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INNOVATIVE CLEAN COAL TECHNOLOGY
DEMONSTRATION PROJECT

PASSAMAQUODDY TECHNOLOGY RECOVERY SCRUBBER™

FINAL REPORT, VOLUME 1 OF 2

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ABSTRACT

This Final Report provides available design, operational, and maintenance information, and marketing plans, on the Passamaquoddy Technology Recovery Scrubber™ demonstration Project at the Dragon Products Company's cement plant at Thomaston, Maine. In addition, data on pollutant removal efficiencies and system economics are reviewed. The Recovery Scrubber was developed to simultaneously address the emission of acid gas pollutants and the disposal of alkaline solid waste at a cement plant. The process, however, has general application to other combustion processes including waste or fossil fuel fired boilers.

Selected chemistry of the exhaust gas, (before and after treatment by the Recovery Scrubber), selected chemistry of the cement plant kiln baghouse dust catch (before and after treatment by the Recovery Scrubber), and Dragon cement plant economics are presented. Current marketing efforts and potential markets for the Recovery Scrubber in several industries are discussed.

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TABLE OF CONTENTS

VOLUME I

	PAGE
DISCLAIMER	i
ABSTRACT	ii
ACKNOWLEDGMENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
LIST OF ACRONYMS AND SYMBOLS	vii
SELECTED CONVERSION VALUES	viii
SELECTED MOLECULAR AND EQUIVALENT WEIGHTS AND SOLUBILITIES	ix
EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	10
2.0 PROCESS DESIGN DESCRIPTION	15
3.0 DETAILED SYSTEM/EQUIPMENT DESCRIPTION	23
4.0 CONTINUOUS EMISSION MONITORS	32
5.0 FORMATION OF SO_2 AND NOx IN CEMENT KILNS	40
6.0 EMISSIONS RESULTS	44
7.0 OPERATING RESULTS	55
8.0 MAINTENANCE AND RELIABILITY	65
9.0 PASSAMAQUODDY TECHNOLOGY RECOVERY SCRUBBER™ ECONOMICS, POTENTIAL MARKETS AND COMPETITION, AND CURRENT MARKETING EFFORTS	71
10.0 SUMMARY AND CONCLUSIONS	93
REFERENCES	99

VOLUME 2

APPENDICES

A. List of Feasibility Studies
B. Typical Dragon Plant Coal Analyses
C. Continuous Emission Monitor Proposal from Enviroplan
D. Enviroplan Certification Tests (Field Certifications and Factory System Test Documentation)
E. CEM Calibration Gas Certifications
F. Examples of Completed Dragon Daily CEM Inspection Checklists
G. Tabulation of Daily Emissions by Time Period
H. Tabulation of Selected Inlet/Outlet SO_2 Data and Corresponding Removal Efficiencies
I. Graphs of Daily Inlet and Outlet SO_2 Emissions versus Time for 14 Operational Time Periods
J. Graphs of Daily Inlet and Outlet NOx Emissions versus Time for 14 Operational Time Periods
K. Report for Research Triangle Institute
L. Environmental Science Services report for MEC on "Reactor Removal of Alpha-Pinene Efficiency"
M. EPA's "Draft Strategy for Combustion of Hazardous Waste in Incinerators, Boilers and Furnaces"

LIST OF TABLES

Page

1. Chemical Reactions in the Recovery Scrubber 14
2. Gas Handling Train Equipment and Motor List 24
3. CKD Processing Equipment and Motor List 28
4. Potassium Sulfate Crystallization System Equipment ... 30
   and Motor List
5. Common Equipment 31
6. SO_2 Analyzer - Selected Specifications 35
7. NOx Analyzer - Selected Specifications 36
8. Typical Chemistry of Kiln Feed, Untreated CKD, ... 45
   and Treated CKD
9. Calculated Chemistry of Combining Typical 46
   Cement Kiln Feed with Treated CKD
10. SO_2 Removal Efficiency at Various Inlet SO_2 Ranges ... 48
11. Summary of Dragon Scrubber Emissions and 49
    Removal Efficiencies
12. Chemical Analysis of By-Product Potassium Sulfate 60
13. Typical Operating Parameters 61
14. Typical Recovery Scrubber Inputs and Outputs 62
15. Sulfur and Potassium Balance 63
16. Anticipated Annual Maintenance Costs 68
17. CKD Landfill Capital Costs 74
18. Revenue and Avoided Costs at Dragon 78
19. Chemistry of Biomass Ash 86

LIST OF FIGURES

Page

1. Location Map 2
2. Recovery Scrubber Process Flow 17
3. Average Inlet and Outlet SO_2 versus Time Periods ... 50
4. Average Inlet and Outlet NOx versus Time Periods ... 51
5. Hourly Process Flowsheet 64

LIST OF ACRONYMS AND SYMBOLS

Btu	British thermal unit
CAAA	Clean Air Act Amendments of 1990
CCT	Clean Coal Technology program
CEM	Continuous Emission Monitor
CKD	Cement Kiln Dust
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
^{o}F	degrees Fahrenheit
FRP	fiberglass reinforced plastic
ft	foot or feet
gpm	gallons per minute
gr/scf	grains per standard cubic foot
HP	horsepower
inch H_2O	pressure in inches water gauge
kW	kilowatt
kWh	kilowatt hour
Lb	pound weight
LbEq	pound equivalent
LbMole	pound mole
LOI	Loss on Ignition
MACT	Maximum Achievable Control Technology
mg/NM^3	milligrams per normal cubic meter
mW	megawatt
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
T/H or TPH	(short) tons per hour
VOC	Volatile Organic Compounds

SELECTED CONVERSION VALUES

Length:

1 M	=	3.28 ft
25.4 mm	=	1 inch
1 mm	=	0.039 inch

Volume:

1 M^3	=	35.31 ft^3
28.32 L	=	1 ft^3
4.546 L	=	1 gal(US)
3.785 L	=	1 gal(Imp)

Area:

1 M^2	=	10.76 ft^2
1 HA	=	2.47 acres
1 acre	=	4840 yd^2

Pressure:

1 Atmos	=	1034 g/cm^2
	=	14.7 psi
	=	101.8 KPA
	=	760 mm Hg
	=	407.4 inch H_2O
1 MPa	=	145.2 psi
	=	10.2 Kg/cm^2

Miscellaneous:

1 gal(US)	=	8.345 Lb(H_2O)
1 bbl(oil)	=	42.0 gal(US)
1 MT(oil)	=	7.4 bbl(oil)
1 bbl(cement)	=	376 Lb
1 gMole gas	=	22.4 L
1 LbMole gas	=	359 scf
2.29 mg/NM^3	=	0.001 grain/scf
2.86 $mg(SO_2)/NM^3$	=	1 ppm(SO_2)
1 KW	=	0.860 KCal
	=	3413 BTU
	=	1.34 HP
0.5557 KCal/Kg	=	1 BTU/Lb
1 KCal/Kg	=	3600 BTU/ST
239 KCal	=	1 MJ

SELECTED MOLECULAR AND EQUIVALENT WEIGHTS AND SOLUBILITIES

	Molecular Weight	Equivalent Weight	Solubilities @ 60°C g/100g H_2O
CaO	56.1	28.0	
$CaSO_4$	136.1	68.1	0.205
$CaCO_3$	100.1	50.0	0.001
Na_2O	62.0	31.0	
$NaCl$	58.4	58.4	37
Na_2SO_4	142.0	71.0	45
K_2O	94.2	47.1	
KCl	74.6	74.6	46
K_2SO_4	174.3	87.1	18
$K_2Ca(SO_4)_2 \cdot H_2O$	328.4	82.1	0.25

EXECUTIVE SUMMARY

Introduction

The Passamaquoddy Technology Recovery Scrubber™ (the Recovery Scrubber) was selected for partial funding under Round II of the U.S. Department of Energy's (DOE) Clean Coal Technology (CCT) program. This project has been partially funded pursuant to Cooperative Agreement Number DE-AC22-90PC89657, issued December 20, 1989. A full-scale prototype of the Recovery Scrubber was constructed at the Dragon Products Company's cement plant in Thomaston, Maine ("Dragon") (see Figure 1 - Location Map) and began operation in December 1990. Various engineering problems, none of which were relevant to the fundamental technology, were encountered. Resolution of these problems was delayed by extended cement plant down-time because of poor market conditions. However, essentially all of the problems have been solved and the system has achieved reliable operation.

Gaseous emissions from cement kilns, particularly of sulfur dioxide and those produced by the burning of hazardous waste fuels, are being more stringently regulated and the only alternative responses available to kiln operators are elimination of the use of hazardous waste fuels (for which a tipping fee is paid to the cement plant) or use of low-sulfur fuels (which command increasing price premiums). Both options have a substantial adverse effect on plant or company economics. Sulfur dioxide emissions can also be reduced by installation of conventional lime or limestone scrubbers. However, these types of scrubbers are both expensive to build and operate, and result in an additional disposal problem, scrubber sludge.

There are approximately 2,000 portland cement kilns in the world of which about 250 are in the United States and Canada. Most of these use raw materials which contain volatile contaminants (potassium, sodium, sulfur, chlorine). These volatile elements, and compounds of these elements, become concentrated in the dust entrained in kiln exhaust gas which is subsequently recovered in dust collection equipment before the gas is released to the atmosphere. In the absence of

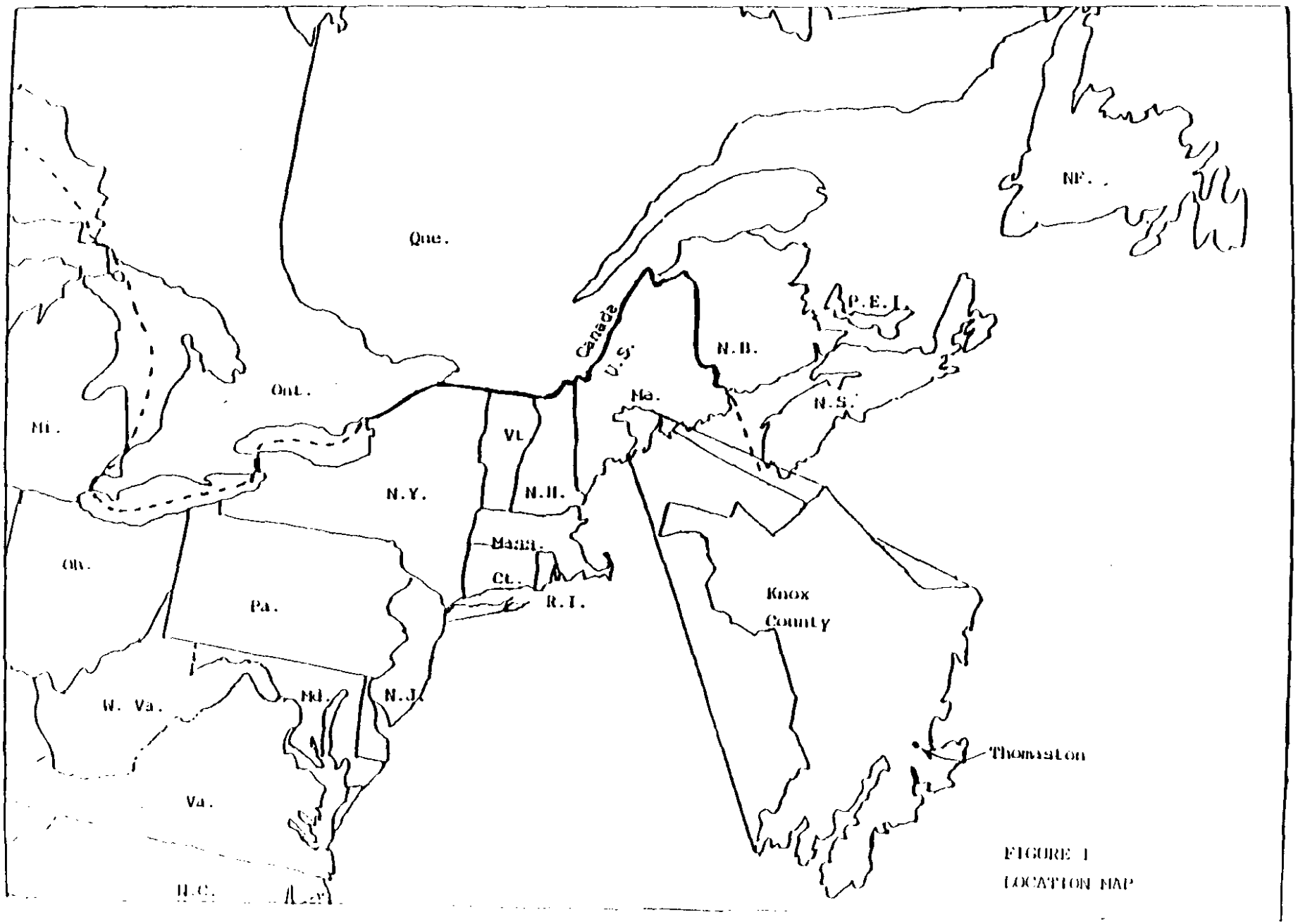


FIGURE 1
LOCATION MAP

significant volatile constituents, the dust collector catch, or cement kiln dust (CKD) as it is known in the industry, may be returned to the process. Where volatiles levels are excessive, CKD must be discarded or "wasted" in order to avoid kiln operating and cement quality problems. Virtually all CKD now wasted is landfilled on-site, a practice subject to increasing scrutiny and criticism, particularly for kilns which burn hazardous waste fuels. There is presently no method of waste dust recovery, other than the Recovery Scrubber, in commercial use.

At Dragon, over one million tons of process waste dust had been landfilled during the life of the plant, and further landfilling was becoming more difficult as regulations were tightened, while wasting 10% of feed materials was becoming untenable as production costs came under increasing market pressure. Simultaneously, sulfur dioxide emissions in the exhaust gas were coming under increasingly stringent regulation, and the alternative to scrubbing was limiting fuel sulfur levels; progressively, these low sulfur fuels are commanding a premium which, again, cannot be supported by the economics of cement production. It should be noted that, typically, 30-40% of cement direct manufacturing costs are due to fuel.

The Recovery Scrubber operates at the Dragon plant by combining the alkali component of CKD (mainly potassium) with sulfur species in CKD and exhaust gas. Both exhaust gas and CKD are cleaned, and the reaction product (potassium sulfate) is extracted as a saleable by-product.

Process Description

The Recovery Scrubber is designed to exploit the chemical reactions between acidic and alkaline waste components; most commonly between acidic exhaust gas constituents and alkaline solid wastes. The products of reaction are salts of alkali metals which can be recovered for profitable recycling.

The Recovery Scrubber involves a reaction tank in which flue gases are intimately mixed with a liquid waste or a solid waste in slurry form. Such a reaction system is versatile, and allows for a variety of waste treatment processes according to the particular needs of each application.

The Dragon prototype uses highly basic CKD to react with and remove acidic (SO_2, HCl, and CO_2) components from exhaust gas. Soluble alkali compounds are removed from CKD, renovating it for reuse as feedstock in the cement plant while the soluble salt products are recovered for subsequent sale. Waste heat from the treated exhaust gas stream is used for evaporation, concentration, and crystallization of dissolved salts (K_2SO_4, KCl, etc).

Environmental Performance

At the Dragon plant, all of the currently produced CKD (an average of 10 TPH) is now renovated in the Recovery Scrubber and recycled back to the cement plant as a portion of the raw material feedstock of the plant.

The percent SO_2 removal efficiency, defined as:

$$\frac{[(\text{pounds of } SO_2 \text{ input}) - (\text{pounds of } SO_2 \text{ output})] \times 100}{\text{pounds of } SO_2 \text{ input}}$$

has averaged 89.2 percent for the entire Phase III operating period (see Section 6 - Emission Results). During the final three months of Phase III operation (these months represent 27% of the operating hours during Phase III), the Recovery Scrubber has demonstrated a time weighted SO_2 removal efficiency of 94.6 percent. Often during this time, the SO_2 input to the Recovery Scrubber was so low that an outlet SO_2 of between 2 and 10 pounds of SO_2 per hour resulted in a calculated removal efficiency of less than 85 percent. During operations in 1993, when the inlet SO_2 was between 100 and 200 pounds per hour, the calculated removal efficiency was better than 94 percent. When the inlet SO_2 was greater than 200 pounds per hour, the removal efficiency was 98.5 percent.

