.

Changing raw materials may also reduce sulfur dioxide emissions. If a raw material contains sulfide sulfur, organic sulfur or carbon, substituting another raw material that does not contain these compounds may reduce SO₂ emissions. If a single raw material component contains sulfide-bearing minerals, its replacement may minimize SO₂ emissions in most cases. If a single raw material component contains carbon that is responsible for decomposing sulfates into SO₂, replacing it may substantially reduce SO₂ emissions. Finally, if sulfur (and chloride) is present in excess of alkali on a molar basis, either reducing the sulfur (and/or chloride) input to the system or increasing the alkali input to the system may reduce SO₂ emissions. However, replacing one raw material with another raw material may not be economically feasible and increasing alkali input may not be possible because of product quality limits on total alkali concentration in the cement.

Scrubber technologies that capture SO₂ after it has been generated in the kiln system can be divided into four classes: dry reagent injection, hot meal injection, lime/limestone spray dryer absorber, and wet scrubbers. The overall sulfur capture efficiency is dependent on the type of absorbent injected, temperature of the injection zone, fineness of the absorbent, and residence time.

An example of a dry reagent system is the addition of calcium hydroxide (Ca(OH)₂) to the kiln feed or its injection in the riser duct between the two upper cyclones of a preheater. The removal efficiency for a dry reagent system is between 20-85% of the SO₂ in the off-gases. A hot meal injection system uses calcined material from the kiln system as a source of lime (CaO) for the absorption of SO₂. Kilns utilizing these systems have demonstrated an SO₂ reduction in the range of 0-30%.

A lime/limestone spray dryer system injects a slurry of lime or limestone into the conditioning tower of the preheater. The spray dryer SO₂ removal efficiency is between 50-90%. A few wet scrubber systems have been placed after the particulate matter control device (PMCD) with all or a portion of the exit gases passing through them. These gases are passed through a slurry of absorbent such as pulverized limestone. The efficiency of wet scrubber systems is estimated at 80-95%. A residual sludge is produced by a wet scrubber system. The high moisture concentration in the gases leaving the stack may lead to the formation of condensable particulates.

TABLE OF CONTENTS

	<u>Page</u>
Executive Summary	3
Table of Contents	5
List of Acronyms, Chemical Symbols, and Abbreviations	8
Part I. Sulfur Dioxide Formation Mechanisms	9
Introduction	9
Portland Cement and Its Manufacturing Process	9
Forms of Sulfur in the Cement Kiln System	12
Raw Materials	12
Fuels	14
Raw Mill	14
Preheat Zone	15
Calcining Zone	16
Upper Transition Zone	19
Burning Zone	21
Summary of Zones	24
Formation of Other Sulfur Compounds	24
Reduced Sulfur Species	25
Sulfur Emissions	26
AP-42 Emission Factors	26
Short-Duration Testing	27
Long-Term CEM Testing	27
PCA Database	28
Plant Studies	29
Plant A	29
Plant B	30
Plant C	33
Plant D	34
Plant E	36
Plant F	36
Part II. Sulfur Dioxide Control Technologies	37
Potential Sulfur Dioxide Control Technologies	37
Fuel Switching	37
Inherent Sulfur Dioxide Removal	37
Sulfur Dioxide Scrubbers	37
Evaluation of Sulfur Dioxide Control Technologies Applicable to Cement Kilns	38
Fuel Switching	38
Inherent Removal	39
Process Alterations in the Cement Manufacturing Industry	40
Sulfur Dioxide Scrubbers	43
Sulfur Dioxide Control Techniques Applicable to Cement Kilns	48
Acknowledgements	49
Bibliography	49
Appendix A – Equipment Schematics	52

LIST OF TABLES

	<u>Page</u>
Table 1. Principal Compounds in Portland Cement Clinker.....	11
Table 2. Emissions as a Function of Raw Mill Operation [Rose and Brentrup, 1995]	15
Table 4. 1982 Emissions of SO ₂ as a Function of Process Type [Nielsen and Jepsen, 1990].....	19
Table 5. Sulfur Distribution during Manufacture of White Cement [Borgholm, 1993].....	21
Table 6. Volatilities (ε)* for Alkalies from Kiln Feed, Hot Meal, and Hot Meal with Added Carbon [Garcia and Bonifay, 1986].....	23
Table 7. Formation and Removal of SO ₂ in the Various Zones of the Cement Kiln [Nielsen, 1991]	24
Table 8. USEPA AP-42 Document SO ₂ Emission Rates by Process Type [USEPA, 1995].....	27
Table 9. PCA Database of SO ₂ Emissions [Hawkins, 2001].....	28
Table 10. Average SO ₂ Emissions from 1982 PCA Survey, USEPA AP 42, and PCA Environmental database [Nielsen and Jepsen, 1990; USEPA, 1995; Hawkins, 2001]..	29
Table 11. Particle Size Distribution of Hot Meal, De-SO _x Material, and Bypass Dust, Plant B.	31
Table 12. Chemical Analysis of Hot Meal, “De-SO _x ” Material, and Bypass Dust, Plant B.....	32
Table 13. Analysis of Raw Materials for Plant “D” (Analyses on Ignited Basis)	35
Table 14. Inherent SO ₂ Removal in Rotary Kilns Producing Cement Clinker.....	39
Table 15. Inherent SO ₂ Removal in In-line Raw Mills.....	40
Table 16. Typical DynaWave Process Parameters	47
Table 17. SO ₂ Control Techniques Applicable to Cement Kilns.....	48
Table 18. Achievable SO ₂ Reduction Using Various Control Techniques	48

LIST OF FIGURES

	<u>Page</u>
Figure 1. Equilibrium constant vs. temperature for the scrubbing of SO ₂ by CaO from Silikattechnik 9 [E. Vogel, 1958, p. 361, 449, 502]	17
Figure 2. Log plot of the total pressure, in atmospheres of the decomposition products of various sulfates occurring in the cement kiln [Choi and Glasser, 1988]	20
Figure 3. Plant A preheater and bypass configuration	30

LIST OF ACRONYMS, CHEMICAL SYMBOLS, AND ABBREVIATIONS

acfm	actual cubic foot per minute
CaCO ₃	calcium carbonate, a major component of limestone
CaO	lime
Ca(OH) ₂	calcium hydroxide
CaSO ₄	anhydrite
2CaSO ₄ • K ₂ SO ₄	calcium langbeinite
CaSO ₄ • 2H ₂ O	gypsum
CO	carbon monoxide
ESP	electrostatic precipitator
FeS ₂	pyrite and/or marcasite
FGD	flue gas desulfurization
HAPs	hazardous air pollutants
ID fan	induced draft fan
KF	kiln feed
kg	kilogram
kg SO ₂ /mt clinker	kilograms SO ₂ per metric ton of clinker
K ₂ SO ₄	potassium sulfate
3K ₂ SO ₄ • Na ₂ SO ₄	apthitalite
lb	pound
lb/hr	pounds per hour
lb SO ₂ /st clinker	pounds SO ₂ per short ton of clinker
LOI	loss on ignition
MgCO ₃	magnesium carbonate
mg/Nm ³	milligrams per normal cubic meter
mt	metric ton
NaHCO ₃	sodium bicarbonate
NaOH	sodium hydroxide
Na ₂ SO ₄	sodium sulfate
NH ₃	ammonia
NO ₂	nitrogen dioxide
O ₂	oxygen
PCA	Portland Cement Association
PMCD	particulate matter control device
ppm	parts per million
ppmv	parts per million by volume
scfm	standard cubic feet per minute
SO ₂	sulfur dioxide
st	short ton
USEPA	United State Environmental Protection Agency

Formation and Techniques for Control of Sulfur Dioxide and Other Sulfur Compounds in Portland Cement Kiln Systems

by F. M. Miller^{*}, G. L. Young^{**}, and M. von Seebach^{***}

PART I. SULFUR DIOXIDE FORMATION MECHANISMS

INTRODUCTION

Sulfur in cement kilns is derived from both kiln feed and kiln fuel. The form of sulfur found in the kiln feed dictates the location in the kiln where sulfur dioxide (SO₂) generation takes place. In this report, chemical and physical factors governing the generation of SO₂, its transformation into other sulfur compounds, and removal of sulfur oxides within cement kiln systems will be discussed. Additionally, this report will provide some guidance as to the principles governing the fate of sulfur as well as some of the measures that can be taken to reduce emissions. In Part II of this report: "Sulfur Dioxide Control Technologies," control techniques are reviewed and those technologies applicable to portland cement kilns are identified and described.

To properly describe the principles of SO₂ formation, transformation, and removal, this report is divided into the following sections:

Part I: Sulfur Dioxide Formation Mechanisms

- Portland cement and its manufacturing process
- Forms of sulfur in the cement kiln system
- Sulfur emissions
- Plant studies

Part II: Sulfur Dioxide Control Technologies

- Potential SO₂ control techniques
- Evaluation of SO₂ control techniques applicable to cement kilns

PORTLAND CEMENT AND ITS MANUFACTURING PROCESS

Although the two words "cement" and "concrete" are used interchangeably in common parlance, portland cement is actually one of the ingredients composing concrete. Concrete, the widely used construction material consists of a mixture of 10-20% cement added to a blend of crushed stone or gravel, sand, and water. Other materials, such as chemical or mineral admixtures like fly ash,

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blast furnace slag, or silica fume, may also be used in modern concrete mixes. The water causes the hydration of the cement, which sets to a solid, durable mass. The compressive strength of concrete is chiefly a function of the water-to-cement ratio of the mix. Higher compressive strengths are achieved by increasing the amount of cement and reducing the water content of the mix, while at the same time ensuring that the mix has adequate fluidity.

Portland cement is manufactured from a mixture of naturally occurring raw materials. Limestone is typically about 80% of the raw mix and is the source of calcium in the form of calcium carbonate (CaCO_3). The remaining raw materials may include shale, clay, and/or sand as sources of silica and the necessary small amounts of alumina and iron. Some manufacturing facilities use industrial by-products, such as fly ash, steel slag, etc., to augment the quarried raw materials.

Cement is manufactured exclusively in rotary kilns in the United States, Canada, and other developed nations. Vertical kilns and other technologies are used in some developing countries, but those technologies will not be described in this paper. Modern rotary cement kilns are cylindrical, refractory-lined rotating steel ovens ranging in length from 60 to over 200 meters (200 to >650 feet) with a diameter of 3 to 7.5 meters (10 feet to 25 feet). The mixture of raw materials, also known as raw feed or kiln feed, enters the slightly elevated end of the kiln, and as the kiln slowly rotates, the raw feed tumbles down the length of the kiln toward the flame in the lower end of the kiln. The high temperature of the flame in the combustion zone heats the kiln feed to approximately $1,500^\circ\text{C}$ ($2,750^\circ\text{F}$) in order to chemically transform the CaCO_3 and lesser amounts of silica, alumina, and iron contained in the raw materials into lumps or balls of material called “clinker.” To heat the raw feed, the flame is fueled by pulverized coal, pulverized petroleum coke, natural gas, oil, and/or recycled materials burned for energy recovery.

The clinker falls from the kiln into the clinker cooler where circulating air quickly cools the material and freezes its crystal structure. The heated air from the cooler is used for combustion in the kiln. The cooled clinker is removed from the cooler and subsequently ground with a small amount of gypsum ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$, an agent that controls the setting time of the cement) or other additives into the fine gray powder that is portland cement.

Cement kilns can be classified into two main pyroprocessing types, wet or dry. The raw materials for a wet kiln are mixed and ground with water to produce a slurry. This slurry simplifies the blending of the kiln feed to produce a uniform chemical composition. The water evaporates from the raw feed as it passes down the length of the kiln before the ensuing chemical and physical transformations may occur.

The dry process kilns are further divided into three types: long dry, preheater, or precalciner. The long dry kiln is similar to the wet kiln with the exception that the raw materials enter the kiln as a dry powder. The preheater kiln also utilizes dry raw materials. Before the kiln feed enters the kiln, it passes through one or more cyclone-type vessels and associated riser ducts. The riser ducts transfer heat from the kiln exhaust gases into the raw feed, while the cyclones separate particles from gases. The hot gases rise through the preheater tower as the raw materials pass in a countercurrent pattern down through the vessels. Traditionally, the topmost vessel is numbered Stage I with the lowest vessel receiving the highest number, i.e., Stage IV.

A precalciner kiln usually has a series of preheater cyclones and risers to dry and heat the raw materials with the addition of a vessel known as a precalciner or calciner. A precalciner vessel is a secondary combustion zone outside of the kiln. Heat from the burning of fuel in this vessel nearly completes the first critically important chemical reaction produced in any cement

kiln, calcination. Calcination is the decomposition of CaCO_3 into carbon dioxide (CO_2) and calcium oxide (CaO).

As will be discussed in greater detail later in this paper, alkali and sulfur partially vaporize when exposed to the very high temperatures in the combustion zone of the kiln. In cases of elevated alkali and sulfur content in the raw materials, some preheater and precalciner kilns can accumulate these materials in the kiln system. If these compounds are not removed from the system, they will be discharged from the kiln system in the clinker. They can also create undesirable buildups or accretions in the pyroprocessing unit. In kilns with elevated alkali and sulfur contents in the raw materials, an alkali bypass duct is normally added to preheater and precalciner kilns to provide an outlet for removal of these volatile elements. Passage through the preheater allows for very efficient capture of these elements and subsequent reintroduction into the kiln. Removing a portion of the gas further reduces the amount of alkali and sulfur recirculating in the system, thereby decreasing the alkali and sulfur content in the clinker while also reducing the likelihood of undesirable buildups. The resulting dust cleaned from the alkali bypass exhaust gas is normally discarded.

The raw materials are first calcined regardless of the pyroprocessing system. Then, within the oxidizing environment of the kiln, CaO is combined with silica, alumina, and iron to form the four principal compounds that make up 90-95% of cement clinker by weight. These compounds are shown in Table 1 with their chemical formulas and the cement industry abbreviations.

Table 1. Principal Compounds in Portland Cement Clinker

Compound name	Chemical formula	Cement industry abbreviation
Tricalcium silicate	$3\text{CaO} \bullet \text{SiO}_2$	C_3S
Dicalcium silicate	$2\text{CaO} \bullet \text{SiO}_2$	C_2S
Tricalcium aluminate	$3\text{CaO} \bullet \text{Al}_2\text{O}_3$	C_3A
Tetracalcium aluminoferrite	$4\text{CaO} \bullet \text{Al}_2\text{O}_3 \bullet \text{Fe}_2\text{O}_3$	C_4AF

Various equipment or pyroprocessing zones can describe a kiln. For this paper the following zones are used:

- Raw Mill – Some dry process kiln systems utilize the hot gases from the kiln to dry the kiln feed, as it is being ground in the raw mill; such a raw mill is known as an in-line raw mill. This design ensures intimate interaction between the gas stream and the raw materials.
- Preheat Zone – The first reaction zone of a rotary kiln system is known as the preheat zone. It may be the top preheater stages of preheater or precalciner kilns or the first portion of the wet or long dry kilns. This zone accomplishes four tasks:
 1. The raw material temperature is raised to the water evaporation temperature 100°C (212°F);
 2. The free water is evaporated from the kiln feed;
 3. The chemically combined water is liberated from the clay minerals at a temperature of 550°C ($1,020^\circ\text{F}$) and greater; and

4. The raw materials are raised to the calcining temperature, approximately 800°C (1,470°F).
- Calcining Zone – The calcining zone is characterized as the point within the kiln system when the raw materials are undergoing calcination. In this zone, CO₂ is liberated from CaCO₃ and magnesium carbonate (MgCO₃) found in the kiln feed. The process of calcination fixes the temperature range at from 800-850°C (1,470-1,560°F).
 - Upper-Transition Zone – The upper-transition zone is the portion of the kiln where the raw material temperature is between 900-1,250°C (1,650-2,280°F). This is the location where the last of the kiln feed is calcined. Some of the CaO reacts with the silica, alumina, and iron. Physically, the transition zone is that portion of the kiln between the calcining zone (or precalciner) and the burning or clinkering zone of the kiln.
 - Burning Zone – The region when the raw materials have reached a temperature of 1,250-1,510°C (2,280-2,750°F) is described as the burning or clinkering zone. The final stages of the clinker compound formation occur in this zone, and some of the reactions are exothermic.

FORMS OF SULFUR IN THE CEMENT KILN SYSTEM

Depending on the temperature, excess oxygen (O₂) level, alkali level, chloride level, presence of carbon monoxide (CO) and/or other reducing species, and a number of other controlling factors, the forms of sulfur in the various zones of the cement kiln system can be highly variable. The fate of sulfur in a cement kiln system is dictated both by energy considerations (thermodynamics) and also by reaction rates (kinetics). Some of the variables are amenable to control, while others may require special action. This portion of the report will focus on the individual zones of the pyroprocessing system, and what forms of sulfur are present, decomposed, or formed.