In addition to the excellent SO_2 removal experienced, NOx removal efficiency has averaged 18.8 percent for the entire Phase III operating period (see Section 6 - Emission Results).

In stack testing for the State of Maine conducted during the week of December 16, 1991, particulate emissions were measured at 6.02 pounds per hour or about 0.005 grains per SCF.

In testing performed on a pilot scale Recovery Scrubber, HCl removal efficiency was demonstrated to be about 98 percent. A final report on this test series has not been completed, however a copy of this report will be made available, upon request.

In stack testing conducted September 1 and 2, 1993, the Recovery Scrubber demonstrated a volatile organic compound (VOC) removal efficiency of greater than 70 percent*.

Maintenance and Reliability

Upon initial start-up December 20, 1990, several routine piping and electrical malfunctions, typical of new construction, were experienced and quickly corrected. Compounding these routine new construction type problems, several other problems were experienced. In addition to these start-up problems, the host cement plant was only operating approximately 50 percent of the time because of an extremely poor market for cement in the northeast United States. This low level of operation severely delayed implementation of changes and corrective actions to solve the problems identified during the start-up phase.

By August 1991, most of these problems had been solved and Phase III, operation and data collection, began August 20, 1991.

During the interval between August 20, 1991 and January 14, 1992, the Recovery Scrubber operated in excess of 1,400 hours. The host cement plant kiln was shut down in mid-January, 1992 for winter maintenance and inventory control and was not restarted until May 1992. During the second operating interval, between May 13, 1992 and October 1, 1992, the Recovery Scrubber operated more than 1,300 hours.

*Tests were performed using a specific C_{10} compound.

The Recovery Scrubber was shutdown October 1, 1992 to install the chevron style mist eliminator system and accompanying spray wash system. Before the work was completed, the host cement plant kiln was shut down for winter maintenance and remained down until April 1993 for inventory considerations.

Since completing installation of the chevron style mist eliminator and subsequent start up of the Recovery Scrubber, in April 1993, its availability improved markedly. During the third and final operating interval, between April 13, 1993 and September 22, 1993 the Recovery Scrubber operated 2,600 hours. However, if the host plant down time is ignored since the April start-up, the Recovery Scrubber itself has only been off line twice. When cement plant down time is not counted (i.e., not considered part of the hours available to the Recovery Scrubber) the Recovery Scrubber operated 65 percent of the time in April, 78.6 percent of the time in May, 80.8 percent of June hours, and 99.5 percent of the July 1993 hours. The August and September availability has continued to be very good.

Market Potential

Cement

The Recovery Scrubber, is generally expected to operate at a net annual profit as evidenced in many preliminary feasibility studies conducted for numerous cement companies (see Appendix A). That is, the value of the products produced or expenses that may be avoided when using the Recovery Scrubber exceeds the costs of capital and interest costs plus maintenance and operation of the Recovery Scrubber. Other installations may be justified by the need to meet regulatory requirements on exhaust gas emissions of SO_2, HCl, organics, or particulates, or future regulatory requirements on CKD management. Of the approximately 250 portland cement kilns in the U.S. and Canada, only three kilns currently have SO_2 controls installed (one of which is the Recovery Scrubber). With the continued implementation of the provisions of the Clean Air Act Amendments of 1990 (CAAA), additional plants will have to install SO_2 controls and a number of portland cement kilns may also emit more than 10 tons of HCl per year and trigger the Title III - Air

Toxics, Maximum Achievable Control Technology (MACT) provisions. In addition, the U.S. EPA's Report to Congress concerning CKD disposal pursuant to RCRA 3001(b)(3)(A) (the Bevill amendment), will dramatically tighten CKD disposal requirements. The Recovery Scrubber is the only control method that can simultaneously control SO_2, HCl, particulates, and renovate and recycle CKD both as it is produced and through reclamation of existing old CKD landfills. Not only does the Recovery Scrubber offer these environmental benefits, it generally does so at a net operating profit. To summarize, the market potential in the cement industry is exceptional.

Pulp and Paper/Waste Incineration

Many of the 2,300 pulp & paper mills in the United States, Canada, Western Europe and Japan (of a total of 3,800 world wide), and the 760 waste-to-energy ("WTE") plants in the world produce an alkaline ash which the Recovery Scrubber could use in the same way that it uses alkaline CKD.

Utility

There are also numerous smaller (<100 mW) fossil fuel fired boilers whose emissions could be cleaned with a Recovery Scrubber using an on-site or off-site waste material as reagent. Non-utility installations will typically cost US$7-$30 million depending upon capacity and complexity. In many situations, these installations will be profitable simply on the basis of the benefits produced and conventional pollution control provided.

Installation of a Recovery Scrubber normally involves no interference with operation of the host plant. Tie in of exhaust gas ducting with appropriate dampers can be made during a maintenance or other short term shut-down. Typically, the ash or dust stream is presently being sent to landfill so that dust or ash handling is external to the plant and tie in to the Recovery Scrubber would not present a problem.

Summary and Conclusions

The wet process kiln at Dragon uses about 10 TPH of 2.5% to 3.0% sulfur coal (see Appendix B) as fuel. Prior to installation of the Recovery Scrubber, Dragon was faced with a State of Maine requirement that would have forced the plant to reduce its fuel sulfur content by approximately one-half. This change would have increased operating costs between $1 million and $2 million per year.[1] In addition, the landfill used by Dragon (prior to installation of the Recovery Scrubber) to dispose of CKD was nearly full and it was anticipated that securing permits for a new landfill was going to be both expensive and time consuming.

The two problems outlined above, fuel sulfur limitations and CKD landfilling, led to the development, pilot scale testing, and design and installation of the full-scale Recovery Scrubber prototype at the Dragon cement plant in Thomaston, Maine. Subsequent start-up problems were identified and resolved. Phase III SO_2 removal efficiency was 89.2 percent for the entire time period, but averaged nearly 95 percent in the later stages of Phase III, after fine tuning the exhaust gas distribution in the reaction tank plenum. In addition, when the inlet SO_2 was sufficiently high (i.e., >200 pounds per hour), the calculated SO_2 removal efficiency was 98.5 percent. Phase III NOx removal efficiency was 18.8 percent and increased to nearly 25 percent during the final few months of operation.

Several additional benefits accrued that were not originally planned or foreseen. These include, but are not limited to, HCl scrubbing efficiencies greater than 95 percent, particulate capture resulting in demonstrated emission levels of 0.005 - 0.007 grains/SCF (inlet dust loading was approximately 0.04 grains/SCF), a VOC (represented by α-pinene) removal efficiency of over 70 percent, and potential application of the Recovery Scrubber to several other industries.

After an initial period of debugging and problem solving, the Recovery Scrubber has proven to be a reliable, low maintenance pollution control device. It should be noted that reliability is, among other things, a function of

design. Higher reliability, if desired, may be designed into equipment through use of more expensive, severe duty equipment or through the use of redundant sub-systems, albeit at higher initial capital cost.

Currently, Passamaquoddy Technology, L.P. is actively marketing this technology in the U.S., Canada, and world wide in the cement industry, the pulp and paper industry, to municipal solid waste incinerators, and to a few selected utilities. By early 1994, Passamaquoddy Technology expects to have a contract for installation of a second Recovery Scrubber in the cement industry. Negotiations and marketing efforts continue in the other industries and definitive agreements may be reached for at least one non-cement industry installation during 1994.

1.0 INTRODUCTION

This final report describes the start-up and operating experience of the first full-scale prototype of the Passamaquoddy Technology Recovery Scrubber™ at the Dragon Products Company cement plant in Thomaston, Maine. It also presents sections on the process design and equipment, a system description, a brief description of the continuous emissions monitors (CEM) used, a brief discussion of SO_2 and NOx formation in cement kilns, emission control results, operating results, maintenance and reliability of the Recovery Scrubber, the economics of the Dragon installation, potential markets, competition, and current marketing efforts by Passamaquoddy Technology, L.P.

The Recovery Scrubber was selected for partial funding in Round II of the U. S. Department of Energy's (DOE) Innovative Clean Coal Technology Program (CCT) and Cooperative Agreement Number DE-AC22-90PC89657 was issued December 20, 1989. Construction was completed and the Recovery Scrubber began operation one year later.

1.1 BACKGROUND

Pollution control at cement plants, in the past, was primarily concerned with particulate control. Recently, the Clean Air Act Amendments of 1990 (CAAA) have tightened restrictions on several air pollutants, primarily sulfur dioxide, SO_2, and added a list of toxic air pollutants that may require more stringent control, including HCl and several heavy metals or their compounds. In addition, the U.S. EPA will submit a Report to Congress concerning recommendations on regulations of CKD pursuant to the Bevill amendment.

1.1.1 SO_2 Provisions of the CAAA

Although the SO_2 provisions of the CAAA primarily addresses utility boilers larger than 25 megawatts (mW), EPA is required to inventory industrial sources of SO_2 emissions every five years and to then project industrial SO_2 emissions 20 years into the future. The CAAA caps industrial emissions at 5.6 million tons of SO_2 and requires EPA to take appropriate action to bring emissions below 5.6 million tons

if the projection predicts levels exceeding the cap.

1.1.2 Cement Kiln Dust (CKD)

Calcium, silica, iron, and alumina are some of the necessary elements and compounds required to produce portland cement. Also, several volatile trace elements that are not required are present. Potassium is one of these volatile elements that is present and is not only not required but is deleterious to the long term durability of cement products. Potassium has a relatively low boiling point; and, at the temperatures achieved in a cement kiln (i.e., 3,000°F), several potassium compounds boil or vaporize. As gases travel to cooler parts of the kiln, potassium compounds condense onto fine dust particles in the exhaust gas stream. Consequently, CKD captured in the dust collector at the rear of a portland cement kiln contains elevated levels of potassium and, in many cases, can not be returned to the process.

Cement plants dispose of cement kiln dust (CKD) as a means of reducing the concentration of alkalis (K and Na), sulfur compounds, chlorides, and other volatile metals in the kiln system.[2] Soluble alkali sulfates are known to affect the strength development of portland cement[3] and are one reason cement plants have typically disposed of CKD in the past. In addition, on preheater type cement kilns, if the alkali salts accumulate to more than approximately 2% in the feed materials, material build-ups within the kiln system and resulting kiln operating problems will occur[4]. Until recently, landfill disposal of this waste CKD has been virtually unregulated.

The Environmental Defense Fund sued the US EPA to force it to perform a study of CKD as required by the Bevill amendment. The suit has been settled and EPA is under a consent order and is scheduled to report the results to Congress by the end of 1993.

Additionally, the Boiler and Industrial Furnace (BIF) regulations were established February 21, 1991 (56 Fed. Reg. 7134) and a number of industry and environmental groups have filed lawsuits contesting various parts of the rules.[5] One side of the issue argues that EPA has unlawfully construed

the Bevill amendment to allow cement kilns to escape RCRA controls on combustion residues derived from burning hazardous waste.[6] EPA claims that the residues are covered by Bevill because the residues are not significantly different from the residues that result from processing normal or virgin raw materials (53 Fed. Reg. at 7197, col. 1)[7].

In the past, CKD was generally hauled to an abandoned area of the cement plant quarry and discarded. Whatever the final result of EPA's Bevill determination regarding CKD or the outcome of the various lawsuits related to the BIF regulations, it appears that CKD will fall under much tighter regulations.

1.1.3 Air Toxics Provisions - Title III of the CAAA

Generally, the Air Toxics provisions are aimed at reducing routine emissions of air toxics from major sources. Title III establishes a list of 189 chemicals (including HCl) subject to the new air toxics provisions. EPA must establish a list of major source categories (e.g., chemical plants, pulp and paper mills, cement plants, etc.) for the purpose of issuing emission standards for the listed chemicals. Major sources are defined as those which emit 10 tons per year (TPY) of a listed pollutant or 25 TPY of any combination of all the listed pollutants. EPA must list sufficient area source categories to ensure that 90% of the emissions of the 30 most serious area source pollutants are regulated.

For each major source category, EPA is to promulgate a standard which requires the installation of Maximum Achievable Control Technology ("MACT") by new and existing sources in the category. MACT is intended to be the best available control technology (cost is to be considered when making a MACT determination). MACT standards may distinguish among classes, types, and sizes of sources in a category. For new sources, MACT standards must be no less stringent than the emission control achieved in practice by the best controlled similar source in a category. For existing sources, standards must be no less stringent than the emission control achieved by the best performing 12% of sources in the category (or best 5 sources in a category with less than 30 sources). All MACT standards are to be

promulgated within 10 years, with standards for 40 source categories required within two years. Existing sources must comply with MACT standards no later than three years after they are issued (with a possible one year extension). Any source making a voluntary reduction of 90% below 1987 emission levels receives a six year extension of the MACT compliance date. The voluntary reduction must be achieved before the applicable MACT standard is first proposed.

The cement industry has been targeted as one of the source categories that will be investigated by EPA first in their efforts to establish standards for 40 source categories during the first two years. As mentioned in the Executive Summary in the section on market potential in the cement industry, a number of cement kilns will likely exceed the 10 TPY limit for HCl established by Title III of the CAAA. EPA, recognizing this possibility, contracted with Entropy, Inc. to perform testing (during the week of September 9, 1993) on the Dragon Recovery Scrubber as a prelude to possibly establishing the Recovery Scrubber as MACT control for HCl emissions from portland cement kilns.

1.2 The Passamaquoddy Technology Recovery Scrubber™

The Recovery Scrubber uses CKD or other alkaline wastes to efficiently scrub SO_2, HCl, particulates and other exhaust gas emissions, and simultaneously recycle CKD into fresh feedstock for a cement kiln and produce fertilizer and distilled water as saleable or reusable by-products. Exhaust gases are cleaned of acid rain producing compounds; potassium is removed from CKD and it can therefore be recycled; and valuable products are produced from waste materials.
Table 1 - Chemical Reactions in the Recovery Scrubber, provides a list of the pertinent chemical reactions and accompanying changes in form, by dissolution or precipitation, occurring in the process. The reactions have been grouped into the following: exhaust gas reactions, CKD reactions, and reactions between products of the former two reactions[8].

TABLE 1

Chemical Reactions in the Recovery Scrubber.

Exhaust Gas Reactions

$SO_2 + H_2O \longrightarrow 2H^+ + SO_3^=$ (in solution)

$H_2SO_3 + \frac{1}{2}O_2 \longrightarrow 2H^+ + SO_4^=$ (in solution)

$CO_2^* + H_2O \longrightarrow 2H^+ + CO_3^=$ (in solution)

CKD Reactions

$CaO + H_2O \longrightarrow Ca^{++} + 2OH^-$ (in solution)

$Ca(OH)_2 + CO_2^* \longrightarrow CaCO_3 + H_2O$ (insoluble)

$CaSO_4^{**} \longrightarrow Ca^{++} + SO_4^=$ (in solution)

$K_2SO_4 \longrightarrow 2K^+ + SO_4^=$ (in solution)

$K_2O + H_2O \longrightarrow 2K^+ + 2OH^-$ (in solution)

Reactions Between Products of Exhaust Gas and CKD Reactions

$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$ (soluble)

$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2H_2O$ (insoluble)

$Ca^{++} + CO_3^= \longrightarrow CaCO_3$ (insoluble)

$2K^+ + SO_4^= \longrightarrow K_2SO_4$ (soluble)

* Slurry in reaction tank is saturated with CO_2.

**Greater than 100 times more soluble than $CaCO_3$ at Recovery Scrubber reaction conditions (in water, 140°F)

2.0 PROCESS DESIGN DESCRIPTION

2.1 Overview

A number of industrial processes involving combustion give rise to solid or liquid wastes containing appreciable quantities of alkali metal compounds (K, Na). The Recovery Scrubber is designed to exploit the chemical reactions between acidic and alkaline waste components; most commonly between acidic exhaust gas constituents and alkaline solid wastes. The products of reaction are salts of alkali metals which can be recovered for profitable recycling.

The Recovery Scrubber involves a reaction tank in which flue gases are intimately mixed with a liquid waste or a solid waste in slurry form. Such a reaction system is versatile, and allows for a variety of waste treatment processes according to the particular needs of each application.

The Dragon prototype uses highly basic CKD to react with and remove acidic (SO_2, HCl, and CO_2) components from exhaust gas. Soluble alkali compounds are removed from CKD, renovating it for reuse as feedstock in the cement plant while the soluble salt products are recovered for subsequent sale. Waste heat from the treated exhaust gas stream is used for evaporation, concentration, and crystallization of dissolved salts (K_2SO_4, KCl, etc). In addition to the gaseous pollutants, the Recovery Scrubber is also an efficient particulate collector. Recent stack testing demonstrated a particulate emission level of about 15 mg/NM^3 (0.006 grains per SCF) after treatment in the Recovery Scrubber. Sale of by-products, avoidance of landfill costs, savings on raw material, and savings resulting from the use of less expensive fuels can result in operation at a profit.

In the Recovery Scrubber, dry cement kiln dust is mixed with water to form a dilute slurry. Exhaust gas, generally 200°F. or warmer, and containing the acidic oxides of sulfur, nitrogen, and carbon, is passed through a heat exchanger where it is cooled to the point of condensing moisture. The CKD-water slurry and cooled flue gas are then brought into contact with each other, and allowed to react to perform both CKD renovation and flue gas scrubbing.

Reacted CKD undergoes significant chemical change during the process. It is freed of soluble alkali (Na and K) and significantly reduced in calcium sulfate content. Calcium, from dissolved gypsum ($CaSO_4 \cdot 2H_2O$) and calcined limestone (CaO) is precipitated as calcium carbonate ($CaCO_3$). Reacted CKD at this point in the process is essentially the same composition as cement kiln raw material feed.

Reacted slurry is separated into a liquid and a solid fraction (thickened slurry). The liquid fraction containing dissolved material is pumped to an evaporator where water is removed from the potassium salt solution leaving solid crystalline potassium sulfate. The processed CKD solids, as a concentrated slurry, are washed with distilled water (derived from the evaporation process) and returned to the cement plant raw material preparation system.

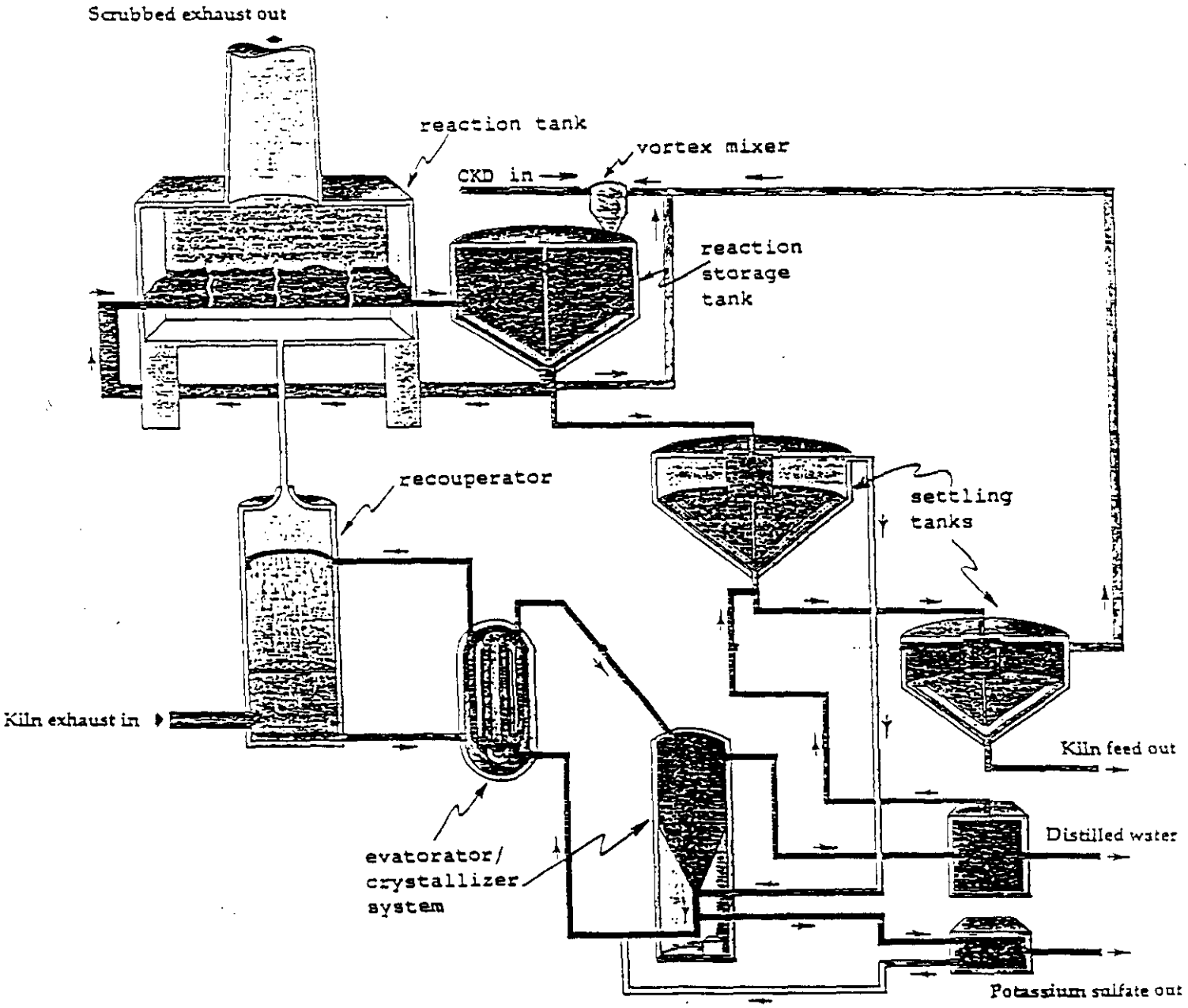
Waste CKD, exhaust gases (including waste heat), and waste water are inputs to the process. Renovated CKD, potassium based fertilizer (either KCl or K_2SO_4), scrubbed exhaust gas, and distilled water are process outputs. There is no waste. Nothing goes to landfill. Nothing goes to the sewer.

2.2 Detailed Process Description

Figure 2, Recovery Scrubber - Process Flow, is a schematic illustration of the system components and material flows. The following discussion refers to the labeled components in that diagram.

2.2.1 Vortex Mixer

A vortex type mixer is located on top of the reaction storage tank. CKD is conveyed to the vortex mixer by a screw conveyor - elevator combination. Reacted slurry from the reaction storage tank is pumped to the vortex mixer at 300 - 500 GPM and injected tangentially at four points around the periphery of the vortex. CKD is dropped into the center of the vortex, mixed with reacted slurry and immediately discharged into the reaction storage tank. Process make-up water is added to the reaction storage tank to maintain the desired slurry moisture content.



Recovery Scrubber
Process Flow

Figure 2

2.2.2 Reaction Tank

After CKD is mixed to form a slurry (approximately 20% CKD solids : 80% water, by weight), it is used as the scrubbing reagent in the reaction tank. The reaction tank is a dual purpose sub-system where CKD is used as the scrubbing reagent for the flue gas, and where flue gas, dissolved in water, simultaneously renovates CKD. Exhaust gas bubbles through a depth of slurry rather than having the slurry sprayed into the gas stream. This method of gas-liquid contact provides for very efficient scrubbing of the gas while maintaining a chemical solution capable of dissolving calcium sulfate and precipitating calcium carbonate. This result is the direct opposite of limestone based scrubber systems where calcium carbonate is reacted to form a calcium sulfate waste sludge.

Process chemistry is based on the relative solubilities of limestone ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and potassium sulfate (K_2SO_4), and on the ability to maintain a reaction solution saturated in carbon dioxide obtained from the flue gas. Both calcium carbonate and gypsum are present in the scrubbing medium and flue gas provides a constant input of both carbon dioxide and sulfur dioxide or sulfur trioxide. The solubility of gypsum is approximately 0.22% and that of calcium carbonate 0.002%. That is, gypsum is more than 100 times more soluble than limestone. As gypsum from waste cement kiln dust dissolves in the slurry to approach saturation (0.22% in solution), the Ca^{++} ion is continuously precipitated as calcium carbonate due to the constant presence of carbon dioxide in solution. Gypsum, therefore, cannot reach saturation and gypsum scaling is avoided. Alkali, for example potassium from CKD, is available to combine with the $SO_4^{=}$ liberated from $CaSO_4$ to form a highly soluble salt. The $SO_4^{=}$, therefore, remains in solution.

2.2.3 Reaction Storage Tank

The reaction storage tank affords a long residence time for CKD slurry to be in contact with water and flue gas. A long residence time is necessary to dissolve and react minerals of low solubility such as the calcium sulfate reactions described in Section 2.2.2. Reacted CKD slurry from the reaction tank is pumped to the settlement system.

2.2.4 Settlement System

Separation of renovated CKD from the water solution of alkali sulfate may be accomplished by a variety of means including filtration, centrifuging, or settlement. Because processed CKD floculates, settling tanks were selected as the preferred method.

There are two settling tanks. The first recovers the most concentrated alkali sulfate solution. The water is then evaporated to crystallize potassium sulfate (see Section 2.2.6 Recouperator-Crystallizer). Settled CKD from the first tank is rinsed with distilled water (derived from the process) and conveyed to the second settling tank. Settled solids from the second tank are conveyed to the cement plant raw material preparation system for use as a portion of the raw material for the kiln. Water separated in the second settling tank is recycled to the reaction storage tank to provide process make-up water.

2.2.5 Renovated CKD Output

CKD which has been through the process exits the second settling tank as a slurry of 40 to 50 percent solids, by weight. At Dragon, where the cement kiln is a wet process kiln, a slurry is useful as direct feed to the raw mill. The water content of the slurry is not a problem, simply a replacement for raw mill make-up water.

For application to a dry process plant the slurry should be dewatered before reentering the raw material stream. Water may be removed in cyclones, filter presses, additional settlement, or thermal drying. The drying method to be applied to a specific plant should be selected after detailed evaluation of that plant. Careful study of a specific plant will determine heat availability and the best auxiliary method for water reduction.

The potassium oxide content of reacted CKD is reduced to the level of normal kiln feed or below so that its return will not increase the alkali content of the total raw material mix. The sulfate content of reacted CKD is also significantly reduced. Trace metals, particularly those that

could render potassium salts unsuitable for fertilizer use, and those that could become progressively concentrated by reuse of CKD, must also be considered. Heavy metals, not already present as insoluble oxides, generally precipitate as the insoluble oxide, sulfate or carbonate in the Recovery Scrubber process. The heavy metals are, therefore, separated from the liquid fraction which feeds the crystallizer. They are pumped with the reacted CKD and returned to the cement plant as raw material. Therefore, the crystallized solid potassium sulfate salt contains nondetectable to very low levels of heavy metals.

2.2.6 Recouperator-Crystallizer

The recouperator-crystallizer (evaporator) is a multiple function sub-system. It is the beginning of the process for input of gaseous material and is also the source for much of the water, and the major portion of the heat, used by the process. The recouperator first cools the hot flue gas prior to use of the gas for CKD renovation. Cooling is necessary to prevent excessive evaporative loss of water from the CKD-water slurry during reaction. Cooling also condenses exhaust gas moisture for recovery and use in the system and permits use of fiberglass as an economical construction material.

The recouperator also captures energy for evaporating water from the potassium sulfate solution obtained by CKD renovation. The recouperator is a direct contact heat exchanger where water is sprayed countercurrent to the exhaust gas flow, thus cooling the gas and heating the water. The heated water is circulated to a flash tank operating under vacuum where the water flashes to low temperature steam. This steam is circulated through a shell and tube heat exchanger which transfers the thermal energy to the crystallizer circuit. The resulting recovery of the potassium sulfate solids in the crystallizer is desirable as a means of preventing discharge of potential water pollution and as a means of providing significant income by operation of the system. If the large energy requirement for evaporation were supplied by purchased energy instead of using waste heat, system economics would be less desirable.

Water vapor from the crystallizer is condensed for reuse. Because it is good quality distilled water (less than 50 ppm total dissolved solids) it could be made available for plant use or, with some additional treatment, for boiler make-up water.

2.2.7 Pelletizer/Dryer/Storage (K_2SO_4 Output)

Potassium sulfate crystals produced in the crystallizer pass through a centrifuge and to a pelletizer to form small spheres suitable for fertilizer use. The pellets are dried and conveyed to storage for shipment.

2.3 Typical Cement Plant Installation

The process description above has been for the wet process kiln at the Dragon Products Company, Inc. plant at Thomaston, Maine. Several changes would be made to the Recovery Scrubber if it is installed on other kiln process types.

2.3.1 Long Dry Process Kilns

If the Recovery Scrubber is installed on a long dry kiln, generally the only change would be the method of returning the renovated CKD to the plant process. Typically, long dry process kilns must cool and condition the exhaust gas after it exits the kiln and before it enters the particulate collection device (electrostatic precipitator or baghouse). Water is generally sprayed into the exit of the kiln countercurrent to the exhaust gas flow to both cool the gases and to increase the humidity for more efficient operation of ESPs.

Renovated CKD could be sprayed into the kiln as part of the exhaust gas cooling water. If necessary, the renovated CKD could be dewatered by filtration or other methods of drying prior to return to the raw material preparation system. The method of reintroducing treated CKD would have to be examined for each specific case and the most economical method selected.

2.3.2 Preheater and Preheater/Precalciner Kilns

A preheater or preheater/precalciner kiln will present other design considerations. Generally, exhaust gas in such plants passes through a raw mill or dryer before being dedusted so that the dust eventually collected is principally raw material rather than CKD. Volatiles (potassium, sulfur, chlorine) are typically removed by a gas bypass. A proportion of the kiln exhaust gas is taken from the kiln riser, cooled, passed through a dust collector and released to atmosphere. The dust extracted contains a high proportion of volatiles and is usually landfilled. With a Recovery Scrubber, however, it may be possible to use a meal bypass and avoid the operational and maintenance difficulties inherent in a gas bypass. While the concentration of soluble alkalis and sulfur will be lower in the cyclone underflow than in entrained dust, heat loss per ton of material extracted will be substantially lower.

A more serious concern with taking alkalis out of a preheater kiln system is that the shorter kiln residence time can result in reduced volatilization. This is particularly true with precalciner kilns. If soluble alkalis, sulfur or chlorine are present in the cyclone underflow or the bypass dust, however, the Recovery Scrubber can remove them.

3.0 DETAILED SYSTEM/EQUIPMENT DESCRIPTION

3.1 Gas Handling Train

A hole was cut into the existing metal cement plant stack at Dragon to retrofit the Recovery Scrubber to the cement kiln. Kiln exhaust gas is withdrawn from the stack through a guillotine type damper at the stack-Recovery Scrubber ductwork interface. A butterfly type damper is located in the existing metal stack above the Recovery Scrubber exhaust gas takeoff. The guillotine damper is driven by a 5 HP motor automatically operated from the cement plant control room. The butterfly damper is pneumatically operated and is also automatically actuated from the plant control room.

Exhaust gas is withdrawn from the stack by a centrifugal fan operating at 1250 RPM and driven by a 700 HP, 4160v motor. Exhaust gas flow is controlled by a pressure sensor located at the base of the existing stack. A 1.0 HP drive modulates a set of inlet dampers on the FD fan to maintain a constant pressure at the base of the stack. The exhaust gas passes through metal ductwork containing internal water quench sprays designed to insure the gas temperature does not exceed 240°F, in order to protect the fiberglass recouperator that follows.

The exhaust gas is cooled in the direct contact heat recouperator. The recouperator is a fiberglass cylinder 44 feet tall and 20 feet in diameter. A water pump powered by a 150 HP motor provides an internal water spray, countercurrent to the exhaust gas flow, to accomplish a dual purpose. The gas is cooled to approximately 140°F before reaction with the scrubbing medium (CKD slurry) and a portion of the sensible and latent heat contained in the exhaust gas is recovered to provide energy for evaporation later in process. The cooled gas is then conveyed to, and scrubbed in, the reaction tank. Entrained water droplets are collected in the ductwork and are drained, via a PVC line, to a tank (carryover tank) and conveyed back to the recouperator by a 15 HP pump.

The reaction tank is a rectangular, carbon steel tank, 48 feet wide and 36 feet long, lined with a vinyl ester resin designed to resist the extremely corrosive atmosphere

produced when bringing the exhaust gas through it's dew point. The gas enters a plenum through a series of baffles used to properly and evenly distribute the gas into the plenum. The gas then passes up through a stainless steel perforated tray. A slurry of water and CKD flows across the top of the perforated tray while the gas percolates up through the tray. This method of gas/liquid contact provides intimate mixing and promotes the high scrubbing efficiency demonstrated by the Recovery Scrubber.