Raw Materials

In raw materials [Rother and Rose, 1991; Nielsen and Jepsen, 1990; Bonn and Hasler, 1990; Goldmann et al, 1981], sulfur can exist in the form of metal sulfides, organic sulfur compounds, elemental sulfur, or sulfates. The kiln feed sulfides are usually iron sulfides, most commonly pyrite and marcasite (both FeS₂). Others are monosulfides (typified by FeS) belonging to the pyrrhotite group. All these sulfides are formed under reducing conditions during the formation of the deposit, and any included organic matter will be simultaneously pyrolyzed, sometimes all the way to carbon. For limestone deposits of this type, carbon contents of about 0.2-0.4 % may indicate the presence of reduced sulfur compounds. A portion of the sulfur that enters in the form of organic sulfur compounds or sulfides may be transformed into SO₂. Sulfides, such as pyrite, are oxidized in the temperature range 300-600°C (570-1,110°F) [Sprung, 1964; Steuch and Johansen, 1991; Rother and Rose, 1991; Nielsen and Jepsen, 1990; Bonn and Hasler, 1990; Wolter, 1987].

The sulfates most commonly found in raw materials are gypsum (CaSO₄ • 2H₂O) and anhydrite (CaSO₄), which are stable at temperatures below those prevailing in the burning zone of the kiln. By and large, sulfur that enters the kiln in the raw materials in the form of sulfates

will tend to be retained within the kiln system [Rother and Rose, 1991]. This will be discussed in more detail later. However, sulfides, such as pyrite, are oxidized in the temperature range 300-600°C (570-1,100°F) [Sprung, 1964; Steuch and Johansen, 1991; Rother and Rose, 1991; Nielsen and Jepsen, 1990; Bonn and Hasler, 1990; Wolter, 1987]. Wolter claims,

“It was found that in nearly all cases, SO₂ emissions are nearly independent of the sulfur input by the fuel or of sulfate recirculation between kiln and preheater. The SO₂ emissions in cement plants seem to be closely correlated exclusively to the amount of sulfides in the raw materials. A portion of the sulfides forms SO₂ during oxidation at temperatures between 400-600°C (750-1,110°F), preferably in cyclone Stage II.”

Steuch and Johansen [1991] have also found that most of the sulfur introduced (70-95%) to a cement kiln is not emitted as a gas, but is typically scrubbed out in the process. They also indicate that one of the main factors affecting SO₂ emission is the amount of sulfides and organic sulfur in the kiln feed. They cite as an example a preheater plant that experienced high SO₂ emissions. When the plant was designed and constructed, it had been projected that the sulfate equivalent of the alkalis in the mix would be tied up and not emitted, and that about half of the remaining sulfate would be tied up in the form of calcium sulfate. Actual emissions were considerably higher than expected, due to the pyritic source of the sulfur. The plant found that calcium hydroxide was the most effective scrubbing agent to remove this SO₂, and that it was effective when added to the kiln feed. Adding it to the raw mill or to the conditioning tower was less effective. In no case was the efficiency high. It was found important to be close to the dew point of the gases to obtain effective sulfur capture at temperatures significantly below calcination.

Although part of the SO₂ generated by pyrite oxidation is absorbed during its flow through the upper preheater stage(s), and, where applicable, the spray tower and the raw mill, the remaining SO₂ may still require additional measures to achieve further reduction. In the temperature range characteristic of the upper preheater stages, calcium is largely in the form of calcium carbonate. The only calcined lime (CaO) normally present is that carried back by the combustion gases from hotter kiln regions. Calcium carbonate is known to be a relatively inefficient dry scrubbing material for SO₂ at temperatures below about 600°C (1,110°F) [Ritzmann, 1971; Sprung, 1964; Bonn and Hasler, 1990]. The rate of the reaction is slow, particularly in the absence of water [Sprung, 1964], and the retention time in the kiln system before emission from the stack is quite short [Nielsen and Jepsen, 1990]. As a result, very high SO₂ emissions are possible; values of 1,400-1,700 milligrams per normal cubic meter (mg/Nm³) (500-600 ppm) with peaks to 3,000 mg/Nm³ (1,050 ppm) were found for one Swiss plant [Bonn and Hasler, 1990].

Not all authors agree that the efficiency is always this low. Goldman et al. [1981] indicate, at least in one case, that a single preheater cyclone stage has been shown to scrub out about 82% of the SO₂ generated from pyrites.

Organic sulfur and elemental sulfur are less usual than pyritic sulfur in cement raw materials. According to Goldman et al. [1981], the presence of organic carbon in raw materials is an indication that organic sulfur compounds are likely. This certainly has been the experience of one of the authors (Miller), with raw mixes containing organics in the form of kerogens (low-grade oil shales). When organic sulfur compounds are present, they behave similarly to pyrites in

that they are oxidized at low temperatures, making it difficult to remove the resulting SO₂. There is indeed some anecdotal evidence suggesting that such sulfur compounds may be oxidized to SO₂ at even lower temperatures than pyrites.

To summarize, the forms of sulfur in the raw materials are sulfides (such as pyrite), sulfates (such as gypsum), organic sulfur compounds, and very rarely, elemental sulfur.

Fuels

The forms of sulfur in fuels are the same as those in raw materials—sulfates, sulfides, and organic sulfur. However, the form of sulfur in fuels rarely affects emissions of SO₂ because the fuels are burned either in the burning zone of the kiln or in the calciner. The SO₂ produced in the burning zone of the kiln can be readily scrubbed out in the calcining zone or combined with alkalis in the burning or transition zones. In the calciner, abundant free CaO is available for scrubbing, and the temperature is optimum for the desulfurization reaction. The most important exceptions to this rule apply if:

- Combustion is carried out under reducing conditions, which severely curtail scrubbing efficiency (and also produces an inferior product),
- The burning zone is exceptionally hot, which may occur in kilns burning mixes of very hard burnability (mixes requiring high burning zone temperatures), or
- There is a substantial excess of sulfur (+ chlorine) over alkalis in the kiln charge. (This situation does not ordinarily apply unless unavoidable, since it has a negative impact on clinker quality.)

Raw Mill

In the raw mill, the process is continually generating fresh surfaces on limestone (CaCO₃) for potential reaction with SO₂ [Rother and Rose, 1991; Steuch and Johansen, 1991]. Furthermore, especially in roller mills, the relative humidity is often high, as the temperature in these regions of the pyroprocessing system often drops below 200°C (390°F). This combination of circumstances is quite favorable for removal of SO₂, despite the low temperature and the relatively slow reaction rate that characterize this temperature. Goldmann et al. [1981] conclude that when the kiln has a roller mill associated with it, the roller mill reportedly scrubs about half the SO₂ (other authors cite higher efficiencies). It is scrubbed out as calcium bisulfite, which is oxidized in the kiln to sulfuric acid and calcium sulfate. Sprung [1964] states that,

“with excess sulfur in the kiln gas phase, it still possible to reduce the SO₂ emissions to less than 160 mg/Nm³ if the off-gases are passed through a drying/grinding unit. SO₂ reacts there with calcite to form CaSO₄, accelerated by the high content of water vapor.”

Rother and Rose [1991] agree, stating that the moisture level of the gases may be approaching the dew point in the raw mill. Rose and Brentrup [1995] give a quantitative measure of the efficiency of the raw mill in scrubbing SO₂, shown here as Table 2. The mill is seen to remove some nitrogen dioxide (NO₂) from the gases as well as significant quantities of ammonia (NH₃). In this case, the raw mill scrubbed out over 61% of the SO₂.

Table 2. Emissions as a Function of Raw Mill Operation [Rose and Brentrup, 1995]

Compound	Emission with raw mill off, milligrams per normal cubic meter	Emission with raw mill on, milligrams per normal cubic meter	Total Emissions, metric tons/year
SO ₂	1,465	560	971
NO ₂	2,695	2,495	2,351
NH ₃	80	20	49

To summarize, in a raw mill that recovers heat from the gases from the pyroprocessing system, the CaCO₃ in the kiln feed scrubs out a substantial portion of the SO₂ from the process. The foregoing discussion applies principally to roller mills. While ball mills swept with preheater exit gases will indeed scrub out some of the SO₂ that enters them, the intimacy of interaction between gas stream and raw mix is of a lower order, and the efficiency of scrubbing will be correspondingly reduced. The literature provides insufficient information on ball mill efficiencies to permit a quantitative estimate.

A minor amount of SO₂ can also be captured in the dust collector. If a baghouse is used instead of a precipitator for dedusting combustion gases from the kiln, the efficiency may be somewhat better although no documentation for this intuitive conclusion has been found. Such sulfur removal as occurs here does so principally because of intimate gas-particle contact and because of high relative humidities.

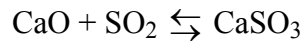
Preheat Zone

While the raw mill is fairly effective in removing SO₂ with CaCO₃, the preheat zone of the kiln, particularly at the lower temperature end, is much less efficient. This is due to the combined effects of low relative humidity and temperature. No new limestone surface is being generated. Also, as indicated above, the amounts of CaO or Ca(OH)₂, both of which are more effective than CaCO₃, are very small. Sprung [1964] ran a number of laboratory tests that showed that in the temperature range of 400-500°C (750-930°F), SO₂ reacts with CaCO₃ forming CaSO₄. The degree of conversion increases with increasing temperature and increasing specific surface of the calcite (1,300-8,200 cm²/g). The presence of water vapor enhances the conversion. The activation energy can be determined from the temperature dependence of the reaction rate constant. It is 27.9 kcal/mol for the conversion of SO₂ to CaSO₄ in dry atmospheres, but only 18.7 kcal/mol for an atmosphere with 2% water vapor by volume. It is clear that water vapor catalytically enhances the degree of reaction of SO₂ with CaCO₃. Rother and Rose [1991] and Nielsen and Jepsen [1990] however, point out that in the temperature range of 300-600°C (570-1,110°F), in the top stages of the preheater, absorption conditions for SO₂ generated from oxidation of pyrites are poor, due to low temperature and the presence of only calcium carbonate as a scrubbing medium.

It should not be concluded that the top preheater stages are totally ineffectual. Bonn and Hasler [1990] found that the preheater scrubbed out 70% of the SO₂ liberated from the pyrite. The calcium sulfite that was the initial reaction product was effectively oxidized in the preheater and kiln above 450°C (840°F) so that SO₂ levels from this source were minimal. Freshly generated free lime or alkali oxides effectively remove most of the SO₂ that may be formed in

the kiln and again carried back to the preheater. The effectiveness of the capture is reflected in the fact that a reduction in the ratio of alkali-to-sulfur from the normal value of at least 1.0 to only 0.4 only increased SO₂ emissions by 8%. The advantage of preheater and calciner kilns, in this regard, is that the contact between flue gases and incoming material is much more efficient than in long kilns. Indeed, Nielsen [1991] provides data and rationale to show that the emissions should in fact be much less, and that the presence of pyrite in the raw mix is less problematic for preheater kilns. Although emissions from calciner kilns usually are lower than from long kilns, they may be higher than from preheater kilns because bypass gases will tend to be quenched (cooled rapidly), severely reducing the time (at favorable temperature) for the reaction of quicklime with SO₂ in the bypass.

For SO₂ removal, Vogel [1958] demonstrated that CaO should be more effective than CaCO₃. He showed that SO₂ reacts very readily with alkali or alkaline earth oxides in the presence of water to form salts. In the presence of dry CaO, the reaction reportedly occurs only above 300°C (570°F) in the following manner:



In summary, in the preheat zone, sulfides in the feed are oxidized to SO₂. Some of the SO₂ generated in this zone and some of the SO₂ from the burning process will be scrubbed out by the CaCO₃ in the kiln feed, together with small amounts of free CaO that are carried back from hotter zones by the combustion flue gases.

Calcining Zone

The calcining zone is the optimum place for dry scrubbing of SO₂ to occur. Rother and Rose [1991] indicate that the newly generated CaO is very reactive toward SO₂ in this region of high reaction rate and favorable thermodynamics. The reaction is optimum both with respect to rate and equilibrium in the 800-950°C range (1,470-1,740°F) typical of the lower preheater cyclone stages. Nielsen and Jepsen [1990] point out that preheater and calciner kilns have much lower SO₂ emissions than do long kilns, due in large part to the intimate contact between kiln exit gases and raw meal in the cyclones and riser ducts. In essence, the riser duct and the bottom cyclone stages reportedly act like fluidized beds. Steuch and Johansen [1991] provide the following data (Table 3), further confirming the high efficiency of the preheater in scrubbing SO₂.

Table 3. Measurements of SO₂ from Two Calciner Kilns with 30-40% Bypass [Steuch and Johansen 1991]

	SO ₂ Emissions, parts per million (ppmv)	
	Kiln A	Kiln B
After bypass	1,010 ± 720	3,200 ± 700
After preheater	135 ± 35	860 ± 60
% scrubbing efficiency	86.6	73.1

Ritzmann [1971] measured high removal efficiencies with raw meal at 800-850°C (1,470-1,560°F). The efficiency was better with a cyclone vessel as the reaction chamber rather than in a stationary apparatus. The efficiency of removal at higher and lower temperatures was far lower than in this optimum zone. Laboratory tests and phase thermodynamics calculations convinced Choi and Glasser [1988] that CaO and sulfur oxides could react very favorably in the temperature zone represented by the calcining zone of a cement kiln.

Vogel [1958] made a number of measurements of the reaction equilibrium of free lime and SO₂ to generate calcium sulfate and calcium sulfide. This is the reaction that is favored when the excess O₂ is very low. His results are plotted in Figure 1.

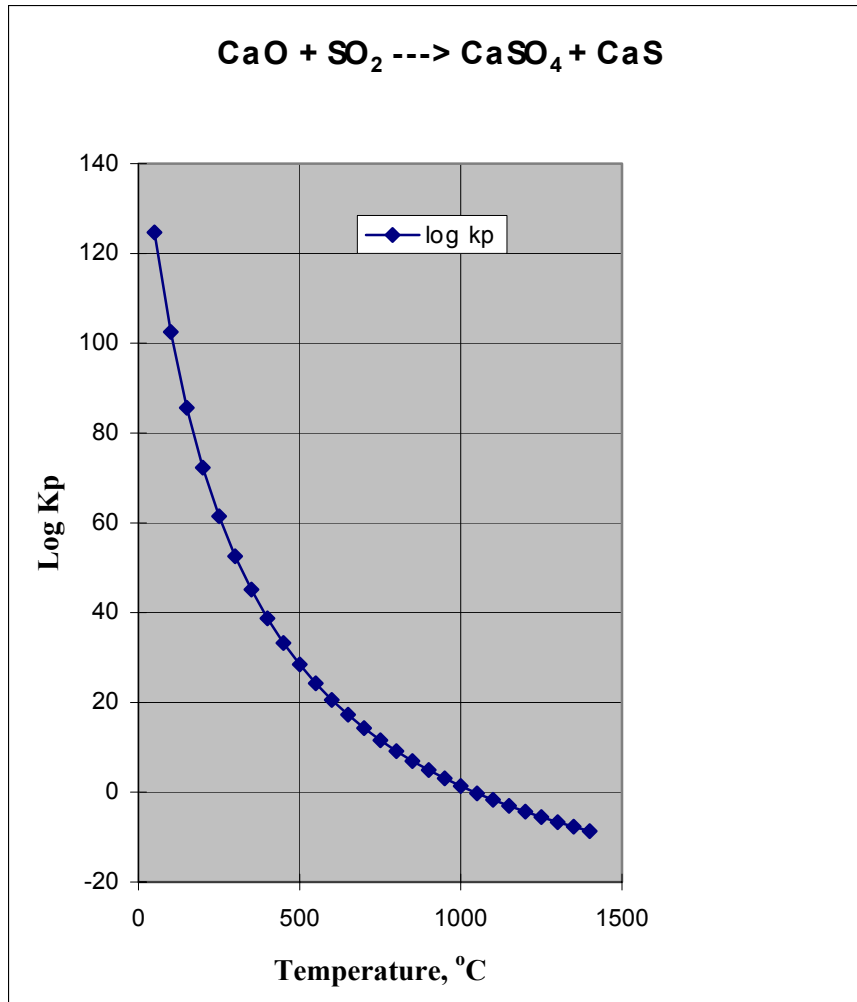


Figure 1. Equilibrium constant vs. temperature for the scrubbing of SO₂ by CaO from Silikattechnik 9 [E. Vogel, 1958, p. 361, 449, 502]

Where the value of log Kp is zero, the forward and reverse reactions are equally favorable. It is clear that above 1,045°C (1,910°F), calcium sulfate will tend to decompose, while below this temperature, the capture reaction is more favorable. The reaction is slow, however, below about 500°C (930°F). This further illustrates that the calcining zone is the optimum location for SO₂ removal.

The decomposition of calcium sulfate is also a function of the excess oxygen of the flue gases and, conversely, the CO concentration. Therefore, the scrubbing of SO₂ in the calcining zone is also strongly affected by these parameters. Lowes and Evans [1993] discuss the interrelationship of the levels of kiln exit oxygen, kiln exit CO, and SO₃ content of the Stage IV discharge material. The authors indicate that avoiding reducing conditions is a must for any wet or semi-wet kiln to meet SO₂ emissions regulations. While for a dry process kiln, reducing conditions do not necessarily increase SO₂ emissions to the same degree as in a wet kiln, considerable process problems occur due to sulfate deposits at the kiln inlet, in the riser duct and cyclones. Lowering the back end oxygen from 2%, which is normal, to 1.0-1.5% resulted in an increase of SO₂ emissions of about 50-800 ppm. The molar sulfur/alkali ratio was 1.0; alkalis were 0.6% in the clinker.