TABLE 2

Gas Handling Train Equipment and Motor List

Vessels

Item	Material	Capacity or Size
Heat recouperator	Fiberglass	44'(H) x 20'(D)
Carryover tank	Polypropylene	1,500 gallons
Chevron spray tank	Polypropylene	1,500 gallons

Motor List

Motor for:	Number of Units	Service	Rated HP	RPM
Exhaust FD fan	1	cont	700	1250
FD fan inlet damper	1	int	1.0	
Inlet guillotine damper	1	int	4	
Inlet damper seal fan	1	cont	3	
Chevron spray pump	1	cont	25	
Recouperator circulation pump	1	cont	150	1800
Recouperator carryover pump	1	int	15	

int = intermittent operation
cont = continuous operation

The scrubbed gas then passes through a chevron type mist eliminator to remove any entrained slurry or water droplets and is vented to atmosphere. The chevron mist eliminator is continuously washed with a spray. The spray water is withdrawn from a tank and is pumped, with a 25 HP pump, to a set of nozzles which provide full coverage of the chevron mist eliminator inlet surface.

3.2 CKD Processing System

CKD is mixed with water to form an alkaline slurry which is then used in the reaction tank as the scrubbing reagent for reaction with acidic components of the flue gas. In the reaction tank, acid gas and caustic CKD undergo dissolution and neutralization reactions in which gas is used to process CKD, and CKD is used to process gas.

CKD is withdrawn from the cement plant dust holding bin through a rotary feeder and discharged into the lower screw conveyor. The lower screw conveyor transfers CKD to a bucket elevator which transports it to the top of the reaction storage tank where it is discharged into the upper screw conveyor. This screw transfers CKD to a vortex mixer which discharges the dry CKD into the reaction storage tank where it is thoroughly mixed with freshly reacted CKD-water slurry.

The vortex mixer is a short cylinder with a steeply inclined conical shaped bottom. Reacted slurry is injected tangentially into the vortex mixer at four (4) equally spaced locations at about 400 GPM while the CKD is dumped into the center of the whirlpool formed by the injected slurry. The material is then discharged into the reaction storage tank directly in the path of the 9,000 GPM return flow of CO_2 saturated, reacted slurry from the reaction tank. The reaction storage tank contains 72,000 gallons of reacted slurry which provides approximately 7 hours of residence time for the slurry. The residence time required, and hence the reaction storage tank volume, is a site specific consideration and will vary greatly from installation to installation.

Leachate from No. 2 settling tank and excess leachate from No. 1 settling tank (leachate production exceeding the

evaporation rate in the crystallizer) is conveyed to the reaction storage tank through the reaction tank sump pump. Additional makeup water necessary to maintain a slurry solids content of approximately 20% is added to the reaction storage tank. The 20% solids CKD-water slurry is circulated, via two axial flow pumps, from the reaction storage tank across the top of a horizontal, perforated tray in the reaction tank. The CKD-water slurry and cooled flue gas, percolating up from the plenum below, are brought into contact with each other and allowed to react to perform both CKD renovation and flue gas scrubbing. CKD undergoes significant chemical change during the process. It is freed of soluble alkali (Na and K) and significantly reduced in calcium sulfate content. Calcium, from dissolved gypsum ($CaSO_4 \cdot 2H_2O$) and calcined limestone (CaO) is precipitated as calcium carbonate ($CaCO_3$). Reacted CKD at this point in the process is essentially the same composition as cement kiln raw material feed (see Section 5.2 - CKD Recovery and Renovation).

Recovery Scrubber chemistry requires an approximate stoichiometric balance between cationic K and Na and anionic SO_2 and Cl. This commonly occurs naturally in cement manufacturing processes. Where an imbalance occurs, most usually a deficiency of alkali, the alkali can be augmented either by incorporating an alkali-rich waste material such as biomass ash, or by using commercially available sources of alkali, such as KOH or ammonia.

A minor, but significant, effect of the Recovery Scrubber is the absorption of carbon dioxide from processed gas. The absorption results from recarbonation of, primarily, calcium oxide in the dust, and recovery is typically in the range 1-3% for a cement kiln. This does, however, contrast with lime and limestone scrubbers which result in a net evolution of CO_2.

Products resulting from the above reactions in the reaction tank are separated into solids, which are returned to the kiln as raw material, and liquid, containing dissolved materials, which is transferred to the crystallizer for evaporation of solution water and crystallization of dissolved potassium sulfate. Since CKD flocculates, the solid-liquid separation is accomplished in two settling tanks operating in series.

Reacted slurry from the reaction storage tank is pumped from the reaction storage tank to the stilling well of the first, or No. 1, settling tank. In No. 1 settling tank, the heavier solids settle and thicken at the bottom of the tank while the leachate, containing dissolved potassium sulfate, overflows a weir into a collection trough and flows, by gravity, to the centrate tank for later introduction into the evaporator/ crystallizer system for subsequent evaporation of solution water and recovery of the crystallized salt product. The leachate contains dissolved salt which, at Dragon, is predominantly potassium sulfate. In other applications, the salt product may be a mixture of compounds, for example potassium sulfate with ammonium sulfate or sodium chloride. Mixed salts may require separation by selective crystallization, or other methods, to maximize by-product income.

The underflow (thickened slurry) from No. 1 settling tank is pumped to No. 2 settling tank and mixed with distilled water (distilled water is not required, however, it is derived from the process and is used as a portion of the make-up water rather than being discharged) to dilute the interstitial water which contains dissolved potassium sulfate. The slurry solids, including precipitated $CaCO_3$, and liquid are then separated for recovery. The solids, as recovered at this point, are substantially free of alkali and sulfate. The reacted solids are therefore suitable for use as raw material in cement manufacture and are returned to the kiln raw material preparation system. Leachate from No. 2 settling tank overflows a weir into a collection trough and flows, by gravity, to either the chevron spray tank or the reaction tank sump.

3.3 Potassium Sulfate Crystallization System

Leachate from No. 1 settling tank, contains dissolved salt which, at Dragon, is predominantly potassium sulfate. In other applications, the salt product may be a mixture of compounds, for example potassium sulfate with ammonium sulfate or sodium chloride. Mixed salts may require separation by selective crystallization or other means to maximize by-product income. Energy for evaporation is

TABLE 3

CKD Processing Equipment and Motor List

Vessels

Item	Material	Capacity or Size
Vortex mixer	Carbon steel	6'(H) x 4'(D)
Reaction storage tank	Carbon steel	32' diameter 72,000 gallons
Reaction tank	Carbon steel /w vinyl ester resin liner system	48'(W) x 36'(L)
Tray wash tank	Polypropylene	500 gallons
Settling tank No. 1	Carbon steel	36' diameter 35,000 gallons
Settling tank No. 2	Carbon steel	20' diameter 25,000 gallons

Motor List

Motor for:	Number of Units	Service	Rated HP	RPM
CKD rotary feeder	1	cont	0.2	1800
Lower CKD screw conveyor	2	cont	15	
Bucket elevator	1	cont	3	
Upper CKD screw conveyor	1	cont	10	
Vortex mixer slurry pump	1	cont	25	
Reaction circulation pumps	2	cont	50	1200
Reaction tank sump pump	1	cont	3	1200
Reaction tank HP tray wash pump	1	int	60	
Reaction tank HP tray wash drive	1	int	1.5	
Storage tank discharge pump	1	cont	3	1200
Storage tank rake arm	1	cont	2	1200
No. 1 settling tank discharge	1	cont	3	1200
No. 1 settling tank rake arm	1	cont	2	1200
No. 2 settling tank discharge	1	cont	30	1200
No. 2 settling tank rake arm	1	cont	2	1200

int = intermittent operation
cont = continuous operation

derived from the flue gas during cooling. The collected heat is transferred to the evaporator and discharged as steam. The steam is condensed and the condensate is returned to the process as part of the make-up water requirement.

Exhaust gas from the portland cement kiln is passed through a direct contact heat exchanger (recouperator) where it encounters a 3,000 GPM countercurrent water spray. The water spray cools the gas through the dew point (to about 140°F) and the water is heated by the sensible and latent heat from the exhaust gas. The heated water is collected in a sump (the bottom 13 feet of the recouperator) and is recirculated through the exhaust gas.

A portion of the heated (about 135°F) water is withdrawn from the recouperator sump, transferred to a flash tank operating under partial vacuum (-26" Hg) where it flashes into low temperature steam. The low temperature steam is conveyed through a polypropylene pipe to the shell side of a shell and tube (non-contact) heat exchanger where it transfers heat energy to the leachate (potassium sulfate solution), from No. 1 settling tank, circulating from the vapor body. The potassium sulfate solution flows through the tube side of the heat exchanger. The shell and tube heat exchanger is made out of a corrosion resistant alloy (1925 HMO) because of the highly corrosive nature (pH < 2) of the liquid from the recouperator. The shell was originally carbon steel, which quickly suffered severe corrosion damage.

The vapor body operates under a partial vacuum (-28" Hg). When the heated potassium sulfate solution enters the vapor body, solution water flashes into steam. Low temperature steam is vented through a mist eliminator to a condenser where the steam is condensed into distilled water. Cooling water is provided by water pumped from an impoundment in an abandoned part of the cement plant quarry. The heated cooling water is cooled by spraying it over a quarry face as it is returned to the impoundment. Water lost through evaporation is made-up by natural precipitation. Condensation of steam in the condenser induces the vacuum, however, a small vacuum pump (rated capacity is about 536 ACFM) is required to remove noncondensable gases (i.e., O_2, CO_2, N_2, etc.) that are dissolved in the liquid.

TABLE 4

Potassium Sulfate Crystallization System
Equipment and Motor List

Vessels

Item	Material	Capacity or Size
Flash tank	Hetron 980 resin	12'(L) x 8'(D)
Heat exchanger	HMO 1925	20'(L) x 5'(D)
Centrate tank	Vinyl ester FRP	6,000 gallons
Vapor body	Carbon steel w/ vinyl ester lining	26'(H) x 16'(D)
Condenser	Carbon steel	22'(L) x 5'(D)
Hot well	Vinyl ester FRP	400 gallons
Salt product silo	Carbon steel	300 tons

Motor List

Motor for:	Number of Units	Service	Rated HP	RPM
Flash tank vacuum pump	1	cont	40	1800
Vapor body vacuum pump	1	cont	50	1800
Vacuum pump seal water pump	2	cont	0.5	2875
Vapor body circulation pump	1	cont	150	1800
K_2SO_4 slurry pump to centrifuge	1	cont	5	1750
Leachate (centrate tank) pump	1	cont	3	1750
Centrate tank mixer	1	cont	3	1200
Centrifuge	1	cont	30	5000
Distilled water (hotwell) pump	1	cont	5	1750
Cooling water pumps	4	2-3 cont	60	
Pin mixer (pelletizer)	1	cont	25	1800
K_2SO_4 bucket elevator	1	cont	2	

int = intermittent operation
cont = continuous operation

Distilled water is collected in a tank (hotwell) and transferred to No. 2 settling tank where it is used to rinse the thickened slurry from No. 1 settling tank, as described in Section 3.2 above. As water is evaporated, the concentration of potassium sulfate increases to the point that crystals begin to grow in the leachate. The volume lost through evaporation is made up by fresh leachate pumped into the vapor body from the centrate tank.

A small (5-8 GPM) slipstream of the slurry of potassium sulfate crystals is withdrawn from the vapor body and is passed through a centrifuge to separate crystals from slurry. The liquid portion is returned to the centrate tank and recovered potassium sulfate crystals are passed through a pin mixer for pelletization. The pellets of potassium sulfate are then dried and conveyed by bucket elevator to a storage silo for later sale.

3.4 Miscellaneous or Common Equipment

In addition to equipment that can be attributed to specific areas, there is some equipment common to several or all of the systems. Among this equipment is heat tracing for process pipelines, area lighting, seal water pumps, an instrument air compressor, and air activated slurry line pinch valves.

Table 5

Common Equipment

Equipment:	Number of Units	Service	Rated HP/kW
Seal water pump motors	5	cont	1 HP
Heat tracing	8,000'	int	5 watt/ft
Area lighting		int	10 kW
Instrument air compressor	1	cont	25 HP
Slurry line pinch valves	10	int	

4.0 CONTINUOUS EMISSION MONITORS

The Dragon cement plant monitored O_2 and CO in their portland cement kiln exhaust gases prior to installation of the Recovery Scrubber. A gas sample is extracted at the kiln exit prior to the existing dust collection device (baghouse) for an O_2 determination. Another gas sample is extracted between the baghouse and the kiln induced draft (ID) fan for a CO determination. Dragon requested proposals from suppliers of SO_2 and NOx continuous emission monitors (CEMs) in late 1989 and selected the proposal submitted by Enviroplan (59 Main Street, West Orange, NJ, 07052) (see Appendix C) to provide the necessary monitoring equipment. Enviroplan guaranteed that the system would pass certification testing (see Appendix D) or they would make equipment corrections or adjustments and repeat testing if necessary to assure certification.

The following description of the Enviroplan CEMs is taken from the Enviroplan proposal. Enviroplan is not a manufacturer of gas measuring equipment. Each instrument selected is best suited to the needs of the portland cement kiln, based on Enviroplan's in-depth knowledge derived from long-term use of these instruments.

4.1 CEM System Description

4.1.1 Dilution Probe Sampling System

The dilution probe sampling system has been in use in the U.S. for more than eight years and has been widely accepted overseas for substantially longer in applications similar to portland cement kilns.

The 12-inch probe tip is designed in such a manner as to effectively extract a sample at a pressure of approximately 17 feet, water gauge, at a rate which varies between one and five cubic feet per day. Low sample volume results in less maintenance of filters. High pressure extraction prevents probe plugging. The sample is mixed in the probe tip with clean, dry air at ratios varying from 10:1 to 500:1. This dilution ratio is selected to prevent any possibility of condensation in the sample line and to provide the ideal

range of gas for the gas analysis equipment. The probe tip is manufactured of non-corrosive material.

The sample is delivered, under pressure, through sample lines to the EPA approved instruments for measurement.

4.1.2 Pumpless Source Sample Extraction

Low volume, high pressure extraction is accomplished by means of clean, dry air. The air, delivered through the umbilical sample line, drives a highly efficient venturi which extracts the sample through a coarse screen, then a fine quartz filter, and finally through a sonic orifice metering device.

After mixing the sample with air in the dilution chamber, the pressured air carries the diluted sample to the analyzer. Because the sample is always under pressure, sample integrity is guaranteed.

4.1.3 True Dynamic Calibration

Calibration gas is delivered through the sample umbilical line to the probe tip. The entire extraction chamber is flooded with calibration gas which then checks the fine filters, sonic orifice, mixing chambers, etc. back to the analyzer. Dragon uses calibration gases that have been certified traceable to National Bureau of Standards versus EPA traceability Protocol No. 1, Procedure G1, and analyses performed per Section 3.0.4 (see Appendix E).

Continuous functional checking is accomplished by means of a vacuum line in the umbilical line which checks the efficiency of the venturi chamber continuously.

4.1.4 Installation

The equipment is mounted through a standard 4-inch port and held in place by a 4-inch flange. These are mounted to a two inches outside diameter tube extension which supports the probe tip.

Because the sample line is not heat traced, service loops are provided for periodic maintenance. That is, the sample line need not be detached for removal of the probe tip. In fact,

the system can remain on and functional through the entire maintenance process.

4.1.5 Sequence/Controller

The sequence controller is located at the analyzers at ground level for easy access. Air supply and calibration gases are attached to the controller, and the sample gas is delivered to the analyzer from the sequencer. The sequencer can be used to provide sample gas from up to six probes to a single set of analyzers.

4.1.6 Rack Mounting

The sequencer and analyzers are mounted in a standard rack. A stable environment is provided (i.e., 50°F to 95°F and a maximum humidity of 95 percent).

4.1.7 Environmental Enclosure

At Dragon, the equipment, other than the probe and sample line, is mounted in a heated, air-conditioned room, with a walk-in door, within the Recovery Scrubber motor control center (MCC) building.

4.2 SO_2 Analyzer

The SO_2 analyzer used at Dragon with the Enviroplan system is a Thermo Electron Model 43A Pulsed Fluorescence SO_2 Analyzer. It is EPA approved (EQSA-0486-060; see Fed. Reg. April 10, 1986, Volume 51, No. 69 for definitions and federal specifications). The analyzer is specific to SO_2 and has a linear response through all ranges.

The analyzer works by passing a pulsed ultraviolet light through a reflection mode optical filter system to a measurement chamber where it excites SO_2 molecules. As these molecules return to the ground state they emit a characteristic fluorescence with intensity linearly proportional to the concentration of SO_2 molecules in the sample. The emitted light then passes through a second filter to illuminate the sensitive surface of a photomultiplier tube. Electronic amplification of the output of the photomultiplier tube provides a meter reading and an

electronic analog signal for recorder output. A second U.V. detector senses lamp intensity and maintains a constant U.V. excitation level by a closed loop feedback control of the lamp power supply. This assures longterm span stability. The reflective fiber optics result in a very low and unvarying level of scattered light. This assures longterm zero stability.

Table 6

SO_2 Analyzer - Selected Specifications

Linearity	1% of Range
Noise (At Zero)	0.5 ppb (Fast Time Response)
	0.3 ppb (Slow Time Response)
Response Time (0-95%)	2 minutes (Fast Time Response)
	4 minutes (Slow Time Response)
Lower Detectable Limit	1 ppb (Fast Time Response)
	0.6 ppb (Slow Time Response)
Precision	1% of Reading or 1 ppb
Zero Drift	<1 ppb per day
Span Drift	±0.5% per week
Temperature Dependence	
Zero	±0.05% per °C
Span	±0.1% per °C

4.3 NOx Analyzer

The NOx analyzer used at Dragon with the Enviroplan system is a Thermo Environmental Instruments, Inc. Model 42 Chemiluminescence NO-NO_2-NOx Analyzer. This instrument is a second generation analytical instrument capable of measuring oxides of nitrogen at levels from sub parts per billion to 20 parts per million. It is EPA approved (RFNA-1289-074) and is linear at all ranges.

Sample gas enters the analyzer, flows through a sample capillary and then either flows through the mode valve (NO or NOx) and the NO_2 to NO converter to the reaction chamber. There the NO reacts with ozone to produce a characteristic chemiluminescence. Reacted gas is drawn from the reaction chamber through an internal pump. The pump exhaust is fed

through a charcoal trap where any residual ozone is removed and vented.

Table 7

NOx Analyzer - Selected Specifications:

Zero Noise	0.25 ppb RMS (60 sec time const)	
Lower Detectable Limit	0.5 ppb (60 sec time const)	
Zero Drift (24 hours)	0.5 ppb	
Span Drift (24 hours)	±1% of full scale	
Response Time	10 sec average	40 sec
	60 sec average	80 sec
	300 sec average	300 sec
Precision	±0.5 ppb	
Linearity	±1%	

The Model 42 is of a single chamber, single photomultiplier tube design and automatically cycles between the NO and NOx modes. Signals from the photomultiplier tube are conditioned and then fed to the microprocessor where a sophisticated mathematical algorithm is utilized to calculate three independent outputs: NO, NO_2, and NOx. With this algorithm, more accurate NO/NOx measurements are possible than by varying NO/NO_2 samples.

4.4 CEM Operation and Regular Checks

Operation of the system is completely automatic. A timer controls cycling of the samples, the output relays, sample and hold circuits, auto purge, and the calibration cycle. However, normal operation of the system should include a site/system check daily to assure proper operation. This check includes the following:

- The output of the system should be reviewed to assure proper zero and span data. Plotting of the zero and span data will indicate if the charcoal SO_2 scrubber needs replacement and, when combined with the minimum and maximum temperature reading of the CEM enclosure, it can indicate a temperature control problem.

- Proper cycling of the system should be observed to assure no errors in the timer programming. If a problem is detected, the timer programs can be reviewed without disrupting operating sequences.

- Inspection of the air filtering system should include:

  a) observation of proper cycling of the regenerative dryer
  b) inspection of the air supply moisture indicator
  c) inspection of filters for proper moisture removal and draining by the automatic drains
  d) proper delivery pressure to the air filtering system (80-100 psig)

- Inspection of the dilution air pressure gauges and the vacuum gauges to assure proper dilution of the stack sample.

- A check of the analyzers for proper flow.

- A check of the span gas calibration tanks for adequate supply of calibration gases.

- A minimum/maximum thermometer should be inspected and the heating or air conditioning system adjusted, if necessary, to maintain proper control.

- A daily checklist should be filled out and the following information recorded (see Appendix F):

  a) system DA pressure per probe.
  b) system vacuum per probe
  c) zero and span values for each gas channel
  d) system or room temperature
  e) observe each analyzer for proper flow and operation
  f) check probe heater temperature settings

- A weekly check should include:

  a) observe the air filtering system for indications of proper operation
  b) check the inlet filters to assure no accumulation of moisture in the bowls (visual)

c) check the silica gel indicator for proper color

4.5 System Preventive Maintenance Schedule

4.5.1 Recommended quarterly maintenance

Recommended quarterly maintenance includes:

- Probe:

  a) remove probe from process
  b) clean coarse filter
  c) inspect and replace fine filter (quartz wool)
  d) ensure cal/purge line is clean

- Air system: Inspect and replace, if necessary, all reagents

- Analyzers:

  a) inspect and replace analyzer filters
  b) clean fan screens
  c) inspect and replace any reagents, if necessary

4.5.2 Dragon's current maintenance schedule

Dragon's current maintenance schedule is as follows:

- Probe:

  a) Recovery Scrubber outlet checked quarterly
  b) Recovery Scrubber inlet checked once every 6 months

- Air System: checked daily

- Analyzers:

  a) filters/screens checked quarterly
  b) reagents checked weekly

- Room Air Conditioner: filter checked every 6 months

- Cleaning and Maintenance: performed as needed

4.5.3 Zero - Span Checks and Corrective Action

On a daily basis the zero and span checks are examined and:

- The data is acceptable and no analyzer adjustment is needed when:

  a) Zero limits are <±25 ppm
  b) Span limits are <±10% of full range

- Recalibrate the analyzer and data is acceptable if corrected when:

  a) Zero limits are >±25 ppm but <±50 ppm
  b) Span limits are >±10% but <±25% of full range

- Data is invalid. Troubleshoot and recalibrate the analyzer when:

  a) Zero limits are >±50 ppm
  b) Span limits are >±25% of full range

5.0 FORMATION OF SO_2 AND NOx IN CEMENT KILNS

5.1 SO_2 Formation in Portland Cement Kilns

Sulfur may enter a portland cement kiln system with the fuel source, like utility boilers or other fossil fuel fired combustion sources, but may also enter with the raw materials being processed in the cement kiln, unlike other combustion processes. However, in addition to providing another source for SO_2 emissions, the raw material in a cement kiln has the ability to adsorb considerable quantities of SO_2 produced as a result of fuel combustion[9]. The long retention times, temperature profiles, intimate gas/solids mixing, and the presence of vast quantities (compared to the quantity of sulfur in the system) of calcium, potassium, and sodium compounds result in favorable conditions for the chemical reaction of acidic SO_2 with basic compounds contained in the raw materials[10]. However, because of many factors, the scrubbing efficiency of each cement kiln system is unique. An investigation at one cement kiln has found SO_2 contents in cement kiln exhaust gases, attributable to fuel combustion, consistently below the limits of detection of the CEM in use (this is with a defined raw material chemistry and on a preheater/precalciner type of kiln system in one set of tests)[11].

However, in the same process, a direct correlation between total sulfur in the raw material feed to the kiln and SO_2 emissions from the kiln was demonstrated[12]. Although the data was somewhat variable, it was found that an important contributor to the variability of the data was the oxidation state of the sulfur in the raw materials. It was found that sulfide sulfur in the raw materials produces SO_2 under cement process conditions and that the amount of sulfide sulfur was more strongly correlated to SO_2 emissions than the total sulfur in the raw materials[13]. It was also determined that calcium sulfite or sulfate in raw materials do not contribute to SO_2 emissions when put back into the kiln system[14].

Further, to quote from an English translation of an article appearing in the March 1989 Cement-Lime-Gypsum ZKG International by Schutte,

> "Results from investigations over a good many years show that the formation of SO_2 emissions are caused predominantly by the raw material employed."[15]

Other investigators have also found that sulfates decompose only in the temperature range of the sintering zone (combustion zone) of kiln systems. However, in these areas of a kiln, vast quantities of reactants (e.g., alkalis and free CaO) are present and ideal reaction temperatures of 800 to 900°C transform any SO_2 generated into solid sulfates or sulfites[16], providing sufficient oxygen is present.

Schutte found that all forms of sulfur, except sulfate, have the property of releasing SO_2 in the temperature range of 300 to 600°C. However, some SO_2 will be adsorbed (about 50-85 percent) in a preheater type kiln system and that the balance would be emitted[17].

The above discussion is of importance to the Recovery Scrubber process because stoichiometric balance between the anions ($SO4^{=}$, Cl^{-}) and cations (K^{+}, Na^{+}) does not always exist. Typically, in a portland cement kiln application, an excess of anions will exist. The Recovery Scrubber will remove a stoichiometric amount of anions to balance all of the soluble cations and will convert any remaining sulfur into calcium sulfate, which will be returned to the kiln system with the other raw material solids.

5.2 NOx Formation in Portland Cement Kilns

The following discussion is taken from a report to the South Coast (southern California) Air Quality Management District, concerning the feasibility of NOx emissions reductions from a portland cement kiln[18].

Nitrogen is the most abundant element in the air and also occurs in the fuel and raw material used in cement production. Nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NOx, are formed during fuel

combustion. High temperatures (2,800°F and above)[19] are required to disassociate nitrogen and oxygen molecules into radicals; only after disassociation can NOx formation occur, as shown in Equations 1 through 4[20].

$$O_2 \longrightarrow 2O \qquad \text{Equation 1}$$

$$N_2 \longrightarrow 2N \qquad \text{Equation 2}$$

$$O + N_2 \longrightarrow NO + N \qquad \text{Equation 3}$$

$$N + O_2 \longrightarrow NO + O \qquad \text{Equation 4}$$

A limiting factor in NOx formation is the amount of oxygen in the kiln combustion zone. Nitrogen composes about 79 percent of the air introduced into the kiln and oxygen composes only about 21 percent. The fuel combustion reaction itself consumes oxygen but does not require nitrogen; therefore, the oxygen in the air is depleted before nitrogen. In addition, the fuel combustion reaction requires a lower heat of initiation than the nitrogen-oxygen reaction that forms NOx. Therefore, combustion is completed (i.e., has consumed its requisite amount of oxygen) before the nitrogen-oxygen reaction forming NOx. Thus, the availability of oxygen in the combustion zone limits the nitrogen-oxygen reaction.

Although there is a large quantity of nitrogen available from fuel, raw materials, and air, only a small percentage of the nitrogen, particularly in air, is converted to NOx.

Formation of NOx in a cement kiln may occur through at least three separate mechanisms. First, NOx is formed by the direct oxidation of atmospheric nitrogen at elevated temperatures (thermal NOx)[21,22]. Second, NOx is formed through oxidation of nitrogen and nitrogen compounds in the raw materials (feed NOx)[23]. Third, NOx is formed by oxidation of nitrogen contained in the fuel being burned (fuel NOx)[24,25].

The reaction that generates thermal NOx requires very high (>2,800°F) temperatures. A cement kiln generally operates with a material temperature of 2,500 - 3,000°F. The temperature in the flame is higher. The residence time (i.e., length of time that the combustion products remain in this area of elevated temperature) also affects the extent to

which the NOx reactions can proceed to completion. The residence time in a cement kiln, because of the length of the kiln, tends to allow the nitrogen-oxygen reactions (Equations 1-4) to proceed to completion.

Stoichiometrically, the oxygen required for the combustion of fuel is easily estimated; thus, the volume of air required during combustion can be estimated. In the cement industry "one hundred percent combustion air" refers to the exact amount of oxygen required to burn all of the fuel introduced into the kiln. Providing less than 100 percent combustion air results in the inefficient use of fuel. Additionally, insufficient oxygen may result in an explosive mixture of combustible particles and gases with infiltration air in the dust collection device. Providing greater than 100 percent combustion air results in excess oxygen which may react with nitrogen to form NOx. Therefore, operational procedure for cement kilns is to provide slightly greater than 100 percent combustion air (e.g., 110 percent) to avoid unburned fuel and to avoid excess air which unnecessarily absorbs heat and may result in NOx formation. However, although low excess air may reduce NOx emissions from cement kilns, low excess air may also raise SO_2 emissions, as explained in Section 5.1 above.

6.0 EMISSIONS RESULTS

6.1 Background

The wet process kiln at Dragon is rated at 450,000 tons of cement clinker per year and uses about 10 TPH of 2.5% to 3.0% sulfur coal as the primary fuel. Prior to installation of the Recovery Scrubber, Dragon was faced with a State of Maine requirement that would have forced the plant to reduce its fuel sulfur content by approximately one-half. This change would have increased operating costs between $1 million and $2 million per year.[26] In addition, the landfill used by Dragon (prior to the Recovery Scrubber) to dispose of CKD was nearly full and it was anticipated that securing permits for a new landfill was going to be both expensive and time consuming.

The two problems outlined above, fuel sulfur limitations and CKD landfilling, led to the establishment of three performance criteria for successful operation of the Recovery Scrubber prior to installation of the full-scale prototype at the Dragon cement plant in Thomaston, Maine. Those criteria were:

- CKD recovery and renovation,
- SO_2 removal efficiency of greater than 90 percent, and
- use of waste heat for evaporation to concentrate and crystallize potassium sulfate.

Each of these criteria were successfully accomplished during subsequent operation of the Recovery Scrubber.

Several additional benefits accrued that were not originally planned or foreseen. These include, but are not limited to, HCl scrubbing efficiencies greater than 95 percent, NOx scrubbing efficiency of nearly 19 percent, particulate capture resulting in demonstrated emission levels of 0.005 - 0.007 grains/SCF (inlet dust loading was approximately 0.04 grains/SCF), and potential application of the Recovery Scrubber to several other industries.

6.2 CKD Recovery and Renovation

Dragon discarded an average of 250 tons of CKD per day prior to operation of the Recovery Scrubber. One of the three stated performance criterion for successful operation of the Recovery Scrubber prototype was to renovate all of the currently produced CKD at Dragon so that it could be returned to the kiln system as a portion of the kiln feed. The Recovery Scrubber has met this performance criteria. All of the CKD produced at Dragon is processed through the Recovery Scrubber and is then reused as feedstock for the kiln. Typical values for the chemistry of cement kiln feed, unprocessed baghouse CKD, and typical ranges for treated CKD are provided in Table 8.

Table 8
Typical Chemistry of Kiln Feed, Untreated CKD, and Treated CKD[27]

(all values in weight percent)

	Typical Cement Kiln Feed	Typical Untreated Baghouse CKD	Range for Treated CKD Low	Range for Treated CKD High
SiO_2	13.7	13.1	11.6	13.0
Al_2O_3	3.3	2.8	3.2	4.0
Fe_2O_3	1.5	1.3	1.4	1.8
CaO	44.0	46.1	37.8	42.5
MgO	2.9	2.4	2.5	2.9
SO_3	0.3	5.4	2.5	6.0
K_2O	1.1	4.5	1.6	2.6
Na_2O	0.4	0.4	0.3	0.4
LOI	34.5	24.5	30.0	33.0

Treated CKD is returned to the raw mill system at an average rate of approximately 10 tons per hour (TPH) and combined with about 90 TPH of kiln feed for a combined total feed to the kiln of 100 TPH. Table 9, shows the calculated chemistry of the resulting feed to the kiln if 90 TPH of fresh feed and 10 TPH of treated CKD with the "Low" range were combined and likewise, the chemistry if 90 TPH of kiln feed and 10 TPH of the "High" range CKD is used.

As can be seen in Table 9, the chemistry of the combined feed to the kiln is substantially similar to the typical cement kiln feed chemistry.

Table 9

Calculated Chemistry of Combining
Typical Cement Kiln Feed with Treated CKD.

(all values in weight percent, except as noted)

	Typical Cement Kiln Feed	Range for Treated CKD		Calculated Resulting Combined Feed Chemistry	
		Low	High	Low	High
SiO_2	13.7	11.6	13.0	13.5	13.6
Al_2O_3	3.3	3.2	4.0	3.3	3.4
Fe_2O_3	1.5	1.4	1.8	1.5	1.5
CaO	44.0	37.8	42.5	43.4	43.9
MgO	2.9	2.5	2.9	2.9	2.9
SO_3	0.3	2.5	6.0	0.5	0.9
K_2O	1.1	1.6	2.6	1.2	1.3
Na_2O	0.4	0.3	0.4	0.4	0.4
LOI	34.5	30.0	33.0	34.1	34.4
TPH	90	10	10	100	100

The Recovery Scrubber will also permit the excavation and recycling of previously landfilled CKD. The potential benefits to be derived from recycling an existing landfill would include, but would not be limited to:

- savings on mining, crushing, and grinding costs for the production of kiln feed.