With a sulfur/alkali ratio of 2.0, a plot is given that shows that the SO₃ content of the Stage IV discharge material is a strong function of burning zone temperature, back end oxygen, and CO. The plant had found that operating at a Stage IV discharge SO₃ value of less than 3.5% by weight permitted stable operation. As the oxygen went up and the CO down, the Stage IV SO₃ increased with consequent buildup problems. An O₂ level of 2.5% gave 500 ppm CO, while 1.4% O₂ gave 2,500 ppm CO.

Hansen [1985], in his discussion of the use of CO as a process control parameter, offers some additional thoughts on the effect of CO on SO₂ emissions. In keeping with the results of Lowes and Evans [1993], he shows that modest increases in CO concentration at the bypass can significantly increase SO₂ emissions (a clear demonstration of the inhibition of the scrubbing reaction in the calcining zone, or of decomposition of CaSO₄ by CO).

Another factor that can reduce the efficiency of sulfur scrubbing in the calcining zone is the distribution of the hot meal in the riser ducts and cyclones at the bottom of the preheater. Schmidt et al. [1986] performed SO₂ emission measurements on a preheater kiln with a planetary cooler. At the same time, the values relevant to operation of the kiln were measured, stored, and evaluated. It was found that, because of irregular distribution of the meal in the riser duct to the two bottom cyclones, widely differing temperatures were established beyond these cyclones with the consequent SO₂ emission levels being relatively high. Structural changes that improved the meal distribution markedly reduced emissions. It was also found that even with less than 100% balance of the alkalis by sulfur in the clinker, high levels of SO₂ may occur in the calcining zone, partly as a result of high chloride circulation. Low SO₂ emissions occur nevertheless, because the good dispersion of the meal resulted in a high degree of desulfurization of the gases. The calcination reaction was promoted by the energy given off when desulfurization took place. Rother and Rose [1991] also make mention of the importance of good meal distribution for effective capture of SO₂.

Another piece of evidence that confirms the importance of the contact between CaO and SO₂ is the comparison of SO₂ emissions in lb. SO₂/short ton clinker as a function of process type. Nielsen and Jepsen [1990] provide the following, Table 4, which is taken from a Portland Cement Association (PCA) survey in 1982.

The contrast between long wet kilns, long dry kilns, and the preheater/calciner kilns is striking, as also noted by Steuch and Johansen [1991]. In long wet kilns, the contact between CaO and SO₂ is very limited. It may be a bit better on average for long dry kilns because these are more apt to be equipped with baghouses, which may capture acid gases more efficiently than electrostatic precipitators.

Table 4. 1982 Emissions of SO₂ as a Function of Process Type [Nielsen and Jepsen, 1990]

Kiln type	SO ₂ emissions, lb. SO ₂ /short ton clinker		
	Average	Standard deviation	Range
Wet	16.14	11.12	5 – 28
Long dry	7.83	5.82	2 – 13
Preheater	1.86	1.47	0.5 – 3
Calciner	2.41	4.79	0 – 8

With respect to the sulfur cycle and sulfur scrubbing in the calcining zone, Schmidt et al. [1986] further point out that the magnitude of this cycle in an oxidizing atmosphere is subject to an important control parameter—the length of time it takes for the meal to pass through a narrow temperature range, moreover in intensive contact with the rotary kiln gases containing SO₂. The temperature range in question is determined by the kiln feed composition and particle size distribution and also by the partial pressure of CO₂ in the kiln gas.

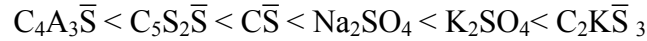
Goldmann et al. [1981] make reference to another reaction that may occur in or near the calcining zone. In dealing with the cyclic phenomena of sulfur capture and sulfur evolution in preheater/calciner kilns, one interesting result in this phase of the discussion is that the KCl content of the hot meal is lower than calculated, and the K₂SO₄ content higher. This would tend to provide support for the mechanism of generation of HCl from the reaction of SO₂ and KCl in the presence of oxygen and water vapor. This reaction has been confirmed in the laboratory [Miller, 1997]. In the calcining zone, some SO₂ may be formed by combustion of fuel in a calciner, or in the calcining zone of long kilns with mid-kiln fuel addition. If the calcining zone is operating under reducing conditions, some calcium sulfate may be decomposed to give CaO and SO₂. Mainly, though, under oxidizing conditions, the calcining zone is the portion of the pyroprocessing system where SO₂ removal is both fast and efficient.

Upper Transition Zone

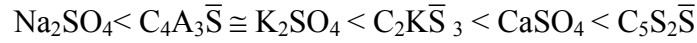
The upper transition zone is short, but is the focus of some important chemistry with respect to sulfur. According to Choi and Glasser [1988], thermodynamic calculations and measurements established that at increasing temperature, reduced species are more favored, and sulfides may survive into clinker. As the oxygen partial pressure increases, sulfites become more stable (but less and less stable at higher temperatures). SO₂ remains prominent in the vapor phase. As oxygen is further increased, sulfate solids, molten sulfates, and SO₃ gas are stabilized.

As has earlier been shown, the scrubbing of SO₂ by lime is no longer particularly favorable in this zone. However, alkali sulfates and alkali/calcium sulfates are very stable. Sulfur dioxide is combined with the alkalis in compounds like potassium sulfate (K₂SO₄), sodium sulfate (Na₂SO₄), calcium langbeinite (2CaSO₄ • K₂SO₄), and apthitalite (3K₂SO₄ • Na₂SO₄). The relative stabilities of various sulfur-containing compounds in the cement kiln, as a function of temperature, are outlined by Choi and Glasser [1988], and shown here as Figure 2 as a plot of the logarithm of the decomposition vapor pressure of sulfate phases as a function of the reciprocal temperature.

At lower temperatures (1,000°C [1,830°F]), the numerical order of increasing pressures is:



However, at 1400°C (2,550°F), it is:



As the temperature increases in the upper transition zone, the calcium sulfate and sulfate spurrite, as well as calcium sulfoaluminate, gradually are destabilized relative to the alkali containing phases.

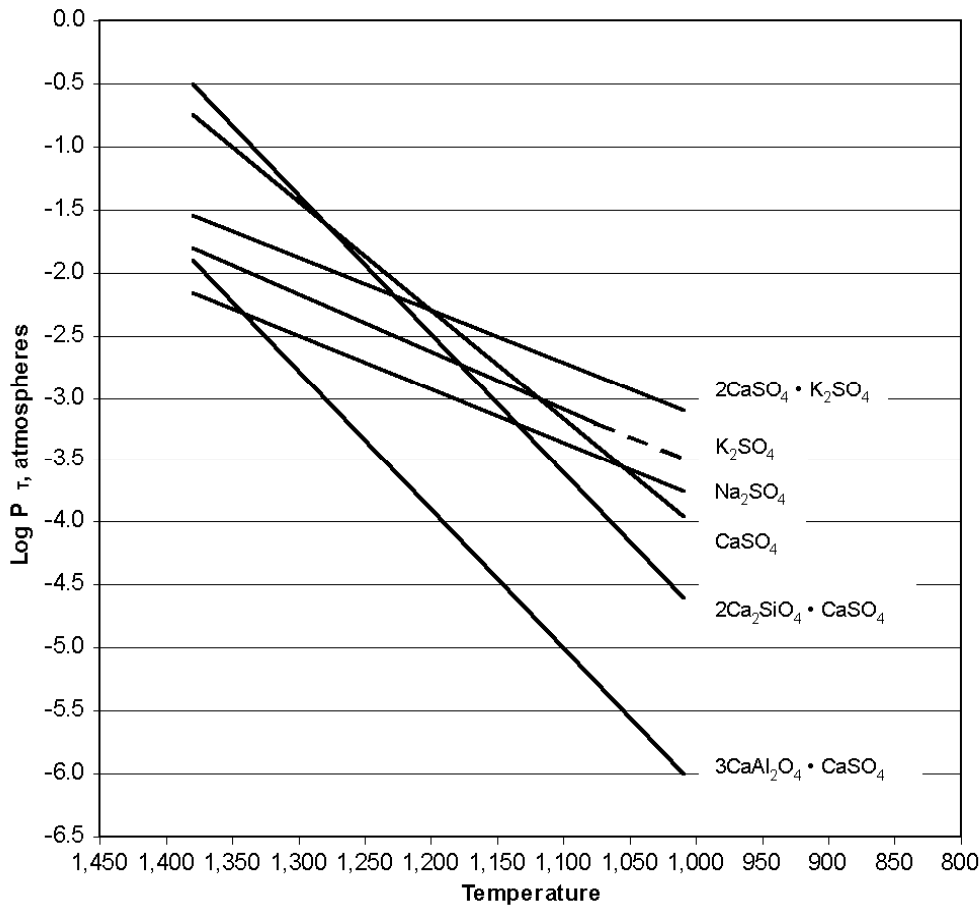


Figure 2. Log plot of the total pressure, in atmospheres of the decomposition products of various sulfates occurring in the cement kiln [Choi and Glasser, 1988]

As earlier noted, the decomposition reaction for anhydrite may occur in the upper transition or the burning zone, depending upon excess oxygen, temperature, and the presence of

CO. Lowes and Evans [1993] claim that anhydrite is stable thermodynamically up to around 1,450°C and even above in the presence of oxygen, as the dissociation is kinetically controlled. In the presence of CO levels of 2,000 ppm, the decomposition will begin above 1,000°C, resulting in substantially increased SO₃ concentrations in Stage IV. CO has a similar effect on the dissociation of alkali sulfates, but at higher temperatures.

In summary, in the upper transition zone some sulfur-containing intermediates, such as sulfate spurrite and possibly anhydrite may decompose to give SO₂ (depending on excess oxygen and CO contents). Some SO₂ will also become bound to alkali or calcium oxides.

Burning Zone

As earlier suggested, the sulfur volatility and circulation, and the amount of sulfur removed in the kiln, is a function of many variables. Included among these is the burnability of the kiln feed. If the feed is too hard to burn, the burning zone temperature will have to be increased to complete the formation of C₃S, which will tend to volatilize more of the alkali and sulfur content in the charge [Steuch and Johansen, 1991]. In an atypical, but elucidating example, Borgholm [1993] has described a system for production of white cement clinker in which four wet process kilns burned a very hard-burning feed with 78.1% C₃S, 14.9% C₂S, 4.3% C₃A, 0.97% C₄AF, and a silica ratio of 11. The raw materials are largely chalk and sand. There was about 0.3% iron oxide and less than 2% alumina in the mix, as well as extremely low alkali, so the sulfur was highly volatile. Because white cement cannot tolerate much fuel ash, the fuel chosen was a mixture of heavy fuel oil and high sulfur petroleum coke. The sulfur balance was as shown in Table 5.

Table 5. Sulfur Distribution during Manufacture of White Cement [Borgholm, 1993]

Parameter	Amount of sulfur	
	kilogram sulfur per 24 hours	Percent of total
Input to 4 kilns		
Kiln feed	96	0.89
Fuel	10,688	99.11
Total	10,784	100
Output from 4 kilns		
Clinker	370	0.34
ESP dust	3,023	28.03
Flue gas	7,391	68.54
Total	10,784	100

Clearly, more than two-thirds of the sulfur was emitted with the flue gases. The new system was a semi-wet system employing saturation of the flue gas with water, and showed

excellent sulfur control. This kiln, before modification, is an extreme example of sulfur emissions from the cement process, in view of the fact that the kilns were wet process, the burnability of the mix was so hard, and the amount of alkali was so low. The very high silica ratio also contributes to volatilization of the alkalis and sulfur.

Sulfur dioxide becomes increasingly stable relative to anhydrite and even alkali sulfates as the temperature increases, as shown earlier in the data of Vogel [1958]. Indeed, Choi and Glasser [1988] claim that SO_2 is the most stable sulfur compound at high temperature. However, as earlier indicated, the relative stability is also a function of other variables. At increasing temperature, reduced species are more favored, and sulfides rarely survive into clinker. As the oxygen partial pressure increases, sulfites become more stable (but less stable at higher temperatures). SO_2 remains prominent in the vapor phase. As oxygen is further increased, sulfate solids, molten sulfates, and SO_3 gas are stabilized.

Also, at temperatures above $1,250^\circ\text{C}$ ($2,280^\circ\text{F}$), decomposition of anhydrite, if still present, will increase rapidly, increasingly controlling the SO_2 and oxygen loss. The presence of SO_2 and oxygen in the kiln gas suppresses these reactions, as does the short residence time. Nonetheless, the processes occur.

The importance of the alkali level and type for sulfur volatility cannot be overstressed. Sprung [1964] carried out laboratory and field measurements to assess this issue. The alkali and sulfur content of the kilns investigated was presented in the form of an alkali-sulfur balance, from which the degree of conversion of the reactions between alkali and SO_2 in the kiln gas phase and in the inner cycle could be computed. From the kiln feed to the suspension preheater kilns, approximately 74-78% of the alkalis vaporized, while from the grate preheater kiln, only 53% were volatilized. In the kiln gas phase, the alkali oxides react with the SO_2 released from dissociation of the alkaline earth sulfates and from the combustion of the fuel, to form alkali sulfates, which make up the majority of the inner alkali and sulfur cycle. From the equilibrium constant for decomposition of the alkali and alkaline earth sulfates, as well as from microscopical observation and extraction tests, it follows that alkali sulfates are the most stable sulfur-containing phases and will leave the kiln with the clinker. The SO_2 content of the off-gases depends on the molar ratio of alkalis to sulfur; when alkalis are in excess, the SO_2 emissions will be extremely low. On the other hand, if the kiln gas phase contains an excess of sulfur, SO_2 emissions will increase. There is almost a linear relationship between the alkali/ SO_3 ratio in the kiln gas phase and the percent sulfur emitted as SO_2 .

Furthermore, the alkalis and sulfur are both more volatile when not combined as alkali sulfates. Sulfur in molar excess of the alkalis is always more volatile than that which is deficient to the alkalis, and alkalis in excess of sulfur are more volatile than alkalis balanced by sulfur. For example, Garcia and Bonifay [1986] studied the volatility of alkalis from the kiln feed, and also from the hot meal. The kiln feed contained very little sulfur, but the hot meal was essentially balanced. They also determined the volatility from the hot meal, when 3% carbon was added to it. The results are shown in Table 6.

The results clearly show high volatility of alkali from raw meal, low volatility from hot meal, and an increase in alkali (and sulfur) removal with carbon added to hot meal. The authors suggested control of SO_2 by stabilizing the burning zone temperature and the secondary air temperature. Oxygen and CO controls were not mentioned as control parameters.

Table 6. Volatilities (ϵ)* for Alkalies from Kiln Feed, Hot Meal, and Hot Meal with Added Carbon [Garcia and Bonifay, 1986]

Material	Additive	ϵ (15 minutes)	ϵ (30 minutes)
Kiln feed	None	0.82	0.90
Hot meal	None	0.24	0.36
Hot meal	3% carbon	0.64	0.82

*- ϵ is the fraction of the element volatilized in the burning zone

Further confirmation of the important interdependence of the alkali and sulfur volatilities, and the kiln feed burnability, is offered by Bonn and Hasler [1990]. They report that alkali sulfates circulate largely undecomposed in the kiln and are finally carried out with the clinker. Because of its decomposition in the sintering zone, calcium sulfate forms a recirculating system, which at higher concentrations leads to the formation of sulfate spurrite and fused salts. According to these authors, where there are sufficiently high partial pressures of SO_2 and O_2 , good nodulization, easy burnability, and a short flame with soft burning, calcium sulfate may leave the sintering zone undecomposed.

Kreft [1985] has emphasized an additional factor controlling the volatilization of alkalies and sulfur; this is the chloride content. Clearly, the presence of chlorine ties up potassium as the volatile potassium chloride (KCl). Any remaining potassium will form K_2SO_4 , after which the excess sulfur, which presumably forms CaSO_4 , will have a much higher volatility. Schmidt and co-workers [1986] conclude that the amount of sulfur that can be discharged with the clinker from a rotary kiln plant is primarily influenced by the SO_2 partial pressure in the burning zone. The partial pressure depends on the amount of sulfur that enters the kiln via the main burner and the amount of sulfur in the cycle between kiln and preheater. This means that, irrespective of the degree of sulfatization of the input materials, the SO_2 emission from the plant can be modified by control of the sulfur cycle between kiln and preheater.

The investigations show also that even with alkali/sulfur ratios greater than one, some of the sulfur supplied to the kiln is discharged with the cleaned gas, giving rise to increased SO_2 emission. The cause of this emission must be that incorporation of sulfur in the alkalies is impeded in the kiln due to large amounts of chloride in the kiln gases. This means that the partial pressure of SO_2 in the kiln must be raised if increased SO_2 emission is to be avoided in situations with high chloride cycles, even if the clinker is undersulfated.

From these results, it may appear that it is difficult to limit CO generation, which will also limit SO_2 emissions, while at the same time avoiding too much excess oxygen (which is wasteful of fuel) and consequent high NO_x emissions. Lowes and Evans [1993] conclude that optimum burner design and operation must ensure that there are enough OH radicals to combust CO in order to avoid reducing conditions in the burning zone. This will minimize sulfur cycles and SO_2 emissions. At the same time, the population of oxygen atoms should be small to avoid the conditions that lead to NO_x generation. To do this, the authors recommend that the coal volatiles be released into an atmosphere low in oxygen. Therefore, the coal jet will have a low primary air velocity, and be heated to devolatilization via a partial penetration of a swirl-induced internal reverse flow zone. These conditions will be most readily achieved via a burner with 5-6% primary air, with a coal jet inside the swirl and axial channels, surrounded by a tulip quarl

which enhances the formation of a swirl-induced internal reverse flow zone without causing the coal jet to expand too rapidly.