- savings on permitting and construction costs for new landfills.

- recovery of useable real estate occupied by the existing landfill.

- elimination of potential future environmental liabilities associated with having a landfill.

- quarry or raw material supply lifetime will be extended by the amount of old CKD recycled.

6.3 Exhaust Gas Scrubbing Efficiency

6.3.1 SO_2

The second of the three stated performance criterion for successful operation of the Recovery Scrubber prototype was to reduce SO_2 by 90%. The percent SO_2 removal efficiency, defined as:

$$\frac{[(\text{pounds of } SO_2 \text{ input}) - (\text{pounds of } SO_2 \text{ output})] \times 100}{\text{pounds of } SO_2 \text{ input}}$$

has averaged 89.2 percent for the entire Phase III operating period (see Appendix G). During the final three months (operating Periods 12, 13, and 14) of Phase III operation (these months represent 27% of the operating hours during Phase III), the Recovery Scrubber has demonstrated a time weighted SO_2 removal efficiency of 94.6 percent.

Because portland cement kiln raw materials are predominantly limestone, a cement kiln has an inherently large capacity to scrub acid gases, as discussed more fully in Section 5.1 -SO_2 Formation in Portland Cement Kilns. Accordingly, in many cases the Recovery Scrubber's inlet SO_2 was so low that an outlet SO_2 of 2 - 10 pounds per hour resulted in a calculated removal efficiency of less than 85 percent (see Appendix H).

Uncontrolled SO_2 emissions from a cement kiln are highly variable. The author has personally observed cement kiln emissions, from several different kilns, vary by nearly two orders of magnitude (e.g., from 2 or 3 pounds per hour to 200 or 300 pounds per hour) in less than one hour. Accordingly, in order to determine if SO_2 inlet loading affected the Recovery Scrubber removal efficiency, one pair of data (inlet and outlet SO_2) were randomly collected from each day of Recovery Scrubber operation during 1993 when the inlet SO_2 was less than 100 pounds per hour. The calculated removal efficiency was 82.0 percent. Likewise, one pair of data were randomly collected from each day of Recovery Scrubber operation (when at least 2 inlet values were above 100 pounds

per hour) during 1993 when the inlet SO_2 was between 100 -200 pounds per hour. The calculated removal efficiency was 94.1 percent. Finally, since there were limited data points when inlet SO_2 was above 200 pounds per hour, all pairs of data with inlet values above 200 pounds per hour were used, which resulted in a calculated removal efficiency of 98.5 percent (see Table 10).

Table 10

SO_2 Removal Efficiency at Various Inlet SO_2 Ranges

Inlet SO_2 Range (in pounds/hour)	Average SO_2 Emissions (in pounds/hour)	Calculated Removal Efficiency (in percent)
<100	4.0	82.0
100 - 200	7.7	94.1
>200	3.6	98.5

The Recovery Scrubber has met this performance criterion.

A tabulation of the average inlet and outlet SO_2 and NOx values, and calculated removal efficiencies for each of 14 different time periods are presented in Table 11. The time periods were arbitrarily selected but attempt to provide a method of dividing the Recovery Scrubber operating data into periods with somewhat equal operating time, while considering periods of extended downtime that occurred (e.g., cement plant winter maintenance and inventory control shut downs). Appendix G presents a tabulation of the same data as in Table 11 but on a daily basis within each of the different time periods.

Figure 3 is a graphical representation of the average SO_2 (in pounds per hour) for the inlet and outlet of the Recovery Scrubber for 14 different operational time periods. Appendix I presents graphs of the average daily inlet and outlet SO_2 emissions in pounds per hour for each of the 14 operational time periods individually.

6.3.2 NOx

In addition to the excellent SO_2 removal experienced, NOx removal efficiency has averaged 18.8 percent for the entire Phase III operating period. However, the NOx removal efficiency increased to nearly 25 percent during the final few months of operation. Reasons for the increased NOx removal efficiency are currently being investigated, but no definitive explanation is available at this time. Figure 4 is a graphical representation of the average NOx (in pounds per hour) for the inlet and outlet of the Recovery Scrubber for 14 different operational time periods. Appendix J presents graphs of the average daily inlet NOx and outlet NOx emissions in pounds per hour for each of the 14 operational time periods individually.

Table 11

Summary of Dragon Recovery Scrubber Emissions and Removal Efficiencies

Period	Operating Time (Hrs)	Inlet* SO_2	Inlet* NOx	Outlet* SO_2	Outlet* NOx	Percent Removal Efficiency SO_2	Percent Removal Efficiency NOx
1	211	73	320	10	279	87.0	12.8
2	476	71	284	11	260	84.6	8.6
3	464	87	292	13	251	85.4	14.0
4	259	131	252	16	165	87.6	34.5
5	304	245	293	28	243	88.7	17.1
6	379	222	265	28	208	87.4	21.3
7	328	281	345	28	244	90.1	29.3
8	301	124	278	10	188	91.8	32.4
9	314	47	240	7	194	85.7	19.0
10	402	41	244	6	218	86.1	10.5
11	460	36	315	6	267	83.4	15.0
12	549	57	333	2	291	95.9	12.4
13	464	86	288	4	223	95.0	22.6
14	405	124	274	9	199	92.4	27.4
Total	5316						
Weighted average		109	289	12	234	89.2	18.8

*Figures are in pounds per hour

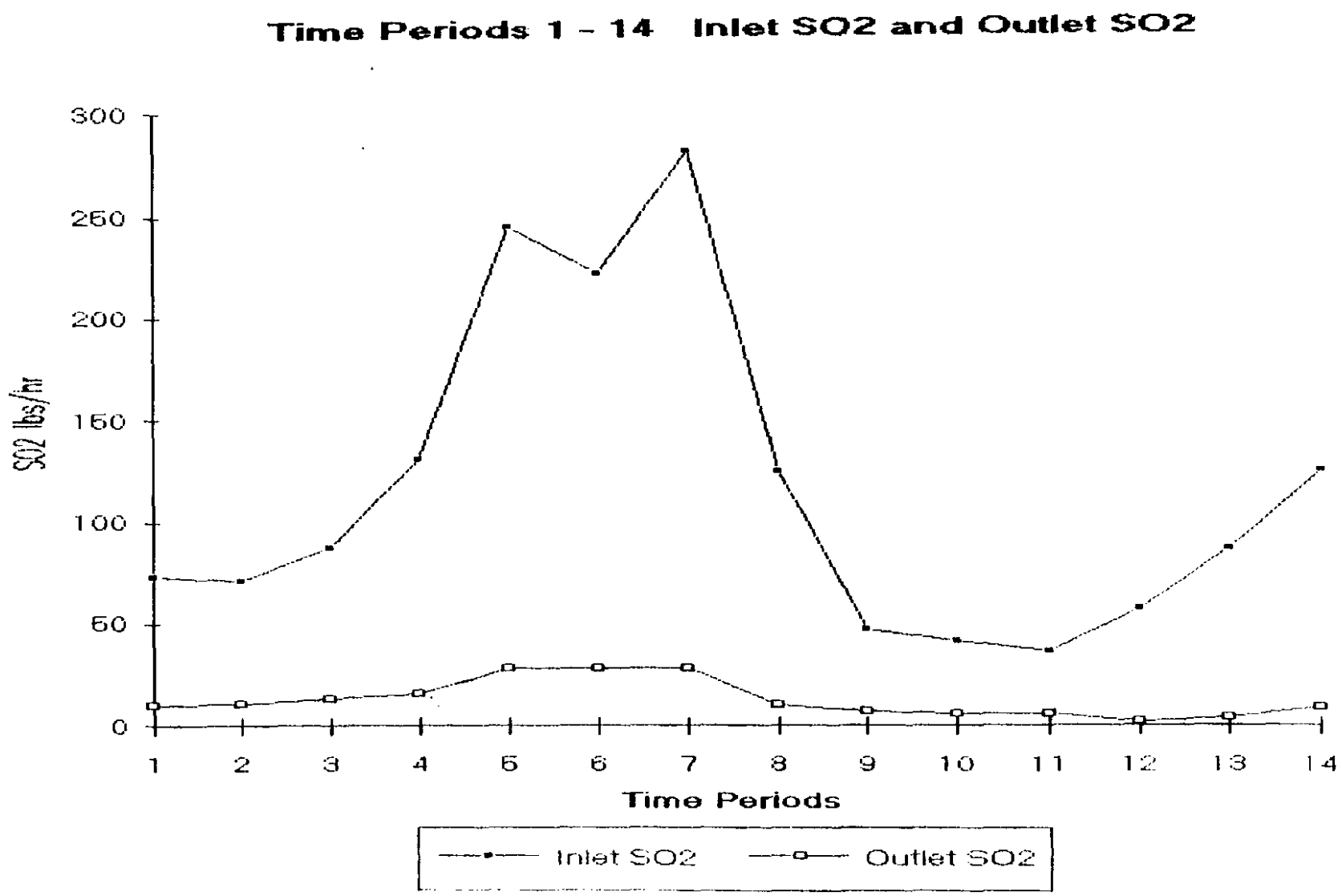

Time Periods 1 - 14 Inlet SO2 and Outlet SO2
SO2 lbs/hr
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Time Periods
Inlet SO2
Outlet SO2

Figure 3

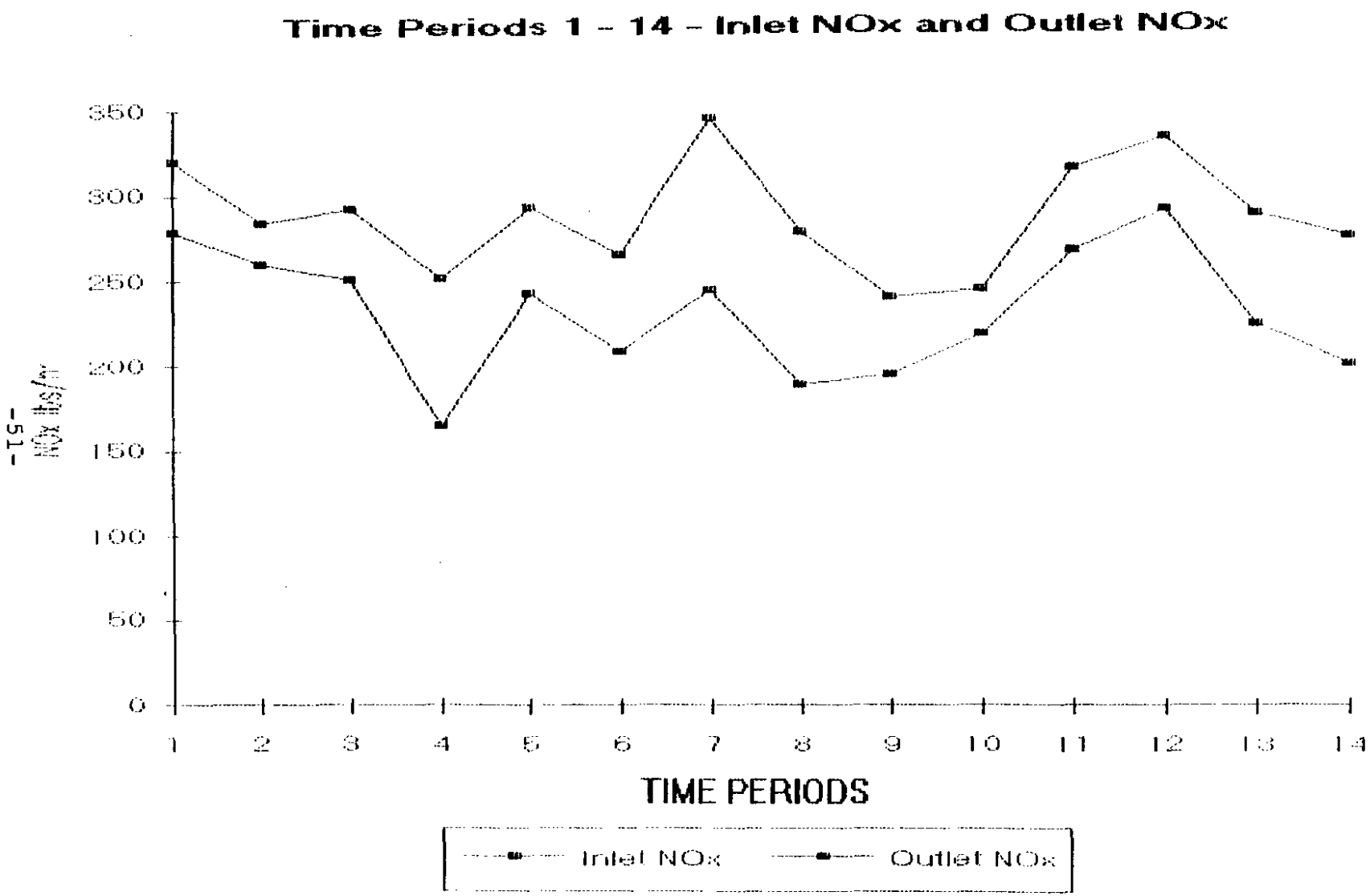

Time Periods 1 - 14 - Inlet NOx and Outlet NOx
350
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
TIME PERIODS
Inlet NOx
Outlet NOx

Figure 4

6.3.3 Particulate

Another unexpected and potentially valuable benefit derived from operation of the Recovery Scrubber prototype is the demonstrated excellent particulate capture efficiency. In recently completed compliance testing for the State of Maine, Department of Environmental Quality (DEQ), the Recovery Scrubber demonstrate a particulate emission rate of 0.005 to 0.007 grains per standard cubic foot (SCF) or approximately 15 mg/NM^3. It should be noted that, as a wet scrubbing process, the Recovery Scrubber efficiently captures even superfine (<10 micron) particulates so that emission levels could be further reduced by more stringent demisting of the scrubbed gas before release; albeit at a cost in fan power to overcome an increased system pressure drop.

6.3.4 HCl

Testing was performed at the U.S. EPA's laboratories at Research Triangle Park, NC by Acurex Corporation, under contract to CalRecovery, Inc., who was hired by Passamaquoddy Technology, L.P. During pilot scale testing to determine, among other things, HCl removal efficiency, it was found that HCl was removed from a simulated incinerator flue gas stream at efficiencies of about 98% (the final report has not been released, however, it will be made available later, upon request)[28]. In these tests, incinerator ash was combined with other alkaline waste in an aqueous slurry and used as the scrubbing reagent.

During the week of September 9, 1993, Entropy, Inc., under contract to the U.S. EPA to test the efficiency of various control technologies applicable to portland cement kilns to establish MACT controls for HCl for cement plants, as directed by Title III, the Air Toxics Provisions, of the Clean Air Act Amendments of 1990, tested the Recovery Scrubber prototype at Dragon as a possible MACT for HCl emissions from portland cement kilns. Although neither a preliminary nor a final report has been issued concerning this test series, the report will be available, at a later date, upon request (PTech estimates that the earliest date the report may be available would be July 1994).

Passamaquoddy Technology, L.P. was asked by Research Triangle Institute (P.O. Box 12194, Research Triangle Park, NC, 27709-2194) to prepare a report on the anticipated environmental and economic performance of a Recovery Scrubber when applied to three different cement plants at three different HCl emissions levels for each plant (see Appendix K). RTI is operating under contract to the U.S. EPA to provide technical support for development of MACT standards for the 189 hazardous air pollutants (HAPs) as called for in Title III of the CAAA.

In all 9 cases examined, application of the Recovery Scrubber resulted in net income to the model plant under study. The calculated capital cost to install a Recovery Scrubber ranged from a high of nearly $19 million to a low of less than $6 million. The estimated net benefits ranged from a low of over $700,000 per year to nearly $3.1 million per year. A simple pay back period was also calculated by dividing the capital cost by the annual net income to get a payback period for the Recovery Scrubber installations. The payback periods ranged from 5 years to 8.4 years. While investment in the models with shorter payback periods may be justifiable on a purely financial basis, it must also be emphasized that even in the least beneficial case studied, in less than 8.5 years, the Recovery Scrubber generated sufficient income to pay for its initial installation.