In summary, with respect to the forms of sulfur in the burning zone, the fuel sulfur will largely be converted to SO₂. Subsequently this SO₂, or SO₂ generated from decomposition of calcium sulfate, may be converted to alkali sulfates, depending on the ratio of alkali to sulfur, the levels of chloride in the load, the temperature of the burning zone, and the concentrations of O₂ and CO in the combustion gases, as well as the combustion process itself.

Summary of Zones

Nielsen [1991] provides a table summarizing the formation and absorption of SO₂ in the various zones of the kiln, as shown in Table 7. These reactions by and large summarize the discussions above, excepting the actions of CO on destabilizing sulfates, the thermal decomposition of anhydrite, and the formation and decomposition of sulfated intermediates such as sulfate spurrite or calcium sulfoaluminate.

Table 7. Formation and Removal of SO₂ in the Various Zones of the Cement Kiln [Nielsen, 1991]

Part of plant	SO ₂ formation	SO ₂ absorption
Raw mill and precipitator	NA	CaCO ₃ + SO ₂ → CaSO ₃ + CO ₂
Preheating zone	Sulfides + O ₂ → Oxides + SO ₂ Organic S + O ₂ → SO ₂	CaCO ₃ + SO ₂ → CaSO ₃ + CO ₂
Calcining zone	Fuel S + O ₂ → SO ₂ [*] CaSO ₄ + C → SO ₂ + CO [*]	CaO + SO ₂ → CaSO ₃ CaSO ₃ + ½ O ₂ → CaSO ₄
Burning zone	Fuel S + O ₂ → SO ₂	Na ₂ O + SO ₂ + ½ O ₂ → Na ₂ SO ₄ K ₂ O + SO ₂ + ½ O ₂ → K ₂ SO ₄ CaO + SO ₂ + ½ O ₂ → CaSO ₄

A minor amount of SO₂ can also be captured in the dust collector. If a baghouse is used for dedusting combustion gases from the kiln, the efficiency may be somewhat better than for a precipitator, although no documentation for this intuitive conclusion has been found. Such sulfur removal as occurs here does so principally because of intimate gas-particle contact, and because of high relative humidities.

Formation of Other Sulfur Compounds

The principal sulfur oxide of concern in cement kiln operations is SO₂, which is by far the most stable compound of sulfur under high temperature, oxidizing conditions. The higher oxide of sulfur of greatest potential significance is sulfur trioxide (SO₃), which can be formed from SO₂ by reaction with oxygen. At moderate-to-low temperatures below about 750°C (1,380°F), the reaction of SO₂ with molecular oxygen is energetically favorable, but is a very slow reaction; the mechanism with a high rate involves the reaction with oxygen atoms. Therefore, it is usually a post-combustion reaction. According to Hunter (1981), the fraction of SO₂ that is converted to SO₃ in gas turbines is 1-10%. In cement kilns, this would be much higher if equilibrium

conditions dictated. The main reason more SO_3 is not formed in cement kilns is related to the fact that when the reaction is favorable, it is very slow.

These considerations apply to dry gas. When water vapor is present, the oxidation of SO_2 is much more likely. It is not presently clear whether the mechanism involves direct oxidation in the presence of water, or whether the water forms sulfurous acid or sulfites first, and then oxygen oxidizes the sulfite to sulfate. The 2nd order rate constant for the reaction of SO_3 with water to form sulfuric acid is 5.48×10^{11} cc/mole per second at 25°C (75°F). This is a fast and favorable reaction at this low temperature—at higher temperature it will be even faster. Perhaps the mechanism involves oxidation of SO_2 , followed by a very rapid hydration of the SO_3 that is formed. Ordinarily, it would be far more likely to find sulfuric acid mist than SO_3 in cement plant stack gases. Of course, this would especially be true in the effluent from wet process kilns, owing to their high humidity.

The neutralization of any SO_3 by alkaline materials like CaO or alkali oxides will remove the SO_3 as it is formed from the equilibrium, which also would tend to increase the degree of oxidation. Whereas, as has been noted, SO_2 is the most stable form of sulfur at high temperatures, sulfates are more stable than sulfites, at almost all temperatures.

Another sulfur compound class that is often found in the stack gas of cement plants is ammonium sulfates. This group of compounds, $(\text{NH}_4)_x\text{H}_{(2-x)}\text{SO}_4$, where x can be anywhere from 0.5 to 1.5, is normally formed by the reaction of water and SO_2 or SO_3 with ammonia usually derived from raw materials. It is often responsible in part for detached plumes seen emanating from cement plant stacks. The value of x , or the degree of neutralization of the sulfur acid, depends on the ratio of SO_3 and ammonia in the effluent. Avoidance of emission of SO_3 , sulfuric acid, and ammonium sulfates depends on many of the same factors as avoidance of SO_2 . The former two materials are strong acids, so that alkaline materials react readily with them if they are in contact. The difficulty with achieving contact with sulfuric acid mist is that it is a mist, not a gas, and therefore scrubbing it depends on particle-to-particle contact with an alkaline scrubbing agent. This contact is hard to achieve in the flue gas stream. Evidence for this fact is found in the observation that acidic attack has damaged stacks downstream of wet scrubbers in the utility industry.

Ammonium salts usually form in very fine aerosol particle sizes, in the range of sizes of visible light (0.3-0.7mm). A relatively low concentration of these particles can result in appreciable opacity above the stack. Detached plumes often appear primarily on cool mornings, especially at high humidity. Avoidance of formation of ammonium salts often involves reduction of relative humidity (since these compounds are usually formed in water droplets), increases in stack gas velocity, or removal of one of the offending materials. In extreme cases, it may be efficacious to reheat the effluent to reduce the relative humidity. If this is done, the plume can disperse before condensation reaches the point where plume formation could occur.

Reduced Sulfur Species

The other sulfur compounds of concern that may be present in cement plant flue gases are reduced species resulting either from raw material organic sulfur compounds that have been driven off in the lower temperature ($<500^\circ\text{C}$ [$<930^\circ\text{F}$]) regions of the kiln, or from reducing conditions during combustion. The generation of these compounds from cement kiln feeds has not been studied systematically, to our knowledge. There is anecdotal evidence that carbonyl sulfide (COS) has been detected in stack gases from at least two plants. Hydrogen sulfide (H_2S)

has also been detected at a few plants. These compounds are such strong reducing agents that they would not ordinarily survive if the sulfur were derived from fuel; therefore, eliminating them usually required replacing the offending raw mix component. If the offending component can be introduced into the pyroprocessing system at a higher temperature, it may be possible to convert the sulfur to SO₂. Of course, if the reduced sulfur species does in fact result from incomplete combustion of fuel components, improving combustion should eliminate them.

SULFUR EMISSIONS

As suggested in the foregoing, some of the primary factors generating SO₂ emissions are the content of reduced sulfur species in the kiln feed, and low scrubbing efficiency of certain kiln systems. Local reducing conditions in the kiln or lack of intimate contact between flue gases and incoming feed can also contribute to SO₂ emissions. Additionally, oxidation of sulfides to SO₂, in some cases, will occur at temperatures too low for adequate removal by the limestone present.

For the cement industry, the estimation of SO₂ emissions can be based on three possible methods: general emission factors; emission rates from facility-specific, short-duration tests; or facility-specific, long-term, continuous emission monitoring (CEM) testing.

AP-42 Emission Factors

An important source of emission factors for various industries is the United States Environmental Protection Agency's (USEPA's) *Compilation of Air Pollutant Emission Factors* (the "AP-42 Document"), 5th edition [USEPA, 1995]. When one uses these emission factors, specific limitations must be considered. In the introduction of the document, the USEPA states the following:

"Because emission factors essentially represent an average of a range of emission rates, approximately half of the subject sources will have emission rates greater than the emission factor and the other half will have emission rates less than the factor. As such, a permit limit using an AP-42 emission factor would result in half of the sources being in noncompliance. . . . Average emissions differ significantly from source to source and, therefore, emission factors frequently may not provide adequate estimates of the average emissions for a specific source. The extent of between-source variability that exists, even among similar individual sources, can be large depending on process, control system, and pollutant. Although the causes of this variability are considered in emission factor development, this type of information is seldom included in emission test reports used to develop AP-42 factors. As a result, some emission factors are derived from tests that may vary by an order of magnitude or more. Even when the major process variables are accounted for, the emission factors developed may be the result of averaging source tests that differ by factors of five or more." [USEPA, 1995]

Emission factors for portland cement manufacturing are located in "Section 11.6 Portland Cement Manufacturing" of AP-42 and the SO₂ factors are contained in "Table 11.6-7 Emission Factors for Portland Cement Manufacturing." The SO₂ factors from AP-42 are summarized in Table 8.

The basis for an emission factor must always be evaluated before assuming that it is appropriate for a given application. The SO₂ factors in AP-42 are provided with an emission factor rating and references from which the emission factor was calculated. Depending on the kiln type, the emission factor rating is either “C” or “D.” From AP-42, the definitions of these ratings are:

“C--Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D--Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.”[USEPA, 1995]

Table 8. USEPA AP-42 Document SO₂ Emission Rates by Process Type [USEPA, 1995]

Process type	Average SO ₂ emission factor		
	Kilograms of SO ₂ per metric ton of clinker	Pounds of SO ₂ per short ton of clinker	Emission factor rating
Wet kilns	4.1	8.2	C
Long dry kilns	4.9	10	D
Preheater kilns	0.27	0.55	D
Precalciner kilns	0.54	1.1	D

Therefore, the limitations of AP-42 emission factors should be considered before applying them to specific modern cement kilns. But when no actual testing information is available, AP-42 may be the only available estimation method.

Short-Duration Testing

Because of the limitations of applying any emission factor to a specific facility or across a whole industry, the preferred emission factor would come from site-specific testing. Any short-duration test provides data that can be directly related to a specific cement kiln, but that data may not be any more representative of the kiln than applying a general emission factor. SO₂ emissions from a cement kiln are variable, and therefore a test limited to several hours, regardless of the precision of the testing equipment, might not provide an emission rate that accurately represents long-term operation of the kiln. Therefore, one must carefully evaluate short-term test data to determine if the application of the results from a short-duration test to the continuous operation of a kiln is appropriate.

Long-Term CEM Testing

Ideally, several months of CEM data must be collected and analyzed to properly quantify the SO₂ emissions from a cement kiln. A longer time period may be necessary if the kiln uses a variety of raw materials, produces several different types of clinker, or has had equipment or other operational changes throughout the testing period.

Any emission factor developed for a specific kiln must account for this site-specific variability. The emission factor should be set at a level that is sufficiently high or cover an averaging period that is sufficiently long to reduce the impact of variability. A thorough statistical analysis is required to ensure that the emission factor selected is accurate.

PCA Database

The Portland Cement Association (PCA) has a database of sulfur emissions based on short-duration testing reports [Hawkins, 2001]. It is clear that all plants are not represented in the database, so quantitative conclusions regarding the industry are not warranted, and are not the intent of this report. With these caveats in mind, the process-related SO₂ results are summarized on Table 9 (the data are presented in terms of pounds of analyte per unit production, to most effectively normalize the results).

Table 9. PCA Database of SO₂ Emissions [Hawkins, 2001]

Kiln type	Number of plants in database	Number of tests in database	SO ₂ emission rates, Kilograms SO ₂ per metric ton clinker (pounds SO ₂ per ton clinker)		
			Minimum	Maximum	Average
Wet	11	20	<0.01 (<0.01)	16.32 (32.63)	2.90 (5.80)
Long dry	9	27	0.01 (0.02)	9.09 (18.17)	1.43 (2.85)
Preheater	11	30	<0.01 (<0.01)	3.27 (6.54)	0.70 (1.39)
Calciner	7	24	<0.00 (<0.00)	4.42 (8.83)	0.96 (1.92)

Expressing the emissions in terms of kilograms per metric ton (kg/mt) (pounds per short ton [lbs/st]) of clinker will tend to shift the results to higher values for the less efficient kilns that use more fuel per ton of clinker, and therefore introduce more fuel sulfur into the kiln. The minimum values achieved show that it is possible, with the right raw materials and good combustion practices, to achieve very low SO₂ emissions. Although not shown on Table 9, SO₂ emission results from two plants with alkali bypasses were also collected. The SO₂ emission values for the alkali bypasses ranged from <0.001-0.019 kg/mt (<0.003-0.038 lb/st) and support the conclusion that raw material sources cannot contribute here. The higher values of SO₃ for wet process kilns emissions may be significant, although the number of data points is limited. The additional water in the gas stream is known to aid in oxidation of the SO₂ to sulfates, as will be discussed later in this report.

The average emission rates from the 1982 PCA survey [Nielsen and Jepsen, 1990], USEPA AP-42 emission factors, and the current PCA environmental database are summarized in Table 10. As can be seen, great variability in emission rates is produced depending on the kiln type, age of the kiln, and the amount of data available.

Table 10. Average SO₂ Emissions from 1982 PCA Survey, USEPA AP 42, and PCA Environmental database [Nielsen and Jepsen, 1990; USEPA, 1995; Hawkins, 2001]

Kiln type	1982 PCA Survey, kg/mt clinker (lbs SO ₂ ./st clinker)	AP 42 Factors, kg/mt clinker (lbs SO ₂ ./st clinker)	PCA Environmental Database, kg/mt clinker (lbs SO ₂ ./st clinker)
Wet	8.07 (16.14)	4.1 (8.2)	2.90 (5.80)
Long dry	3.82 (7.63)	4.9 (10)	1.43 (2.85)
Preheater	0.93 (1.86)	0.27 (0.55)	0.70 (1.39)
Calciner	1.21 (2.41)	0.54 (1.1)	0.96 (1.92)

PLANT STUDIES

The following section is not intended as an exhaustive study of the emissions issues at the chosen plants, but simply an investigation of the sulfur oxide generation mechanisms at these plants, the natural scrubbing available, and the additional measures taken to address the residual emission. The situations described here were those in place as of the plant visits, which took place in 1998.

Plant A

Plant A is a single-stage calciner kiln with a very high sulfur kiln feed. The majority of the sulfur in this kiln feed is either organic or pyritic sulfur, present in a low-grade calcareous oil-shale material. This plant once operated with a normal four-stage preheater kiln, but in order to avoid operational difficulties was obliged to use low-organic, low-sulfur limestone, which exhausted the supply of this limestone. The new kiln system was installed to avoid these operating problems, as well as to avoid organic and SO₂ emissions. The pyroprocessing plant design is shown in Figure 3 below:

The kiln feed is introduced directly into the calciner vessel, where coal is burned. The organic materials in the kiln feed are burned in this location, and the exhaust gases are dedusted by a single cyclone. The exit gases from the cyclone are passed through an air-to-air heat exchanger, which preheats the tertiary air prior to its use in the calciner. The gases pass from the heat exchanger to twin cyclones, whose function is to remove additional material for addition to the kiln feed.

The kiln exit gases are 100% bypassed. Therefore, there is no heat recovery from them for calciner or preheater operation. All the energy for the calcination of the feed is derived from the calciner fuel and the inherent fuel in the kiln feed. Thus, in discussing the SO₂ emissions from this process, the kiln and calciner emissions are treated separately. Despite the very high pyrite and organic sulfur content of the kiln feed, the calciner emits essentially no SO₂. Three material balances, constructed on the calciner system as a whole, show complete retention of the input sulfur, whether derived from feed or fuel. The SO₃ content of the kiln feed, on a raw basis, varied from 1.7-2.31% for these three sulfur balances. This complete retention of sulfur is a dramatic illustration of the ability of freshly generated lime in the calciner to scrub out SO₂.

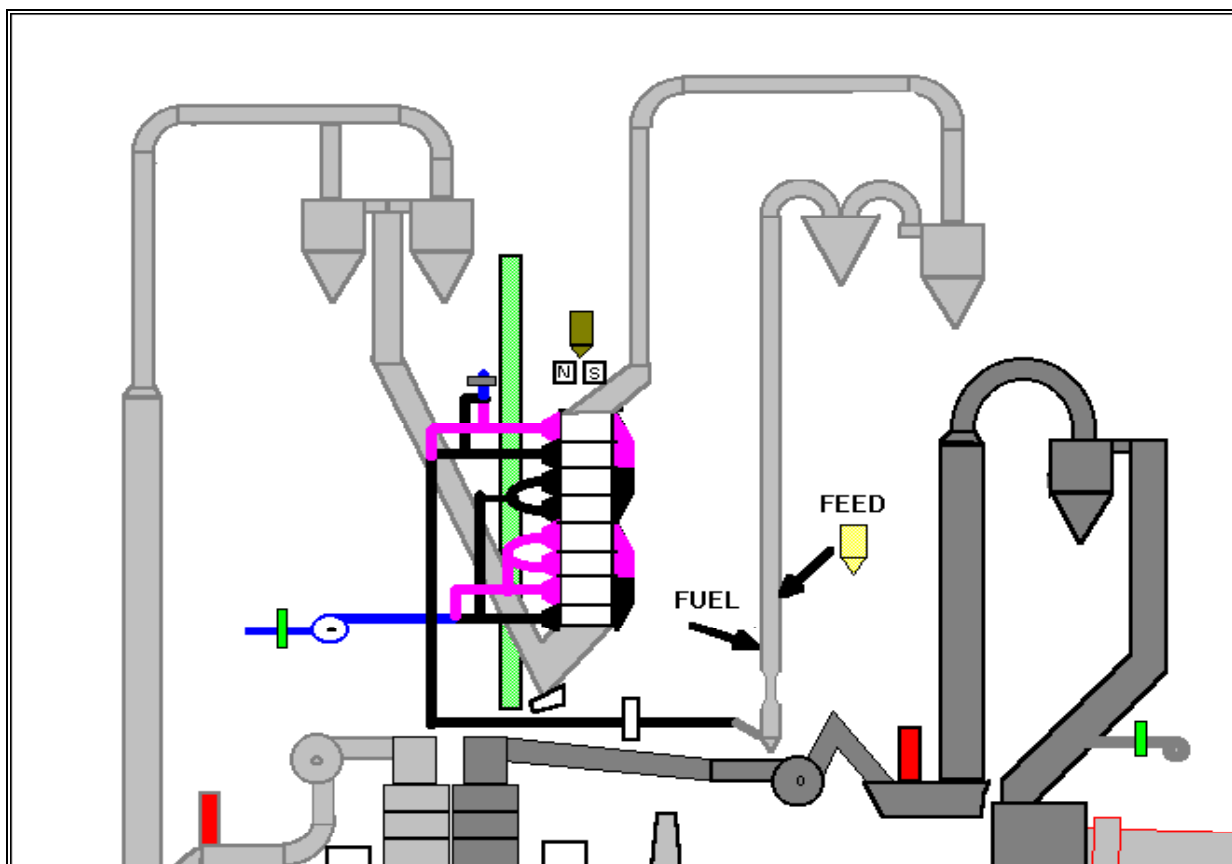


Figure 3. Plant A preheater and bypass configuration

At the time of the visit, Plant A did experience SO_2 emissions from time to time. These were derived from the bypass, and have been shown to be attributable to difficulties in obtaining stable fuel feed to the rotary kiln. When excess oxygen content becomes low as a result of “slugs” of fuel, the SO_2 carryout from the kiln can rise. The bypass dust, by virtue of its high degree of calcination, can scrub out some of this sulfur, but the surface of the dust may be so thoroughly sulfated that the efficiency of removal may not be as good as desired. Controlling SO_2 emissions at this plant was therefore essentially a matter of improving the fuel rate stability to the rotary kiln.

Plant B

Plant B is a four-stage calciner kiln, equipped with a downdraft calciner and an in-line calciner. The plant fires about 65% of the fuel in the calciner and 35% in the kiln. About 30% of the kiln exit gases bypass the preheater. The calciner achieves a calcination degree of 93-99%. The raw materials include as the chief components a weathered and an unweathered marl, which contain 0.37 and 1.5% SO_3 , respectively. About 80% of the sulfur has been shown to be pyritic. Although the weathered marl has lower sulfur content, it also has a low lime saturation factor, and therefore must be supplemented with some of the higher-lime unweathered marl for product quality reasons. Good quarry utilization also demands the use of significant amounts of the unweathered material. The majority of the sulfur is in the form of pyrite, and the emissions of

SO₂, while within present state specifications, were somewhat higher than desired. Furthermore, they correlated extremely well with the input sulfur from the kiln feed.

Therefore, the plant initially installed a cyclone between the first and second cyclone stages, and induced the flow of hot meal from the top of the calciner and the roof of the bottom cyclone stage, so that hot meal could scrub some SO₂ generated from the feed. This system was in place when the plant visit occurred. The modest efficiency of this process induced the plant to install a device that, in its present configuration, recycles hot meal from the top of the calciner at the roof of the bottom cyclone stage, and introduces it directly into the duct between the top two cyclone stages (In other words, the cyclone has been removed). The flow is currently induced by a static pressure difference of about 15" H₂O. The material is aspirated by this pressure difference into the riser duct; the point of introduction is slightly below the point at which kiln feed is introduced. The system is designated a "De-SOx" system. The SO₂ emissions are reduced by about 25-30% when this "De-SOx" system is in operation.

Samples were taken from the earlier configuration, with the cyclone in place. The hot meal material has been analyzed for free lime, loss on ignition, fineness, and particle size distribution, both before and after being exposed to flue gas generated in Stage II and below. Table 11 below shows the particle size distribution of the hot meal, the "De-SOx" material, and the bypass dust. The chemical analytical results for these three materials are shown in Table 12. These analytical data may not be representative of the present situation at this plant, because of the new De-SOx system configuration.

Table 11. Particle Size Distribution of Hot Meal, De-SOx Material, and Bypass Dust, Plant B

Material size	% Passing specified size		
	Hot meal	"De-SOx" material	Bypass dust
104.7 μm	100	78.32	100
48 μm	97.45	45.59	99.50
24 μm	81.98	22.42	92.41
12 μm	58.91	10.50	71.97
6 μm	38.00	5.01	43.13
3 μm	21.10	2.91	20.87
1.5 μm	7.54	0.80	6.42
Specific surface, cm ² /g	4157	990	4197

Table 12. Chemical Analysis of Hot Meal, “De-SOx” Material, and Bypass Dust, Plant B

Parameter	Hot meal	“De-SOx” material	Bypass dust
% SiO ₂	21.78	20.54	18.71
% Al ₂ O ₃	5.03	5.20	4.68
% Fe ₂ O ₃	1.69	1.66	1.48
% CaO	66.39	61.86	58.58
% MgO	1.49	1.52	1.32
% SO ₃	1.02	0.88	3.47
% Na ₂ O	0.12	0.12	0.18
% K ₂ O	0.96	0.85	2.01
% TiO ₂	0.28	0.26	0.26
% P ₂ O ₅	0.17	0.16	0.15
% Mn ₂ O ₃	0.06	0.07	0.06
% SrO	0.08	0.08	0.07
% Loss on Ignition	0.48	5.17	7.12
Total	99.52	98.37	98.09

The hot meal was clearly very fine, and it is surprising that the efficiency of capture of SO₂ was so low. There are, logically, three factors that may have contributed to the fairly poor efficiency of capture experienced at that time:

1. The residence time at temperatures adequate for acceptable efficiency. From the point of De-SOx dust introduction to the point of kiln feed introduction, the residence time was only 0.06 seconds. From the point of De-SOx dust introduction to the exit to the downcomer, the gas residence time is only about 1.7 seconds. After this point, the temperature is very low.
2. The amount of material available for scrubbing. According to calculations, at the time of the plant visit the “De-SOx” cyclone took 6.7% of the exit volume from the in-line calciner before the alteration. This represents about 20,000 actual cubic feet per minute (ACFM), equivalent to 4,700 standard cubic feet per minute (SCFM), which could carry a maximum of 9,500 lb/hr hot meal, even assuming a particle loading of 100-grains/standard cubic ft. This may not have been enough surface area to capture the desired SO₂. After alteration, the De-SOx system took 10-12% of the exit volume. Assuming 11%, the volume, and velocity, of the De-SOx gases increased by 64%. This would significantly increase the amount of material carried by the gases, resulting in the improved scrubbing efficiency measured after removal of the cyclone.
3. The rapid decrease in, and deactivation of, the surface. Comparison of the data in Table 11 shows that there has been a dramatic decrease in the fineness of the material, and in its content of fine particles. Therefore, there has also been a corresponding decrease in available surface for reaction. Chemical analytical results show only a modest increase in sulfate or none at all. (This result seems counterintuitive. It is probable that there is a sampling error—that the coarse “De-SOx” material has been preferentially sampled). Yet the loss on ignition (LOI) has increased significantly. It is reasonable to postulate that this increase in LOI is due to carbonation of the surface of the particles and, as previously stated, calcium carbonate is far less efficient in capturing SO₂ than is CaO or Ca(OH)₂. This interpretation is also consistent with the

finding that removal of the DeSOx cyclone provided more calcined meal for scrubbing, and hence greater surface area, resulting in improved efficiency.

Further evidence of the importance of surface area of the scrubbing material on the efficiency of removal can be gathered from the results with the raw mill on line and off line. The raw mill reduced the SO₂ emissions in July of 1999 from 362 lb./hr to 197 lb./hr. This represents a 45.5% reduction, considerably more than achieved with any scrubbing material added to the preheater. The fresh surface constantly being generated during grinding, and the longer residence time, apparently compensate successfully for the low temperature in the raw mill, and the fact that no CaO or Ca(OH)₂ are present.

To study the effect of fineness, the plant introduced hydrated lime to the discharge line of the De-SOx cyclone at a molar ratio of hydrated lime to SO₂ of 1.83, and achieved a 16.4% removal efficiency, and at a molar ratio of 2.4, a 26.6% efficiency. (The De-SOx system was not used when these hydrated lime tests were run.) The molar ratio, when the De-SOx cyclone is in operation, is estimated by taking 66.39% of 9,500 lbs./hr, or 112 lb.-moles of lime/hr. The De-SOx cyclone removed 46.7 lb. of SO₂ per hour, which is equivalent to a molar ratio of 150. Even if the amount of material is only 10% of that cited, the molar ratio is still 15, which indicates marginal efficiency. The higher removal efficiency of hydrated lime, used at a lower molar ratio, is evidence that the fineness (surface area) of the absorbent is important.

There has been no systematic study varying the oxygen to assess the effect on scrubbing; however, the plant was at one time operating with a significant leak into the preheater system, which increased the oxygen. No increase in scrubbing efficiency was observed. (It must be granted, however, that the pressure drop from the calciner to the “De-SOx” introduction point must have decreased significantly, which would have reduced the flow of gas and material to the “De-SOx” cyclone.) There has also been a short study examining whether changes in temperature could increase the efficiency, but no real effect was seen.

As earlier indicated, the plant and the equipment supplier have modified the system to assess the effect of removing the original cyclone from the De-SOx system. The additional pressure drop increment introduced by the cyclone has been eliminated, increasing the driving force for flow that the material will experience, and significantly increasing the flow of material from the calciner. This has shown an ability to markedly improve scrubbing efficiency.

Plant C

Plant C has a calciner kiln with bypass and a roller mill for raw grinding. The bypass handles about 15-20% of the kiln exit gases. The fuel is western coal with a 0.6% sulfur content. Emissions of SO₂ had been considerably greater than expected (as much as 500 lb./hr) because of pyritic sulfur in the limestone and greater amounts of sulfide sulfur in the shale. There was no economically viable possibility of high-grading the limestone. The weathered shale (called tan shale) contains less sulfur than the unweathered material (gray shale). Thus, the total sulfur input to the kiln system can be reduced somewhat by maximizing tan shale use. This measure, however, is clearly not conservative of quarry resources. Efforts have been made to screen out the coarser, sulfur-rich material in the gray shale with only modest success. About 2% laterite is always used as an iron source in the mix. Replacing shale with fly ash has proven to be expensive. Sand has also been used; the higher silica ratio harms the raw mix burnability,

although the alkali content is reduced. Diatomaceous earth has been examined as an alternate silica source, but the available quantities are small.

The plant experiences no SO₂ emissions from the bypass system, under normal circumstances. This observation confirms the hypothesis that fuel sulfur is not involved in the emissions. The plant has tried varying the kiln exit oxygen concentration from 2-6%, and the Stage III exit oxygen concentration from 3-5%, without affecting SO₂ emissions. The roller mill reduces the emissions by about 50% when it is in operation. This is in general agreement with the results obtained at Plant B. The preheater tower actually does a rather good job of removing SO₂; if all the sulfur in the kiln feed is assumed to be present as sulfides, the tower efficiency may be as high as 78%.

The injection of water into the riser duct from Stage II has achieved about a 10-20% reduction of emissions, but at a substantial energy penalty. The plant has experimented with the injection of calcined kiln feed, at a high ratio of lime to the sulfur to be removed, into the downcomer and into Stage II. The efficiency in the former location (40%) was superior to that in the latter location (30%), in spite of the higher temperature in Stage II. It may be that the relative humidity in the downcomer was higher, and that a layer of moisture on the surface of the particles assisted in transfer of the sulfur to the reacting lime. Further discussion of this hypothetical mechanism will be offered below.

The next step involved the injection of solid hydrated lime into the downcomer and into the Stage II riser. This was hydrated lime obtained as a byproduct from the manufacture of acetylene from calcium carbide. The ratio of lime to sulfur was again very high (40-to-50/1). Efficiencies of 55-65% were obtained. When the injection was made into the roller mill, the efficiency was about 80%. The higher surface area of the hydrated lime was instrumental in improving efficiencies, compared with the results obtained with calcined kiln feed. Finally, the plant decided to inject limewater into the system, at a relatively low (3/1) lime to sulfur ratio. Pebble lime was hydrated in a sump with high-pressure air agitation, and injected into the system. Efficiencies were good, influencing the plant to use slaked lime, introduced into the conditioning tower downstream of the preheater. On an ongoing basis, an efficiency of about 45% can be achieved with a lime to sulfur ratio around 3.0, if the conditioning tower temperature is 335°F. The higher the conditioning tower temperature, the lower is the efficiency.

At the present time, calcium chloride is added at the third stage of the preheater, as a measure to help control alkalies. The chloride is largely removed through the bypass dust. The conversion of alkali from the sulfate to the chloride frees some sulfur to become involved in the circulation between preheater and kiln. So far, it has not appeared to increase the SO₂ from the bypass, but may increase the circulation within the tower. The calciner excess oxygen is controlled on the low side to minimize NO_x generation from the fuel. This, too, can increase sulfur circulation. The alkaline injection system is now used when SO₂ emissions exceed 102.3 lb./hr.

Plant D

Plant D is a four-stage calciner kiln with no bypass and a roller mill for raw grinding. The kiln is fitted with a baghouse for dedusting the exit gases from the preheater. The raw materials contain pyritic sulfur as well as kerogen. The alkali level of the kiln feed is unusually low. The chemical analysis of the raw materials used at the plant are shown in Table 13, below – it is notable that

the sulfur content for the kiln feed is higher than that of any of the contributing raw materials. The reason for this discrepancy is not known:

Table 13. Analysis of Raw Materials for Plant “D” (Analyses on Ignited Basis)

Parameter	High rock	Medium rock	Plant clay	Bauxite	Iron	Kiln feed
% SiO ₂	14.67	33.23	44.58	7.76	1.26	22.47
% Al ₂ O ₃	1.19	2.23	5.38	65.56	10.56	3.87
% Fe ₂ O ₃	0.95	1.79	9.35	18.52	90.84	4.16
% CaO	77.86	59.27	29.73	2.69	3.54	67.00
% MgO	0.87	1.44	8.74	0.11	3.84	1.03
% SO ₃	0.62	0.51	0.26	0.06	0.21	0.74
% Na ₂ O	0.09	0.17	1.37	NA	NA	0.14
% K ₂ O	0.16	0.22	0.84	NA	NA	0.24
% Na ₂ O _{eq}	0.16	0.25	1.92	NA	NA	0.30
Loss on Ignition	NA	NA	17.27	24.05	NA	NA
Total	96.57	99.11	100.25	98.10	110.25	99.95
C ₃ S						68.4
C ₃ A						4.5
Silica Ratio						2.80

From these results, it is clear that the sulfur is derived largely from the limestone, and that the alkali level of the limestone is very low. The alkali level in the clay is higher; however, very little clay can be used. Therefore, the ratio of sulfur to alkali in the kiln is very high. This will tend to increase the circulating load of sulfur from kiln to preheater, because the sulfur not balanced by alkali will tend to have a greater volatility. This will be especially true given the relatively poor burnability of the kiln feed at Plant D. The silica ratio of the limestone is very high, and bauxite and iron ore must be added to reduce the silica ratio of the mix to an acceptable level.

It appears as though the calciner at Plant D may be operating under oxygen-starved conditions, at least some of the time. The results from the gas analyzers in the downcomers from Stage I show significant levels of CO. Some of this CO may be derived from the partial combustion of kerogens. In any case, the lack of oxygen increases difficulties with sulfur removal in the upper preheater stages. Further evidence for the reducing conditions in the calciner are the very low NO_x emissions from this plant. Any reducing conditions in the calciner, and further up into the preheater, will tend to make capture of sulfur less efficient, and therefore increase SO₂ emissions.

In spite of the apparent reducing conditions in the calciner, the SO₂ emissions seem, again, to be chiefly a function of the kiln feed sulfur. Reducing these emissions is most effectively accomplished by reducing the sulfur content of the kiln feed. This is a very difficult task to accomplish, consistent with maintaining good quarry utilization. The plant is considering a series of measures to address the problem.

Plant E

Plant E is a calciner kiln, again with pyritic limestone as the main raw material. The plant also uses fly ash, shale, foundry sand, bottom ash, and other materials from time to time. The kiln operates with a substantial bypass. The plant has a special challenge, in that they need to satisfy regulatory limits on SO₂, NO_x and CO emissions simultaneously.