6.3.5 Volatile Organic Compounds (VOC)

Additional testing was performed at the Dragon Recovery Scrubber for two days beginning September 1, 1993 by Environmental Sciences Services (532 Atwells Avenue, Providence, RI, 20909), under contract to MEC Company (P.O. Box 330, Neodesha, KS) to test VOC removal efficiencies of the Recovery Scrubber. The Recovery Scrubber demonstrated removal efficiencies for VOCs (as represented by α-pinene), on three different runs of 72.3%, 83.1%, and 74.5% (see Appendix L).

6.3.6 CO_2

One of the environmental concerns that has recently gained increasing attention is greenhouse warming and emissions of greenhouse gases, with a primary emphasis on CO_2. Portland

cement kilns are large sources of CO_2 emissions because they emit CO_2 from combustion of fuel, as do all combustion sources, but also emit CO_2 from calcination of limestone. Combined, these two sources emit roughly one ton of CO_2 for each ton of clinker produced. One way to reduce CO_2 emissions is to reduce fuel consumption (improve efficiency) in the kiln. However, the cement industry has already reduced fuel consumption substantially over the last two decades and further reductions, in most cases, are not practical. The Recovery Scrubber, however, can help reduce CO_2 in several ways.

One of the most obvious ways the Recovery Scrubber can help reduce CO_2 emissions is by allowing a cement plant to recycle CKD. Although the reduction in CO_2 may be moderate as a percentage of total CO_2 emissions from a cement kiln (i.e., 1 - 5 percent), reuse of CKD can nonetheless, result in meaningful reductions of CO_2. At Dragon, approximately 2 percent of the CO_2 is removed by the Recovery Scrubber.

If the difference in loss on ignition (LOI) is assumed to be only due to calcination of calcium (and magnesium) and if the quantity of CKD wasted is also known then CO_2 reductions may be easily estimated. The CO_2 reduction possible from the reuse of CKD depends on the amount (tons) of CKD that is hauled to the landfill and on the loss on ignition (LOI) or degree of calcination of the freshly produced CKD. The more CKD that is thrown away and the higher the degree of calcination (lower LOI) of the CKD wasted, the greater will be the CO_2 reduction if CKD is recycled.

Another way that the Recovery Scrubber can help reduce CO_2 emissions from a cement kiln is by enabling a cement plant to use alternate raw materials. Biomass ash and municipal solid waste (MSW) ash both contain some of the basic constituents necessary to produce portland cement. However, in both cases the calcium contained in the ash is generally calcium oxide rather than calcium carbonate. Use of one ton of calcium oxide, rather than the 1.78 tons of calcium carbonate necessary to produce one ton of CaO, would reduce CO_2 emissions by 0.78 tons.

7.0 OPERATING RESULTS

7.1 Recovery Scrubber Start-up Problems and Solutions

The Recovery Scrubber was initially started in late December 1990 and, after several minor problems with pump seals and other new construction type problems, operated until the Dragon plant went down for winter overhaul in February 1991. In addition to those random start-up difficulties, there were some problems relating to inadequate or inappropriate design which were identified and corrected. These problems include:

7.1.1 Heat Exchanger Corrosion

As originally constructed, the shell-and-tube heat exchanger in the crystallizer sub-system had tubes made from a high alloy metal (1925 HMO) while the shell was made from carbon steel with a liberal corrosion allowance. After only a few weeks operating time, the shell was showing signs of severe corrosion. The system was shut down and the heat exchanger was examined. The shell was corroded through in places and was exhibiting evidence of severe corrosion elsewhere. The tubes displayed no evidence of any corrosion attack. The heat exchanger was removed from service, taken to a repair facility, and a new shell was fabricated from the 1925 HMO alloy. No further corrosion problems have developed in any area of the Recovery Scrubber.

7.1.2 CKD Slurry Preparation.

Initial design called for waste CKD and water to be mixed in a rubber lined tank with high energy agitation. The mixed slurry was then to be pumped to the Recovery Scrubber reaction storage tank. Although slurry mixing was adequate, it was not possible to pump a slurry of fresh CKD for long distances through pipes. Gypsum formation on pipe interior walls eventually reduced pipe carrying capacity to below useful flows and the pump would cease working.

The rubber lined mixing tank was replaced with a vortex mixer in which dry CKD is introduced as a powder and a high volume flow (400 - 500 GPM) of previously reacted slurry is used as a tangentially introduced carrier fluid. The mixed CKD and

reacted slurry is then immediately discharged into the reaction storage tank. Gypsum cannot form in the reaction tank because the slurry is saturated with CO_2 and calcium preferentially precipitates as the carbonate. This system works well and has eliminated the problems with build-up of scale on pipe surfaces.

It should be noted that there is no problem handling slurries of CKD after it has been processed through the Recovery Scrubber. Its chemical nature has been significantly changed by the processing and it has lost its pozzolonic nature.

7.1.3 Exhaust Gas Distribution.

The gas-liquid contact system in the reaction tank relies on placement of a uniform, moving layer of slurry on top of a perforated tray (sieve tray). Gas moves up through the perforations from below while slurry simultaneously flows across the top of the tray resulting in intimate gas/liquid contact. Because the layer of slurry is of constant thickness across the tray, it is necessary to have constant and equal gas pressure everywhere under the tray. Input gas flow must be evenly distributed to the plenum below the tray surface by careful design of the gas ducting and the plenum geometry.

Flue gas flowing through the duct from the recouperator to the reaction tank must expand into the plenum under the reaction tray and while doing so, convert its velocity pressure to static pressure. This requires careful design of the ducting and plenum. If the ducting and plenum are built without reference to the design, significant problems can result. If the pressure conversion is adequate, the gas will exert equal pressure at all points immediately below the tray surface. The as built system did not follow initial design and did not effectively perform that conversion and gas pressures within the plenum were non-uniform. To achieve the initial design specification, baffles were placed in the gas stream to redirect and distribute gas flow. The baffles achieved the design requirements. The gas flow distribution has been excellent.

7.1.4 Sieve Tray Flatness.

As initially constructed the tray was not sufficiently flat (flat as opposed to level). The sieve tray requires a flatness of at least ± 1/8 inch over its entire area of 48 X 28 feet. This was not a design problem, but rather a construction problem. Correction of the tray flatness to meet design specifications required several tries and considerable time, effort, and expense. The correction has been made and has resulted in excellent operation of the top surface of the tray.

7.1.5 Plugging of the Sieve Tray.

After some operating time it was noticed that small cones of CKD based material were building up on the bottom side of the tray. They are formed from very small quantities of particulate matter in the gas stream. As gas flows through the plenum and changes direction in order to pass through the holes in the tray surface, the entrained particulate tends to continue in its original direction because of its inertia, that is, to impinge the plate surface rather than move through the holes with the gas. As the material accumulates, building gradually downward from the tray surface, its diameter decreases and a cone is formed. With the result that, it gradually plugged the holes and resulted in a progressive increase in the pressure drop across the tray. Several techniques were tried to either prevent or remove the accumulation. The solution was a moving spray header which applies high pressure water flow to the tray bottom surface. The spray system has worked very well and since its addition the tray has performed excellently in all respects.

7.1.6 Mist Eliminator Plugging.

As exhaust gas bubbles through the CKD slurry, some of the slurry was entrained in the gas stream and escaped up the stack. A mist eliminator was installed above the reaction tank at the inlet to the stack. This solved the slurry entrainment problem and resulted in excellent particulate control (15 mg/NM^3 or 0.006 gr/SCF). However, the mist eliminator plugged with particulate.

Droplets impinging on the mist eliminator accumulate, coalesce into large droplets, and drop back into the slurry flowing across the tray surface. If particulate matter is present in the captured droplets, it too must fall back into the slurry on the tray, but may not do so if the particulate loading on the mist eliminator surface is excessive. As originally designed, with a mesh type mist eliminator, it was necessary to wash the mist eliminator in an attempt to completely remove the particulate build-up.

The mist eliminator wash system did not perform as well as desired. It was necessary to temporarily stop gas flow through the scrubber periodically and enter the reaction tank for manual cleaning of the mist eliminator. Accumulated material, which was not removed during automated spray washing, reduced the cross sectional area of the mist eliminator and increased the operating pressure.

The first wash system used, an array of nozzles placed under the mist eliminator surface and spraying water upward toward it, did not provide the long-term, low maintenance solution desired. It was replaced with a high pressure spray array installed on a rotating arm. The high pressure spray system performed less well than the original low pressure spray. The cause, however, was not failure of the new system, but rather other factors in the process related to material flow rates.

The spray wash system, which cleaned a circle shaped area of a square mist eliminator surface, reduced the effective open area of the mist eliminator to approximately half of the design value. The particulate loading rate per unit area was, therefore, twice the previous value. The mesh type mist eliminator, although very effective as a demister, was deemed unsuitable for the conditions found in the Recovery Scrubber reaction tank.

As described above, several methods were tried to clean the mesh type mist eliminator with varying degrees of success. None of the cleaning methods were entirely successful so small sections of several different types of mist eliminators were tested during actual operation. A test section of a "chevron" type mist eliminator was found to perform as effectively as the mesh type mist eliminator for particulate

removal yet was not blinded with particulate. A new chevron style mist eliminator was designed by the supplier and was installed during the cement plant 1992/1993 winter overhaul.

7.1.7 Pelletizer Operation.

The crystals produced by the crystallization system are a mixture of potassium sulfate, syngenite (potassium calcium sulfate), and minor quantities of gypsum and calcite. Crystals are extracted from the evaporator by passing a small flow through a centrifuge for dewatering. The centrifuge cake is then passed to a pelletizer for formation of pellets suitable for use as fertilizer. Pelletizing of the potassium sulfate crystals has been a problem. Dewatering by the centrifuge results in a centrifuge cake that has a water content too high (because of the presence of syngenite) for pellet formation by the existing pelletizer.

Originally, it was believed that small amounts of CKD was responsible for the poor dewatering performance of the centrifuge. Consequently, sand filters were installed between No. 1 settling tank and the crystallizer centrate tank to remove any remaining CKD solids. The filters did not work satisfactorily because although some CKD solids were present, dissolved gypsum and syngenite were the main contributors to inefficient dewatering.

Changes were made in the crystallizer plumbing so that the concentration of the very soluble K_2SO_4 and the much less soluble syngenite and gypsum could be adjusted to allow for removal of the gypsum and syngenite crystals by filtration while K_2SO_4 remains in solution. This solution did not work either because of the inefficient filtration provided by the sand filters.

In the summer of 1993, the sand filters were removed and hydrocyclones were placed in the crystallizer circuit to separate the very fine gypsum and syngenite crystals from the much coarser potassium sulfate crystals.

Because of the problems encountered with the pelletizer, bulk quantities of pelletized potassium sulfate have not yet been produced for sale. However, recent analysis (see Table 12)

of a sample extracted from the flow in the crystallizer vapor body of the salt product indicates that it will be fully acceptable as a commercial fertilizer.

Table 12

Chemical Analysis of By-Product Fertilizer.
(Dry Basis)

Parameter	Percent as Oxide	Parameter	Percent as Calculated Compounds
Potassium as K_2O	48	K_2SO_4	89
Sodium as Na_2O	0.8	$Na_2SO_4 \cdot 10H_2O$	3.6
Calcium as CaO	1.0	$CaSO_4 \cdot 2H_2O$	1.4
Sulfur as SO_3	43	NaCl	0.3
Chloride as Cl^-	0.2		
Water insoluble matter	3		3
TOTAL	96.0*		97.3*

7.2 Use of Waste Heat for Recovery of Fertilizer

One of the three stated performance criterion (see Section 6.1) for successful operation of the Recovery Scrubber prototype was to use waste heat from the exhaust gas stream as the energy source for evaporation to concentrate and crystallize potassium sulfate from the dilute potassium sulfate salt solution produced by the Recovery Scrubber. The process was designed so that approximately 50 gallons per minute of water needs to be evaporated to recover all of the soluble potassium salts. Heat recovered from the flue gas has proved to be more than adequate for that evaporation rate and excess heat is released with the exhaust gas or is dissipated in an on-site cooling pond. The Recovery Scrubber has met this performance criterion.

*Totals do not match because of assumed hydrated form for gypsum and sodium sulfate and because of a slight stoichiometric imbalance in the original analysis.

7.3 Typical Operating Parameters and Materials Balance

A cement kiln is inherently variable because of the large variety of materials being continuously fed into the process. In addition to a coal firing rate of approximately 10 TPH, about 100 TPH (dry basis) of raw materials (primarily limestone and sand), and approximately 52 TPH of water (used to produce the kiln feed slurry when mixed with the pulverized raw materials) are fed into the system. Because of these variables, typical or average values for operating parameters and materials balances are used rather than instantaneous values.

7.3.1 Typical Operating Parameters

The operating parameters provided below, in Table 13, should be considered to be estimates of typical parameters. These estimates did not change substantially during the duration of the operating periods. It was not possible to associate cement kiln operating parameters, CKD composition or rate, flue gas flow rate, or other parameters to Recovery Scrubber emissions variables (with the exception of the input SO_2 which did noticeably affect the SO_2 removal efficiency - see Section 6.3 Exhaust Gas Scrubbing Efficiency).

Table 13

Typical Operating Parameters

Kiln Raw Material Feed

Raw Material Input Rate to Kiln	100 TPH
Water Input Rate with Raw Materials	52 TPH
Resulting Kiln Feed Slurry Flow Rate	152 TPH

Kiln Exhaust Gas

Volume	160,000 SCF
Temperature	245 °F
CO_2	18.9%
O_2	7.7%
H_2O	12.8%
N_2	60.6 %
SO_2	132 lb/hr

Table 13 Continued

Recovery Scrubber

Slurry Flow Rate Through Reaction Tank	9,000	GPM
CKD Flow Rate In	10	TPH
Renovated CKD Flow Rate Out	11	TPH
Reaction Tank Operating Temperature	141	°F
Make-Up Water Required	48	GPM
Evaporator Cooling Water Flow Rate	2,350	GPM
Cooling Water Temperature Rise	21	°F

7.3.2 Material Balance

The materials balance for the Recovery Scrubber is presented in Table 14. Also, please refer to Figure 5 - Hourly Process Flowsheet.

Table 14

Typical Recovery Scrubber Inputs and Outputs
(all figures are in pounds per hour)

Inputs:

CKD		Exhaust Gas		Make-Up Water	
SiO_2	2,937	CO_2	142,600	H_2O	24,853
Al_2O_3	469	O_2	57,940		
Fe_2O_3	296	H_2O	96,670		
CaO	9,186	N_2	457,000		
MgO	687	SO_2	132		
SO_3	1,166				
K_2O	683				
Na_2O	62				
LOI*	5,334				
Total	20,820	Total	754,342	Total	24,853

* Primarily CO_2 contained in $CaCO_3$ and $MgCO_3$

Table 14 Continued

Outputs:

Renovated CKD		Exhaust Gas		Salt By-Product		Evaporative Losses of Water	
SiO_2	2,937	CO_2	140,000	K_2SO_4	850	H_2O	1,500
Al_2O_3	469	O_2	57,940	Other	150*		
Fe_2O_3	296	H_2O	96,588	H_2O	50		
CaO	9,134	N_2	457,000				
MgO	687						
SO_3	853						
K_2O	224						
Na_2O	52						
LOI	8,197						
H_2O	22,392						
Total	45,241	Total	751,528	Total	1,050	Total	1,500

*Primarily calcium sulfate, sodium sulfate, and insoluble mineral matter.

Table 15

Sulfur and Potassium Balance

Source	Sulfur in pounds/Hr as S		Potassium in pounds/Hr as K	
	In	Out	In	Out
CKD	466	341	567	186
Exhaust	66	Trace	---	---
Salt Product				
K_2SO_4	NA	156	NA	381
Other	NA	35*	NA	---
TOTAL	532	532	567	567

*Primarily from calcium sulfate and sodium sulfate.