As has been observed in connection with the other plants, the SO₂ emissions are largely derived from the raw materials. The plant has established a linear correlation between SO₂ emissions and kiln feed (KF) sulfur as follows (this equation is applicable only to this particular plant):

$$\text{SO}_2 \text{ (lbs./hr)} = 2677.3 \text{ (KF SO}_3\text{)} - 1575.9$$

The correlation coefficient is fairly good for such a one-parameter correlation equation, and could probably be improved by taking into consideration certain operating parameters. The equation confirms that the preheater and the bypass are efficient in removing SO₂ derived from the fuel sulfur, and that the preheater can apparently take out a fixed increment of SO₂ from the gas stream resulting from oxidation of the pyrites. Anything above this amount tends to be emitted.

The plant's challenge is especially difficult because of the simultaneous demands of a limit on NO_x and on CO. Evidence suggests that much of the NO_x is generated in the calciner, from oxidation of fuel nitrogen. To limit the generation of fuel NO_x, it is necessary to operate the calciner at low excess oxygen, or preferably, under reducing conditions. This situation creates a low oxygen gas in the preheater, which cannot be conducive to good capture of the SO₂.

Plant F

Plant F also has a calciner kiln. Their emissions of SO₂, in part from pyrites in the kiln feed, are modest. The very stringent environmental limitations that apply to this kiln have forced the plant to consider adding scrubbing reagents to control emissions. The plant has tried adding hydrated lime to the kiln feed screw, lime slurry to the roller mill, sodium hydroxide (NaOH) to the downcomer, sodium bicarbonate (NaHCO₃) to the kiln feed screw and at the ID fan, and Trona (a natural sodium carbonate/sodium bicarbonate mixture) to the baghouse and at the ID fan. Of these options, the most efficient, in terms of mass required per unit mass SO₂ removed, was sodium bicarbonate. However, this material was expensive, and resulted in an increase in clinker alkali that was undesirable. The most effective from a cost perspective, as well as an efficiency standpoint, was the lime slurry.

PART II. SULFUR DIOXIDE CONTROL TECHNOLOGIES

POTENTIAL SULFUR DIOXIDE CONTROL TECHNOLOGIES

Techniques for SO₂ control have been used in the power industry for a number of years, and have typically been confined to two types of control: either a fuel change to lower sulfur fuels or the addition of a “tailpipe” SO₂ scrubber to the system.

Fuel Switching

In thermal power boilers, SO₂ emissions are directly related to fuel sulfur concentration. If the fuel sulfur concentration is reduced, SO₂ emissions are reduced by a corresponding amount. Some power plants facing stringent SO₂ regulations have switched from a high sulfur fuel, typically a mid-western coal, to a lower sulfur fuel, such as coal from the western United States. An alternative to using a western coal is fuel washing. Some fuel suppliers wash coal to remove impurities including pyrites or other sulfur-bearing minerals.

Inherent Sulfur Dioxide Removal

Combustion devices, like power boilers, do not process raw materials other than the fuel they burn. However, raw material processing and pyroprocessing systems in the cement manufacturing industry offer the opportunity to remove SO₂ that has been previously generated in the system because of process conditions, such as large quantities of pulverized limestone and freshly created lime, that are inherent to the manufacture of cement clinker.

Sulfur Dioxide Scrubbers

Numerous variations of tailpipe SO₂ scrubbers exist and are used in many industries. These scrubbers range in simplicity from in-duct dry reagent injection systems to wet scrubbers that produce a byproduct for reuse, sale, or waste requiring disposal.

Dry reagent injection. Dry reagent systems use a finely pulverized solid reagent that is dispersed into the exhaust gas stream to react with SO₂. Typically, the reagent and captured sulfur compounds are subsequently removed from the gas stream by an existing down-stream particulate matter control device (PMCD). Typical reagents are lime, limestone, trona (a naturally occurring sodium carbonate compound), or other alkali or alkaline earth compounds with a high affinity for SO₂. In thermal boilers and other industries, the spent reagent and other collected dust or ash is usually disposed of in a landfill.

Spray dryer absorber. Spray dryer absorbers are similar to dry reagent injection systems except that the reagent is either an aqueous slurry or the reagent is dissolved in water prior to injection. Sufficient residence time for complete evaporation of the water must exist, be installed as a retrofit, or be designed into a new system. Typical reagents, and reagent collection and disposal are the same as with the dry reagent systems.

Wet scrubbers. Wet scrubbers pass the exhaust gases through an aqueous slurry or water solution of a reagent. In wet scrubbers, the water is not completely evaporated. Depending on the reagent used, the sludge resulting from the reactions between acid gases (in this case SO₂) and the reagent can be either used as a byproduct or disposed of as sludge. When lime or limestone is the reagent, a combination of calcium sulfite and calcium sulfate is produced, which must be disposed of as sludge unless it is further processed. Calcium sulfite may be converted to calcium sulfate, a useable byproduct, if the wet scrubber is designed to include a forced oxidation system. Depending on the chemistry, the calcium sulfate produced may be incorporated into the cement manufacturing process.

EVALUATION OF SULFUR DIOXIDE CONTROL TECHNOLOGIES APPLICABLE TO CEMENT KILNS

This section presents methods of operation, expected SO₂ removal efficiencies of various SO₂ control techniques, and an evaluation of these technologies for use in the cement manufacturing industry. Rotary kilns producing cement clinker have unique characteristics, such as using large quantities of raw materials, which materially differentiate them from systems that only burn fuel. Consequently, cement kilns can employ several techniques to control SO₂ emissions that are not available to other industry groups.

Control techniques for SO₂ emissions from raw material grinding and drying systems and pyroprocessing systems in the cement industry fall into three broad categories; inherent removal by the process, process alterations, and SO₂ scrubbing technologies. Pyroprocessing and raw material grinding and drying systems result in substantial SO₂ removal because of the inherent nature of the process. Process controls reduce the amount of SO₂ generated while scrubber technologies capture SO₂ after it has been generated in the process. These techniques will be discussed in this section.

Fuel Switching

Although switching to a fuel with a lower sulfur concentration is frequently used to reduce SO₂ emissions in thermal power plants, this method is generally not nearly as effective in reducing SO₂ emissions from cement pyroprocessing systems. As previously presented, SO₂ emissions from portland cement kilns are nearly independent of fuel sulfur or from sulfate recirculation between kiln and preheater. Rather, SO₂ emissions from cement kilns depend on, among other parameters:

- Inherent SO₂ removal efficiency of the kiln system,
- The raw material sulfur concentration,
- Form of the sulfur in raw materials (e.g., pyritic or other),
- The molecular ratio between sulfur (and chloride) and alkalies (sodium and potassium),
- Whether oxidizing or reducing conditions exist in the kiln system and where these conditions exist,
- The temperature profile in the kiln system,
- If an in-line raw mill is available and operating, and
- Other conditions that may be unique to a specific cement clinker production line.

Inherent Removal

Pyroprocessing systems and raw materials drying and grinding systems in portland cement plants process large quantities (hundreds of tons per hour) of pulverized limestone and lime. Removal of SO₂ is expected from the pyroprocessing system gases because of inherent process conditions.

Inherent SO₂ removal in pyroprocessing systems producing cement clinker. As previously described in this report SO₂ is effectively scrubbed by lime at 800-950°C (1,470-1,740°F), with most kilns having large zones with these conditions. Cement kilns have large quantities of pulverized limestone and freshly created, highly reactive lime continuously present in the pyroprocessing system. Conditions suitable for efficient SO₂ scrubbing inherently exist in cement kiln systems. In fact, one could describe a cement clinker production line as a huge dry limestone/lime SO₂ scrubbing system with a stoichiometric ratio of reagent to SO₂ that is, in most cases, greater than 100 to 1. In Table 14, several researchers' ranges of inherent removal efficiency for cement kiln systems are presented.

Table 14. Inherent SO₂ Removal in Rotary Kilns Producing Cement Clinker

Reference – author and year	Kiln type	Alkali to sulfur ratio	Reported range of removal efficiency (percent)
Sprung [1964]			79.3-98.8
Ritzmann [1981]	Grate preheater		38-81
	Suspension preheater	>1.0	66-98
	Suspension preheater	<1.0	54-74
Greer [1988]			50-90
Schütte [1989]			50-85
Bonn and Hasler [1990]	Preheater		70
Steuch and Johansen [1991]	Preheater/Calciner		70-95
Pott [1999]	Preheater		>80

From these researchers, the inherent SO₂ removal efficiency in preheater kiln systems ranges from a low of 38% to as high as 98.8%. The range of inherent removal efficiencies is broad because the kiln types vary, the chemical balance between the sulfur and alkali in the raw materials varies substantially, and the chemical form of the sulfur in raw materials can vary significantly.

Inherent SO₂ removal by in-line raw mills. Many cement-manufacturing facilities use an in-line raw mill to dry and grind raw materials. An in-line raw mill uses all or a large portion of the pyroprocessing system's exhaust gases to provide energy to dry the raw materials. The combination of high gas stream moisture concentrations and freshly created limestone surfaces constantly produced by continuous grinding result in favorable conditions for adsorption of SO₂ by CaCO₃. Table 15 summarize several researchers' ranges of inherent removal efficiency of in-line raw mills.

Table 15. Inherent SO₂ Removal in In-line Raw Mills

Reference – author and year	Reported range of removal efficiency (percent)
Goldmann et al [1981]	50
Schütte [1989]	68
Sheth [1991]	50

Summary of inherent SO₂ removal in cement clinker production lines. In summary, rotary kiln systems have SO₂ removal efficiencies ranging between 38-99% of the sulfur input to the system. The literature suggests that 50-70% of the remaining SO₂ will be removed from exhaust gases passed through an in-line raw mill system.

Process Alterations in the Cement Manufacturing Industry

Due to the nature of the portland cement manufacturing process, there are methods to remove and prevent the formation of SO₂ by modifying or controlling conditions in the cement pyroprocessing systems:

- The oxygen concentration of the exhaust gases can be controlled to ensure sufficient oxygen exists to stabilize alkali and calcium sulfate compounds formed in the process.
- The burning zone flame shape can be modified to reduce the possibility of forming localized reducing conditions.
- Raw materials can be altered to affect the alkali/sulfur molar ratio.
- Finally, alterations to the pyroprocessing system can influence SO₂ emissions.

Burning zone oxygen concentration. As noted previously in this paper, O₂ concentration, and more importantly the concentration of CO, have a strong influence on the stability of alkali and calcium sulfates in the burning zone. Higher concentrations of oxygen tend to stabilize sulfates. If oxidizing conditions exist at the high temperatures (1,450°C [2,640°F]) found in cement kiln burning zones, sulfur will tend to be retained in the clinker as either alkali sulfates, calcium sulfate, or combined calcium/alkali sulfates rather than being emitted as SO₂. However, in the presence of trace concentrations of CO (2,000 ppm), decomposition of sulfates can begin at lower temperatures (1,000°C [1,830°F]) which will result in increased SO₂ concentrations.

It was previously pointed out that CO is an efficient reducing agent to convert sulfates back into SO₂, and that the effect of CO on calcium sulfate stability is far stronger than that of oxygen alone. Oxidizing conditions in the burning zone of a kiln producing cement clinker are a required condition for producing quality clinker although transient-reducing conditions may exist. Accordingly, ensuring that oxidizing conditions exist in the burning zone, which also enhances clinker quality, will minimize SO₂ emissions.

Ensuring oxidizing conditions in the burning zone requires proper solid fuel preparation and proper flame shaping and control. This technology is widely practiced in the industry today. For some plants, modernization of the fuel firing system may be necessary to ensure oxidizing

conditions are continuously maintained in the burning zone. In addition, reliable, accurate O₂ and CO gas analyzers at the kiln exit are essential. Carbon monoxide gas analyzers measuring in the parts per million (ppm) concentration range (e.g. 0-5,000 ppmv CO) are recommended.

Control of burning zone O₂ and CO concentration is a control technique applicable to all rotary kilns producing cement clinker. It is particularly applicable to long wet and long dry process kilns. With preheater and preheater/calciner kilns, SO₂ generated in the burning zone will normally be efficiently scrubbed by the intimate contact of the kiln exhaust gases with the freshly created lime in the lower preheater stages. Although freshly created lime exists in long kilns, the intimate mixture of calcined feed and kiln gases does not exist to the same extent. Hence, the importance of fixing the sulfates in clinker is especially critical.

However, it must be noted that oxidizing conditions in the burning zone are favorable for increased generation of NO_x in any rotary kiln.

Avoiding flame impingement. As previously noted, oxygen plays a role in the control of SO₂, but the dependence is weaker than might otherwise be imagined. The effect of CO is far stronger. CO is a powerful reducing agent for CaSO₄ at temperatures of interest in a cement kiln system (1,300-2,100°C [2,370-3,810°F]). In air having temperatures above 1,700°C (3,090°F), CaSO₄ will tend to decompose to SO₂ and CaO. With 0.1% O₂, the temperature at which CaSO₄ decomposes is reduced by about 200°C (360°F). However, the effect of CO on CaSO₄ stability is far stronger than that of oxygen alone.

Hansen [1986] noted that the literature suggests that C or CO reacts with CaSO₄ to form CaS and CO₂ at temperatures below 1,100°C (2,010°F) but that at higher temperatures, such as in the burning zone, SO₂ is formed. Hansen suggests that SO₂ observed is mainly the result of reduction in the burning zone and notes that SO₂ emissions were found to correlate with localized reducing conditions in the burning zone. Hansen [1986] states, "It was found that flame impingement in the hot zone had a major effect on SO₂ emissions from the kiln."

Avoiding flame impingement on the clinker in the burning zone can minimize SO₂ emissions. Localized reducing conditions will be generated and clinker sulfates will be reduced to SO₂ rather than remaining in the clinker if fuel impinges on clinker in the burning zone. These conditions can occur even if the total oxygen concentration may be sufficient to fully combust all of the fuel introduced into the burning zone and excess oxygen is measured at the kiln feed end. In addition, with flame impingement on clinker, the clinker surface temperature can become high enough to thermally decompose sulfate salts.

Ensuring that flame impingement on the clinker is avoided requires proper solid fuel preparation and proper flame shaping and control. This technology is the same as described for ensuring that oxidizing conditions are maintained in the burning zone with the following additional points. Positioning the burner pipe in the kiln is critical. Even with modern fuel preparation and firing systems, if the burner pipe is directed into the clinker, localized reducing conditions can be produced. Additionally, localized reducing conditions can occur if solid fuel particles fail to completely combust before falling into the clinker. This condition can occur when the fuel particles are too large or are injected into the burning zone at a velocity that is too low. Proper combustion of individual fuel particles depends on fuel characteristics, such as volatility, degree of air/fuel mixing and many other factors beyond the scope of this report.

Avoiding flame impingement on the clinker is a control technique applicable to all rotary kilns producing cement clinker. For some plants, modernization of the fuel firing system may be necessary to ensure oxidizing conditions are continuously maintained in the burning zone.

Raw material change. A number of researchers have found that in contrast with the case of utility power boilers, SO₂ emissions from rotary kilns producing cement clinker under oxidizing conditions are nearly independent of the fuel sulfur input. As previously discussed in this paper, emissions of SO₂ from kilns are closely related to the amount of sulfide, such as pyrite, in kiln feed and on the molar ratio of total sulfur to total alkali input to the system. The SO₂ concentration in kiln exit gases depends on the molar ratio of alkalis to sulfur; when alkalis are in excess, the SO₂ emissions will normally be low. If the kiln gas phase contains an excess of sulfur, SO₂ emissions will increase. Additionally, kiln feed containing carbon may directly cause SO₂ emissions.

Schütte [1989] said that kiln feed containing carbon might cause SO₂ emissions according to the following reaction:



According to Sheth [1991], RMC Pacific's current cement plant in Santa Cruz, CA consists of, among other equipment, a four-stage preheater kiln with a calciner and an in-line roller mill. After the plant was constructed, environmental compliance tests conducted found that the SO₂ emissions limit of 73 kg (82 lbs) per hour was not being met. RMC then embarked on a detailed investigation into the causes of the excessive SO₂ emissions and potential methods to reduce them. RMC performed extensive investigations and found that raw materials contained varying amounts of pyritic sulfur. The limestone contained some pyrite; however, it was not possible to selectively mine limestone to avoid the pyrite. The shale quarry was also tested, and it was found that tan colored shale had less pyrite than gray colored shale. When tan shale was used, the SO₂ emissions were reduced. However, the supply of tan shale became the limiting factor on the lifetime of the quarry, reducing the expected quarry life by nine years.

Therefore, changing raw materials may reduce SO₂ emissions. If a raw material contains pyritic sulfur or organic sulfur, substituting another raw material that contains less of these compounds will reduce SO₂ emissions. If sulfur input is in molar excess of alkali input to the system, either reducing sulfur input or increasing alkali input may reduce SO₂ emissions by retaining more sulfur in clinker as alkali sulfates. Sulfur will tend to be retained in the clinker if the raw materials permit slightly reduced clinkering temperatures, and if the burning zone is controlled to achieve these slightly reduced temperatures. Finally, kiln feed containing carbon may produce reducing conditions that generate SO₂ emissions.

Replacing a raw material component to reduce SO₂ emissions can result in emissions reductions ranging from 0-100%. If a single raw material component contains sulfur-bearing minerals, its replacement will eliminate, or nearly eliminate, SO₂ emissions in most cases. If a single raw material component contains carbon and the carbon is responsible for decomposing sulfates into SO₂, replacing it may substantially reduce SO₂ emissions. Finally, if sulfur (and chloride) is present in excess of alkali on a molar basis, either reducing the sulfur input to the system or increasing the alkali input to the system may reduce SO₂ emissions.

However, replacing one raw material with another raw material may not be economically feasible. Additionally, increasing alkali input may not be possible because of cement product quality specifications on total alkali concentration in cement.

Kiln system alterations. Schmidt, et al [1986] found on a kiln with relatively high SO₂ emissions that irregular distribution of kiln feed in the riser duct to two bottom stage cyclones

created widely differing temperatures between them. If a kiln system is operating with this condition, the kiln feed distribution can be corrected to more nearly equalize gas temperatures. The improved meal distribution may reduce SO₂ emissions by up to 20%.

Sulfur Dioxide Scrubbers

As previously presented in this paper, the removal of SO₂ already formed in a kiln system is a function of temperature. At high temperatures (>1,050°C [>1,920°F]) removal is ineffective because the equilibrium is not as favorable. At low temperatures (200-350°C [390-660°F]), the reaction is too slow, so injection of alkaline agents to absorb SO₂ is not effective. However, the reaction is favorable and fast enough in a temperature range of 800-950°C (1,470-1,740°F). Calcium hydroxide can be effective even at lower temperatures because of high surface area. The temperature, fineness of the absorbent, and residence time will dictate the efficiency of sulfur capture. The optimum temperature is 800-900°C (1,470-1,650°F), high fineness hydrated lime is more efficient than low fineness CaO, and longer residence time is helpful.

If kiln exhaust gases are cooled and humidified to near saturation, very efficient SO₂ removal is possible. However, a sludge may be generated that could require disposal. Sulfur dioxide absorption by hydrated lime shows very high efficiency at both low temperatures (<65°C [<150°F]) and high temperatures (>480°C [>900°F]). Sheth [1991] notes that the theoretical maximum efficiency for SO₂ removal by Ca(OH)₂ would be at 50°C (120°F).

Dry reagent injection. Steuch and Johansen [1991] found that Ca(OH)₂ was the most effective scrubbing agent, and that it was most effective when added to the kiln feed. Adding it to the raw mill or the conditioning tower was not as effective. However, in no case was the efficiency high. Having the gases near the dew point improved the effectiveness.

Nielsen [1991], however, reported that adding quicklime or hydrated lime into the riser duct between the two upper cyclones can produce a 50% SO₂ removal efficiency with a 2.5:1 CaO/SO₂ ratio, while a 70% removal efficient required a 4:1 ratio. Introducing lime into the conditioning tower (dry) is far less effective, at most showing 20% removal efficiency.

Schütte [1989] found that the Ca/S ratio for hydrated lime used to capture SO₂ was dependent on the properties of the hydrated lime and on the reaction conditions. The fineness, quality, and manufacture of the additive can cause differences of up to 30% in the SO₂ absorption capacity of the hydrated lime.

RMC Pacific dry Ca(OH)₂ injection. RMC Pacific has experimented with injecting dry Ca(OH)₂ to control SO₂ emissions. Sheth [1991] reported that RMC injected dry Ca(OH)₂ into the Stage II riser and the preheater downcomer duct. The CaO/SO₂ stoichiometric ratio varied between 40:1 and 50:1 and resulted in SO₂ removal efficiencies varying between 55%-65%. The highest SO₂ removal was 80% and was achieved by injecting Ca(OH)₂ into the roller mill. The calcium hydroxide was not metered into the roller mill but was instead unloaded pneumatically from a truck directly into the roller mill, resulting in an undetermined but very high CaO/SO₂ stoichiometric ratio. Similar reduction of SO₂ emissions are observed in a number of plants using Ca(OH)₂ injection into the gas duct to the upper preheater cyclones.

Krupp Polysius Polydesox. Polysius has developed a SO₂ removal process they call the “Polydesox” process. This system uses hydrated lime added at the riser between the first and second preheater stage or in the second stage preheater vessel where SO₂ is formed from pyrites. Polysius claims SO₂ removal efficiencies of as high as 85% for this system.

In summary, the addition of $\text{Ca}(\text{OH})_2$ in the preheater shows removal efficiencies of 20-85% of the SO_2 in preheater off-gases.

Hot meal injection. Fuller Company has developed and patented a “De- SO_x Cyclone” system to reduce SO_2 emissions in a calciner kiln. A portion of the gases is taken from the calciner outlet to a cyclone located near the riser between the top two stages of the preheater. The cyclone gas outlet is ducted to the inlet to the Stage II (from the top) cyclone where pyritic sulfur in kiln feed is decomposing into SO_2 . The meal, containing freshly produced lime, is discharged into the outlet duct of the second stage. Fuller claims an SO_2 removal efficiency of 25-30% at a molar ratio of CaO to SO_2 of 5 – 6 : 1.

RMC Pacific has experimented with injection of calcined kiln feed to control SO_2 emissions. Sheth [1991] reported that calcined kiln feed was collected at the feed end of their four-stage calciner kiln and was injected into the Stage II riser and the preheater downcomer. The SO_2 removal efficiency was about 30% when injecting calcined kiln feed into the Stage II riser and was about 40% when the calcined feed was injected into the downcomer. The injection rate was about 7.5 tons per hour which provided a CaO/SO_2 stoichiometric ratio of over 30:1. A second test series was conducted by taking hot feed (870°C [$1,600^\circ\text{F}$]) from the kiln feed pipe and conveying it into the preheater downcomer duct. The feed rate was kept at 5-7 mt (6-8 st) per hour to obtain data at a high CaO/SO_2 stoichiometric ratio. RMC concluded that the SO_2 reduction was only about 30% and was inconsistent. RMC also reported severe operational problems because of erratic feed to the kiln and problems handling the hot feed.

Lime/limestone spray dryer absorber. The literature indicates that the design stoichiometric ratios for spray dryer systems for SO_2 removal in power plants are typically from 0.54-1.5, with most below 1.0 (because of fly ash alkalinity). Most power plant SO_2 scrubbers are designed for greater than 80% removal efficiency. However, SO_2 removal ranges were from 61-91% for these systems. Some of the design characteristics were:

- Ball mills were used for slaking the lime in 9 of 13 systems
- Rotary atomizers were used in 10 systems while the other 3 used dual fluid (air) nozzles for atomization
- The most common design approach to saturation temperature in the spray dryer is 11°C (52°F).
- Most systems recycled some of the collected particulate to decrease lime stoichiometry
- Most utilities disposed of the waste product in lined landfills.

Sprung [1964] conducted laboratory tests, which showed that SO_2 reacts with CaCO_3 in the temperature range of $400\text{-}500^\circ\text{C}$ ($750\text{-}930^\circ\text{F}$) to form CaSO_4 . The completeness of the reaction increases with increasing temperature and with increasing fineness of the CaCO_3 ($1,300\text{-}8,200\text{ cm}^2/\text{g}$). The presence of water vapor also increases the conversion.

Wolter [1987] found that removing one or two tons per hour of calcined kiln feed from the lowest preheater cyclone stage, hydrating it and then injecting it into the waste gas stream (e.g., in the spray tower) can achieve an SO_2 removal of 30-60%.

The author notes that most of the spray dryer type SO_2 control technologies installed in the cement industry are on preheater or preheater/calciner kilns. However, exit gases from long

dry kilns are generally in the range of 480-650°C (900-1,200°F). Typically, these gases are cooled by either spray water introduced into the feed end of the kiln or by dilution air-cooling after the gases leave the kiln. Adding a conditioning tower to replace water sprays or dilution air would enable the alkaline slurry system to be used to reduce SO₂ emissions (the equivalent of a spray dryer). Exit gases from long wet kilns are generally in the range of 175-315°C (350-600°F) and use of an alkaline slurry spray dryer type scrubber is not possible because the addition of the lime slurry may drop the exhaust gases through the acid dew point. If the exhaust gas temperature drops below the dew point, significant plugging and corrosion problems would be expected in the downstream PMCD, duct work, and ID fan.

RMC Pacific's alkaline slurry injection system (from Sheth [1991]). RMC Pacific uses a hydrated lime, spray dryer absorber to reduce SO₂ emissions. The SO₂ scrubbing system, designed and operated by RMC Pacific, consists of (see Appendix A):

1. A 135 mt (150 st) silo for lime pellets
2. A 3.6 mt/hr (4 st/hr) wet ball mill
3. A vibrating screen to remove oversize material
4. A density meter to control slurry moisture
5. A 17,800 liters (4,000 gallon) slurry tank
6. Two slurry pumps (one standby) to pump lime slurry to the conditioning tower
7. Nine atomizing nozzles in the conditioning tower.

The conditioning tower contains nine spray nozzles arranged in two banks; one bank is used to spray lime slurry and one bank is used to spray cooling water. The amount of lime slurry and/or cooling water is controlled by two control loops; one loop controls conditioning tower exit temperature and one loop controls stack SO₂ emissions. The set point for tower exit temperature depends on whether the roller mill is operating. When the mill is operating, a temperature of 230-260°C (450-500°F) is necessary to supply the heat required to dry the raw material. When the mill is down, a temperature of 160-175°C (325-350°F) is required to properly condition the gases for the electrostatic precipitator (ESP). Stack SO₂ emissions are controlled by varying the amounts of slurry and water under both modes of roller mill operation.

RMC found that the spray nozzles cannot effectively atomize lime slurry with more than 12-13% solids. The sticky nature of the slurry leads to plugging of pumps, lines and spray nozzles and has been found to cause excessive buildup on the preheater ID fan blades. The lime slurry is very abrasive and causes severe wear in pumps, lines and spray nozzles. Tungsten carbide, which is expensive, is used for spray nozzles. When SO₂ emissions are high and preheater exit gas temperatures are low, sufficient lime slurry cannot be added to reduce SO₂ to acceptable levels.

Since lime slurry is added only to condition exit gases from the kiln/preheater, there is no effect on kiln fuel use. However, if gases are cooled below the level required for drying raw materials additional heat could be required for the roller mill.

Once the lime enters the conditioning tower, except for the buildup on the preheater ID fan blades, problems are minimal. Experience shows no wear in the conditioning tower or the ESP and no effects on ESP performance were reported while spraying lime slurry.

At RMC, the captured sulfur compounds are returned as a portion of the raw material feedstock to the roller mill, which results in no scrubber effluent or sludge disposal.

EnviroCare Microfine lime system. According to EnviroCare International's product literature, their system uses the existing gas conditioning tower to introduce the scrubbing reagent consisting of a water suspension of finely pulverized calcium hydroxide, $\text{Ca}(\text{OH})_2$ (see Appendix A). The small size of the lime particles (3-10 microns) allows the particles to dissolve in water droplets quickly and react with SO_2 as it is absorbed into the water droplet. The dried lime continues to react with any remaining SO_2 in the downstream kiln system and PMCD. If desired, incorporating a feedback control loop from an SO_2 monitor to control the lime addition rate can optimize the lime injection rate. EnviroCare claims an SO_2 removal efficiency of greater than 90%.

Wet SO_2 scrubbers. Wet scrubbers have been used successfully in some industries, notably the utility and metallurgical industries. Calcium sulfate scaling and cementitious buildup which occurs in the application of a wet scrubber to the exhaust gas from a cement kiln for acid gas control may not be as serious a problem if these systems are installed downstream of high efficiency PMCD (e.g., fabric filter). Failure of the PMCD can pose difficult problems for a downstream wet scrubber.

Two wet scrubber were selected to serve as examples. The Fuller Company is a cement equipment supplier and the Monsanto DynaWave wet SO_2 scrubber has been installed and previously used on cement kilns in the U.S.

Fuller Company (FLS Miljø). The Fuller Company wet scrubber is designed to remove SO_2 , halide gases, and some particulate matter. The flue gas desulfurization system consists of the following major subsystems (see Appendix A):

- Absorbent feed system,
- Absorption section, and
- Dewatering section.

The scrubber is typically located downstream from the kiln PMCD and is operated under positive pressure. The scrubber is a large tower with the gas inlet near the bottom of the tower and numerous spray nozzles located in the upper portion of the tower. Limestone is typically used as the absorbent and a slurry of approximately 20% limestone and 80% water is produced in the mixing tank. The slurry is sprayed countercurrent to the gas flow and the limestone slurry cools the gases and reacts with SO_2 forming calcium sulfite (CaSO_3) and calcium sulfate (CaSO_4) which precipitates. Air is sparged into the sump at the bottom of the tower to oxidize CaSO_3 to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

A pump removes the gypsum from the sump for dewatering to 10-15% moisture content and the gypsum is of sufficient quality that it can be used as part of the gypsum requirement in cement production. After the gypsum has been removed from the slurry, the water is returned to the mix tank and is used to produce fresh limestone slurry.

After the gas stream has passed through the spray nozzle area, it passes through a mist eliminator to remove entrained water droplets and particulate matter. After passing through the mist eliminator, the cleaned gases are vented to the stack.

Monsanto EnviroChem DynaWave. According to Monsanto literature, the DynaWave is a "Reverse Jet" scrubber that can simultaneously accomplish several gas cleaning/process needs: hot gas quenching, particulate removal, and acid gas absorption (see Appendix A). The reverse jet is an annular orifice scrubber having one to three large-bore

nozzles. These nozzles inject a relatively large volume of scrubbing liquid counter to the gas flow to create a froth zone. The gas collides with the liquid, forcing the liquid radially outward toward the wall. Through balancing the momentums of the gas stream and liquid stream, the liquid reverses direction and returns to the vessel sump for recycle back to the jet. A standing wave is created at the point the liquid is reversed by the gas. The wave or froth zone is an extremely turbulent region where the gas absorption and particulate collection occurs. The key to DynaWave scrubbers is the establishment of this froth zone. A proper balance of gas and liquid momentums and liquid to gas ratio is required in order to achieve the froth zone. The scrubber has the ability to recirculate and handle slurries having as high as 20% solids. According to Monsanto EnviroChem, a typical DynaWave scrubber would have the process parameters summarized in Table 16.

Table 16. Typical DynaWave Process Parameters

Parameter	Units	
	Inlet gas flow rate	200,000 Nm ³ /hr
Inlet gas temperature	100°C	212°F
Inlet SO ₂ content	400 – 900 ppm	400 – 900 ppm
Outlet gas temperature	55°C	131°F
System pH (approx.)	6.5	6.5
Gas side pressure drop	450 mm W.G.	18 inches W.G.

In some cases, scrubber effluent can be purged by using it in the kiln exhaust gas-conditioning tower or in water sprays in the roller mill, which would result in no scrubber effluent or sludge disposal. However, if chlorides are present, the captured chloride compounds must be removed from the kiln system and disposed of. When calcium sulfate/sulfite (reaction products from the example above) are processed through a cement kiln, a substantial portion will normally partition to clinker, depending on several factors including alkali to sulfur molar ratio. The clinker, consequently, serves as the valve or outlet for the captured sulfur. This does not occur with chloride compounds. Chloride compounds will volatilize and build an ever-increasing recirculating load of chlorides until an outlet is provided or until kiln operating problems occur. Since the system is a tail-pipe system generally installed downstream of the PMCD, and since it operates with a saturated gas stream, it would likely be applicable to most if not all cement kilns. A single stage DynaWave scrubber in full-scale operation has a reported SO₂ removal efficiency of about 90%. Monsanto EnviroChem claims that multiple units may be installed in series to achieve whatever removal efficiency is required (e.g., 99.9%).

Sulfur Dioxide Control Techniques Applicable to Cement Kilns

The SO₂ control techniques applicable to the cement industry are summarized in Table 17. The assumed SO₂ reductions that the various control technologies can achieve are presented in Table 18.

Table 17. SO₂ Control Techniques Applicable to Cement Kilns

SO ₂ reduction technique	Applicable to kiln type			
	Long wet	Long dry	Preheater	Precalciner
Process alterations	x	X	x	x
Dry reagent injection			x	x
Hot meal injection			x	x
Spray dryer absorber		x	x	x
Wet SO ₂ scrubber	x	x	x	x

Table 18. Achievable SO₂ Reduction Using Various Control Techniques

SO ₂ control technique	Range of removal efficiency
Process alterations	0–100%
Dry reagent injection	25–85%
Hot meal injection	0–30%
Spray dryer absorber	50–90%
Wet SO ₂ scrubber	80–95%

As presented in Table 18, the achievable SO₂ reduction varies greatly. Even when the same control technology is applied to kilns of the same pyroprocessing type, the removal efficiency will depend on kiln operating parameters, uncontrolled SO₂ emissions rate, and many other site-specific factors.

ACKNOWLEDGEMENTS

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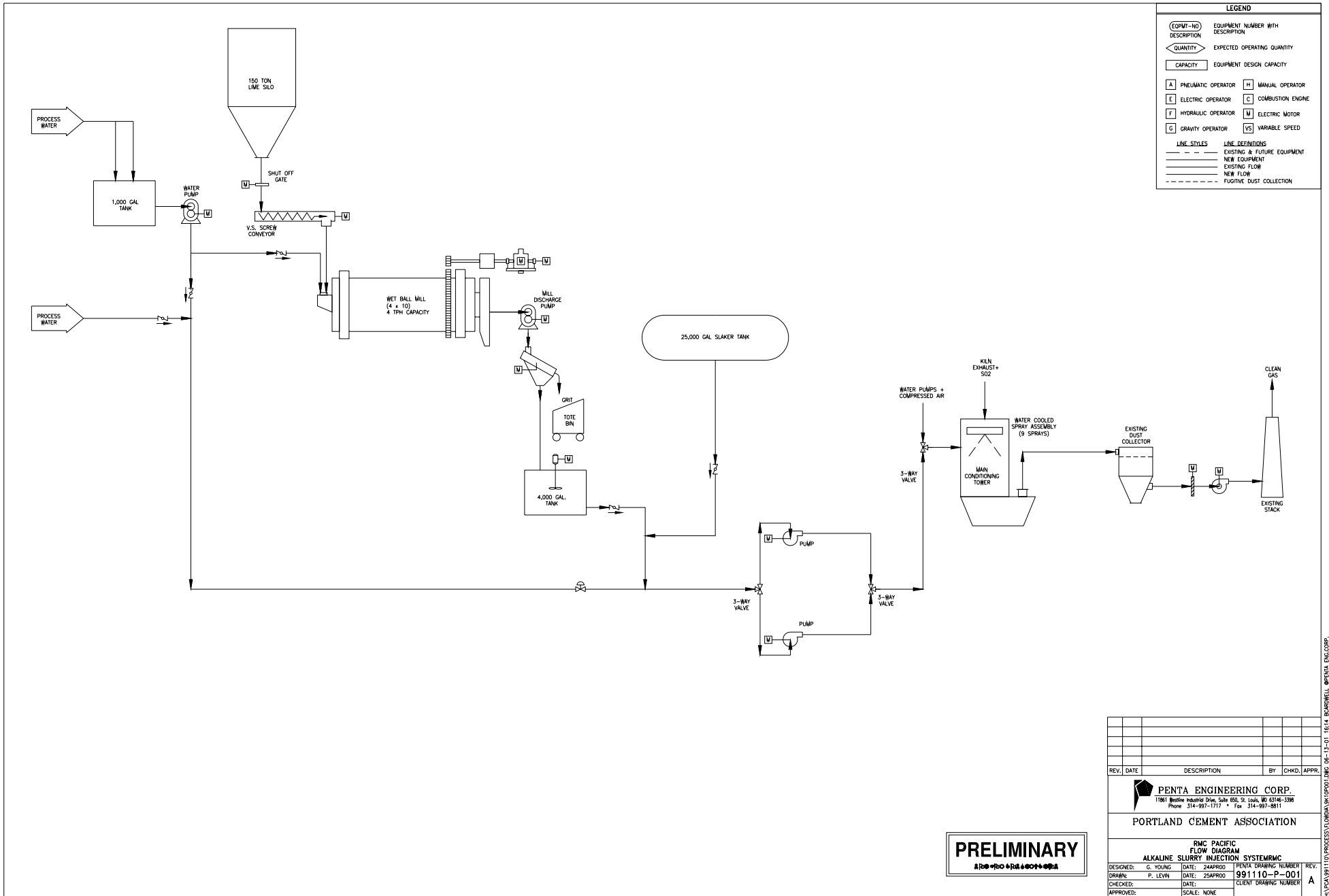
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APPENDIX A – EQUIPMENT SCHEMATICS



LEGEND

(EQUIP-NO) DESCRIPTION	EQUIPMENT NUMBER WITH DESCRIPTION
(QUANTITY)	EXPECTED OPERATING QUANTITY
(CAPACITY)	EQUIPMENT DESIGN CAPACITY
A	PNEUMATIC OPERATOR
E	ELECTRIC OPERATOR
F	HYDRAULIC OPERATOR
G	GRAVITY OPERATOR
H	MANUAL OPERATOR
C	COMBUSTION ENGINE
M	ELECTRIC MOTOR
VS	VARIABLE SPEED

LINE STYLES	LINE DEFINITIONS
---	EXISTING & FUTURE EQUIPMENT
---	NEW EQUIPMENT
---	EXISTING FLOW
---	NEW FLOW
---	FUGITIVE DUST COLLECTION

PRELIMINARY

REV.	DATE	DESCRIPTION	BY	CHKD.	APPR.

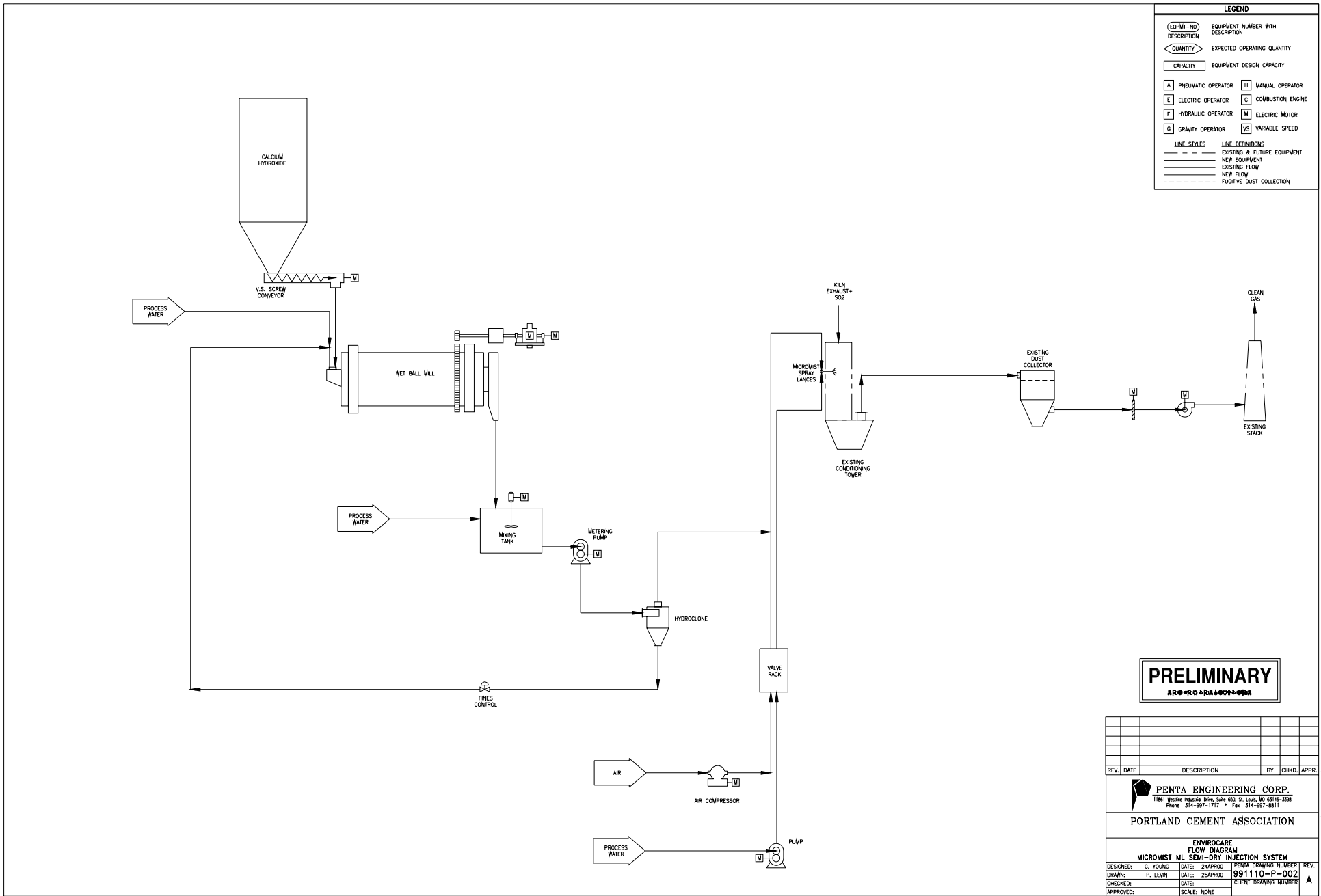
PENTA ENGINEERING CORP.
 11861 Redline Highway Drive, Suite 550, St. Louis, MO 63146-3398
 Phone 314-997-1717 • Fax 314-997-9811

PORTLAND CEMENT ASSOCIATION

RMC PACIFIC
 FLOW DIAGRAM
 ALKALINE SLURRY INJECTION SYSTEM/RMC

DESIGNED: G. YOUNG	DATE: 2/4/2000	TITLE: DRAWING NUMBER: REV.
DRAWN: P. LEVIN	DATE: 2/4/2000	991110-P-001
CHECKED:	DATE:	CLIENT DRAWING NUMBER
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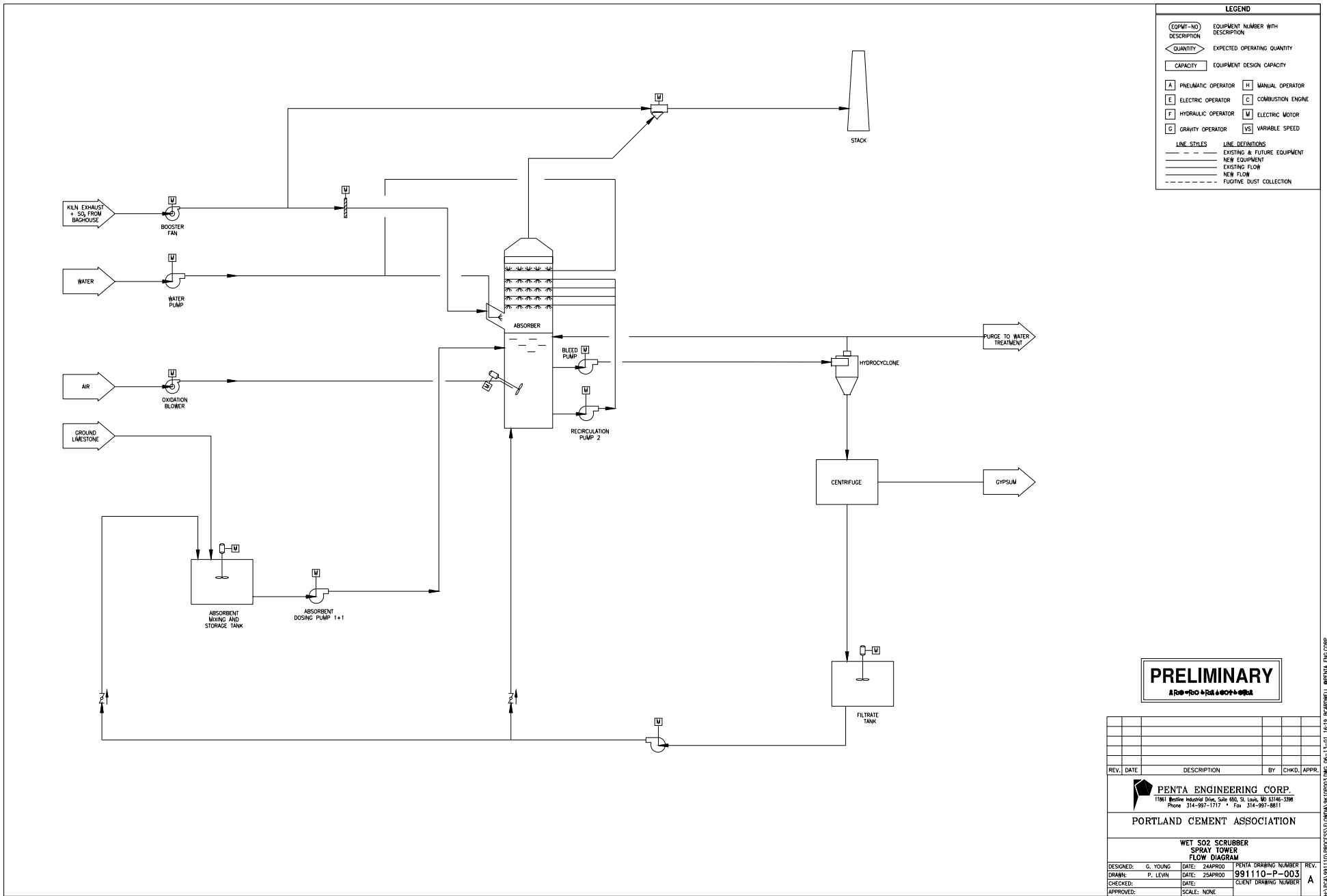
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E	ELECTRIC OPERATOR
F	HYDRAULIC OPERATOR
G	GRAVITY OPERATOR
H	MANUAL OPERATOR
C	COMBUSTION ENGINE
M	ELECTRIC MOTOR
VS	VARIABLE SPEED

---	LINE DEFINITIONS
---	EXISTING & FUTURE EQUIPMENT
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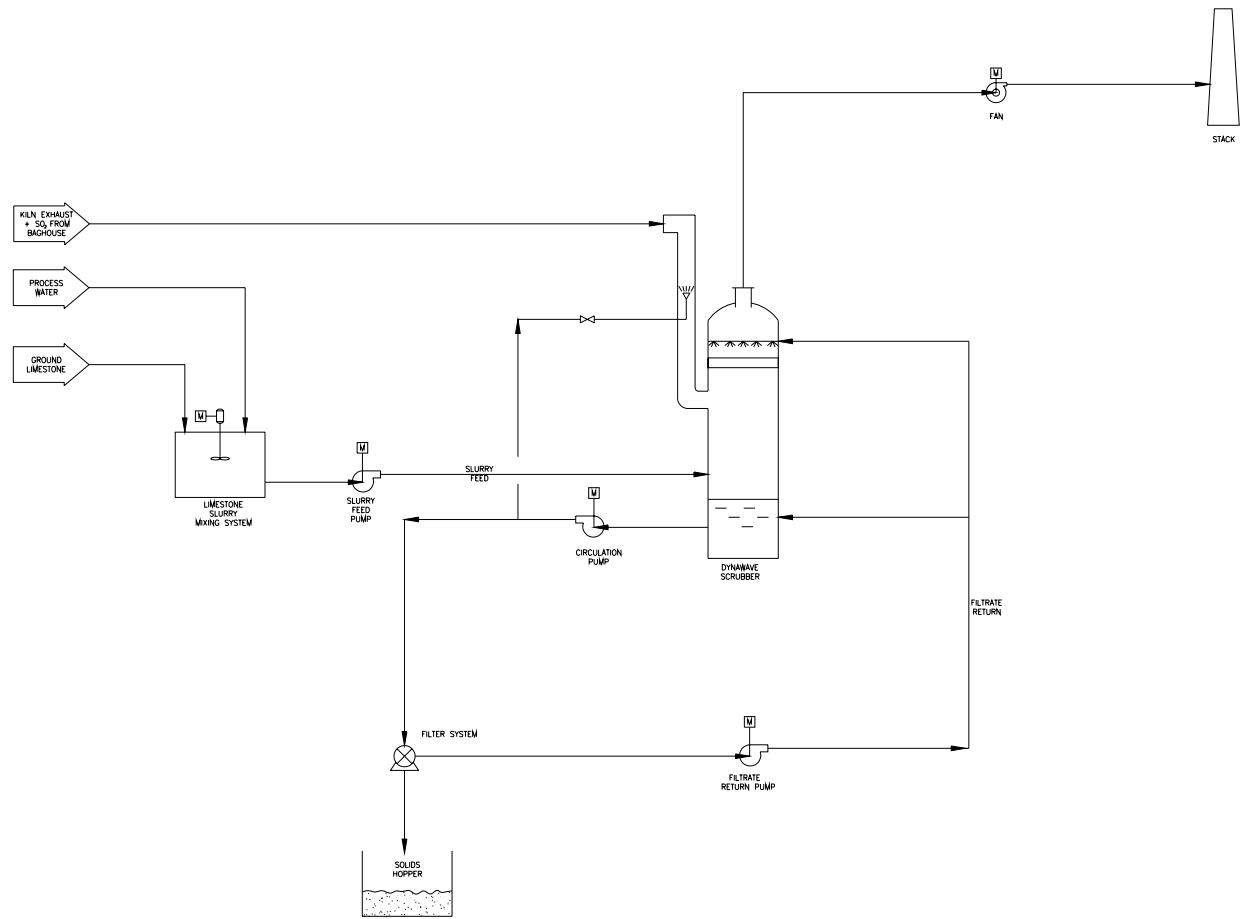
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PENTA ENGINEERING CORP. 1781 Madeline Industrial Drive, Suite 650, St. Louis, MO 63146-3706 Phone 314-997-1717 • Fax 314-997-8811					
PORTLAND CEMENT ASSOCIATION					
ENVIROCARE FLOW DIAGRAM MICROMIST ML SEMI-DRY INJECTION SYSTEM					
DESIGNED:	G. YOUNG	DATE:	2/4/97	PENTA DRAWING NUMBER:	991110-P-002
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F	HYDRAULIC OPERATOR
G	GRAVITY OPERATOR
M	MANUAL OPERATOR
C	COMBUSTION ENGINE
M	ELECTRIC MOTOR
VS	VARIABLE SPEED

LINE STYLES	LINE DEFINITIONS
---	EXISTING & FUTURE EQUIPMENT
---	NEW EQUIPMENT
---	EXISTING FLOW
---	NEW FLOW
---	FUGITIVE DUST COLLECTION

PRELIMINARY
 A B C D E F G H I J K L M N O P Q R S T U V W X Y Z

REV.	DATE	DESCRIPTION	BY	CHKD.	APPR.
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PORTLAND CEMENT ASSOCIATION					
MONSANTO-ENVIRO CHEM FLOW DIAGRAM DYNAMAWAVE WET SO₂ SCRUBBER					
DESIGNED:	G. YOUNG	DATE:	24APR00	PENTA DRAWING NUMBER:	REV.
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