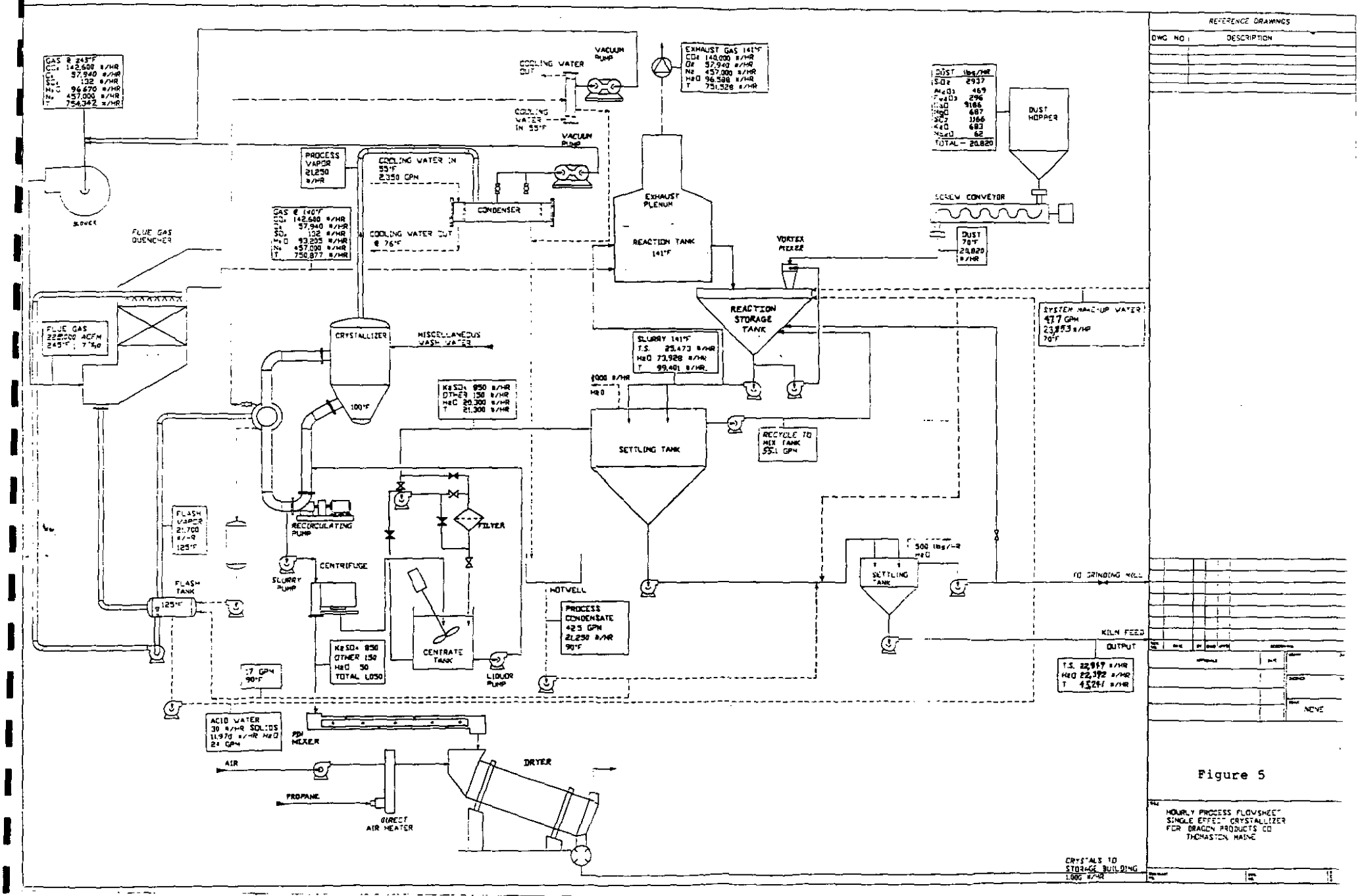


Figure 5

HOURLY PROCESS FLOWSHEET
SINGLE EFFECT CRYSTALLIZER
FOR DRAGON PRODUCTS CO
THOMASTON, MAINE

8.0 MAINTENANCE AND RELIABILITY

Upon initial start-up December 20, 1990, several routine piping and electrical malfunctions, typical of new construction, were experienced and quickly corrected. In addition to these routine new construction type problems, several other problems were experienced. These involved corrosion on the shell of the evaporator shell-and-tube heat exchanger, flatness of the perforated tray in the reaction tank, gas distribution in the plenum below the perforated tray, CKD-water mixing, build-up on the underside of the perforated tray, build-up on the mist eliminator between the reaction tank and the Recovery Scrubber stack, and potassium sulfate pellet formation.

In addition to these start-up problems, the host cement plant was only operating approximately 50 percent of the time because of an extremely poor market for cement in the northeast United States. This low level of operation severely delayed implementation of changes and corrective actions to solve the problems identified during the start-up phase.

8.1 First Operating Interval - Phase III

By August 1991, the problems with corrosion on the heat exchanger shell, the tray flatness, the gas distribution, the CKD-water mixing, and the build-up on the under side of the perforated tray had been solved. Build-up on the mist eliminator and the formation of potassium sulfate pellets remained as operating problems. Also, the cement plant continued to operate on a severely restricted production schedule because of the poor economic conditions in the New England area. Phase III, operation and data collection, began August 20, 1991.

Between August 20, 1991 and January 14, 1992, the Recovery Scrubber operated in excess of 1,400 hours. Although the Recovery Scrubber experienced some downtime during this interval, a substantial portion of the downtime was because of maintenance or operational problems with the host cement plant kiln. The Recovery Scrubber is not operated if the host cement plant's kiln is down or is slowed down or if the raw material storage tanks are inoperative.

8.1.1 Mist Eliminator

During this operating interval, several different methods of removing the build-up from the mesh pad type mist eliminator with various high pressure spray systems were investigated. By the end of this operating interval, it was determined that none of these build-up removal methods were completely satisfactory.

8.1.2 Potassium Sulfate Pelletization

During this operating interval, potassium sulfate pellets were not being dewatered sufficiently in the centrifuge to permit their pelletization in the pin mixer type of pelletizer that had been selected. A set of sand filters were installed between the centrate tank and the vapor body of the evaporator to remove small particles of CKD that had not been removed in the settling tanks. This operating interval offered insufficient time to test the filter's effectiveness in aiding crystal pelletization.

8.1.3 Host Cement Plant Winter Shut Down

The host cement plant kiln was shut down in mid-January, 1992 for winter maintenance and inventory control and was not restarted until May 1992.

8.2 Second Operating Interval - Phase III

Between May 13, 1992 and October 1, 1992, the Recovery Scrubber operated more than 1,300 hours. As before, although the Recovery Scrubber experienced some downtime, a substantial portion of the downtime was related to the host cement plant. For example, the cement plant kiln was down between July 1 and July 15 and again between August 20 and August 30 during 1992 for maintenance problems.

8.2.1 Mist Eliminator

During the second operating interval, several different styles of mist eliminators were installed in selected test sections of the mist eliminator to test their effectiveness and their ability to remain free of build-ups. By the end of

this operating interval, a chevron style mist eliminator had been selected as offering excellent mist elimination and had the ability to remain free of build-ups because the design permitted continuous washing and collection of the spray water used to wash the chevrons.

8.2.2 Potassium Sulfate Pelletization

The filter system installed on the evaporator system near the end of the first operating interval proved to be ineffective. By the end of this operating interval, another method of removing the small crystals of gypsum and syngenite (calcium potassium sulfate) which were hindering dewatering by the centrifuge was developed.

8.2.3 Host Cement Plant Winter Shut Down

The Recovery Scrubber was shutdown October 1, 1992 to install the chevron style mist eliminator system and accompanying spray wash system. Before the work was completed, the host cement plant kiln was shut down for winter maintenance and remained down until April 1993 for inventory considerations.

8.3 Third Operating Interval - Phase III

Since completion, in April 1993, of the modifications described above, the availability of the Dragon Recovery Scrubber has improved markedly. The system now treats and returns to the kiln feed system virtually all of the CKD produced by the cement kin and air emission control meets or exceeds design expectations.

Between April 13, 1993 and September 22, 1993 the Recovery Scrubber operated 2,600 hours. As before, the cement plant experienced several periods of operating difficulty during this operating interval which resulted in Recovery Scrubber down time. However, if the host plant down time is ignored since the April start-up, the Recovery Scrubber itself has only been off line for one cleaning period in May and for one fine tuning adjustment of the gas flow distribution baffles which occurred at the end of May and beginning of June. When cement plant down time is not counted, the Recovery Scrubber operated 65 percent of the available hours in April, 78.6 percent of the available hours in May, 80.8 percent of June

hours, and 99.5 percent of the July 1993 hours. The August and September availability has continued to be very good when the cement plant down time is removed from hours available to the Recovery Scrubber.

8.4 Anticipated Annual Maintenance Costs

Insufficient operating time has yet been accumulated to allow meaningful maintenance costs to be generated from actual records. Although the Recovery Scrubber is an innovative pollution control device, it makes use of standard equipment such as pumps and valves for which many cement and other process plants have existing maintenance records and experience. Annual maintenance costs, including parts replacement costs over a 20 year life, are estimated to be $150,000. Detail is provided in Table 16 - Anticipated Annual Maintenance Costs.

Table 16

Anticipated Annual Maintenance Costs

Item	Anticipated Annual Maintenance Costs
Stack butterfly damper drive	$ 500
System inlet damper drive	500
System fan	12,000
Fan damper drive	500
Reaction tank sump pump	500
Reaction tank circulation pumps (2)	8,000
Storage tank discharge pump	1,000
Settling tank 1 discharge pump	1,000
Settling tank 2 discharge pump	1,500
Potassium sulfate pin mixer	2,000
Potassium sulfate dryer	2,000
Reaction tray high pressure spray pump	3,000
Vortex mixer slurry pump	500
Potassium sulfate conveying system	1,000
Seal water pump	500
CKD rotary feeder	1,000
Tank rake arms (3)	1,500
Chevron spray system	1,000
CKD screw (high level)	1,000

Table 16 Continued

Item	Anticipated Annual Maintenance Costs
CKD elevator	1,000
CKD screws (low level) (2)	2,000
Reaction tank high pressure spray drive	3,000
Distilled water (hotwell) pump	500
Leachate (centrate) pump	500
Crystallizer discharge pump	500
Recouperator spray pump	1,000
Recouperator carry-over pump	500
Recouperator circulation pump	3,000
Crystallizer circulation pump	5,000
Flash tank vacuum pump	5,000
Crystallizer vacuum pump	5,000
Potassium sulfate centrifuge	5,000
Centrate tank mixer	500
System inlet damper purge fan	500
Quarry cooling water pumps (4)	10,000
Leachate filter pumps (2)	1,000
Misc. seal water and lube pumps (5)	3,000
Air activated slurry line pinch valves (10)	5,000
Heat tracing	2,000
CKD weigh feeder	2,000
Instrumentation	10,000
Electrical distribution	10,000
Corrosion repairs	10,000
Slurry line abrasion repairs	5,000
Clearing lines, cleaning, misc.	20,000
Total anticipated annual maintenance costs	**$150,000**

8.5 Summary

After an initial period of debugging and problem solving, the Recovery Scrubber has proven to be a reliable, low maintenance, pollution control device. Extensive use was made of fiberglass as a construction material and particular attention was paid to being sure that corrosion in areas not constructed of fiberglass would not adversely affect the Recovery Scrubber. In future installations, greater use of

fiberglass is anticipated since it is highly corrosion resistant and an economical, low maintenance, construction material.

In addition, it should be noted that reliability is, among other things, a function of design. Higher reliability, if desired, may be designed into equipment through use of more expensive, severe duty equipment or through the use of redundant sub-systems, albeit at higher initial capital cost.

9.0 PASSAMAQUODDY TECHNOLOGY RECOVERY SCRUBBER™ ECONOMICS, POTENTIAL MARKETS AND COMPETITION, AND CURRENT MARKETING EFFORTS

9.1 Recovery Scrubber Economics

9.1.1 Cost to Construct

While nearly $18,000,000 was spent on the Dragon prototype, the cost to reconstruct the Dragon system, absent the revisions involved in the prototype, is estimated to be approximately $10,000,000 in 1990 dollars. This is based on a detailed cost analysis commissioned by Passamaquoddy Technology[29] to determine the cost of the installation "as built" net of modifications and rework. Although further changes have been made since the cost analysis, it is not considered that this has had any significant effect upon the as built estimate.

Cost summary by discipline area:

Civil	20%	$1,997,000
Mechanical	65%	$6,566,000
Electrical & Instrumentation	15%	$1,527,000
Total	100%	$10,090,000

Cost summary by system*:

Exhaust gas related	36%	$3,624,000
CKD related	13%	$1,327,000
By-product related	43%	$4,379,000
Common	8%	$ 760,000
Total	100%	$10,090,000

*Indirect costs, including labor overheads, profit, construction equipment and engineering have been allocated.

The estimated confidence limits were +6.8% or, $686,000 and -7.4% or, $747,000 and the estimates were based on the following assumptions:

- 1990 northern New England non-union labor with average total costs of $36.32 per manhour.
- 1990 materials and equipment prices
- Profit of 10% on direct costs plus labor overheads
- Engineering cost 5% of total
- Construction interest costs excluded
- Sales taxes excluded
- Performance bond excluded
- Site permitting excluded

9.1.2 Cost to Operate

In addition to the anticipated, long term, annual maintenance costs of $150,000 (see Section 8.4), power costs are the only other significant cost to operate. It must be noted that the Recovery Scrubber, unlike other acid gas scrubbers, does not have an operating cost associated with purchase of a scrubbing reagent (the Recovery Scrubber uses and renovates waste materials, in Dragon's case, CKD) and does not have any cost associated with disposal of any waste stream (the Recovery Scrubber is a zero discharge system). Additionally, no dedicated staffing or maintenance equipment is required, effectively all operating costs are variable.

Power costs are based on an average power demand of 787kW, at an average cost of $0.06 per kWh, and 85% operating time. The annual cost is therefore:

(8,760 hours/yr)*(0.85)*(787kW)*($0.06/kWh)= $351,600

Therefore, the total annual estimated maintenance and operating costs are:

Anticipated Annual Maintenance Costs	$150,000
Anticipated Annual Operating Costs	$350,000
Total Annual Costs	**$500,000**

9.1.3 Cost/Benefit Analysis

It must be emphasized that this technology, while providing high level pollution control, also generates both revenues and avoided costs, which offset the operating costs and, in many cases, provide a return on invested capital.

Dragon produces (and the Recovery Scrubber recycles) waste CKD at a rate of 8 tons per hour. This material is considered by Dragon to have a value of $5 per ton. Avoiding the need to landfill this material is considered to be worth, at least $8 per ton.

The Cement Kiln Recycling Coalition (CKRC)* has developed preliminary estimates for implementation costs of a 600,000 ton capacity CKD monofill meeting design criteria believed to be appropriate by the CKRC for CKD from kilns not using hazardous waste and for a 600,000 ton capacity CKD landfill meeting Subtitle C** design criteria. Subtitle C criteria are considered to be appropriate for CKD from kilns using hazardous waste. From a CKRC working draft dated March 29, 1993, the estimated cost for facilities meeting the design criteria are presented in Table 17 - CKD Landfill Capital Costs (numbers have been rounded to the nearest $1,000):

*CKRC is an organization of cement companies and hazardous waste management companies dedicated to promoting the safe and beneficial reuse of waste materials in producing cement.

**Subtitle C is the hazardous waste regulatory program under RCRA for materials defined as "solid wastes" [see RCRA §1004(27)] and that are listed or defined by EPA as hazardous.

Table 17

CKD Landfill Capital Costs

	Monofill	Subtitle C
Construction	$1,470,000	$2,205,000
Contingency	147,000	220,000
Engineering & monitoring wells	220,000	220,000
Permits, etc	300,000*	440,000**
TOTAL	$2,137,000	$3,085,000
Cost per ton	**$3.56**	**$5.14**

* (PTech estimate)
**(CKRC estimate)

In addition to the above costs, annual operating costs will be incurred. During the Spring 1993 PCA-GTC meeting, Mr. Doug Abeln of Schreiber, Grana, and Yonley, Inc. (an Environmental Engineering consulting firm, located in Saint Louis, MO) presented a paper 3/9/93 titled "Contingent Management Practices for CKD" which included the following costs for a 42 acre, Subtitle D landfill for Municipal Solid Waste:

Construction	$5,000,000
Design & Permit	500,000
Annual Operating Costs	1,000,000
Total	$6,500,000

If compacted CKD had a density of 100 pounds per cubic foot*, and the landfill was 25 feet deep, a 42 acre landfill would contain about 2,300,000 tons or the 600,000 ton capacity landfill cited above would be about 26% of the capacity of the 42 acre site. If the annual operating costs were a linear function of landfill size, the annual operating costs of the 600,000 capacity landfills would be about $260,000 per year.

If a typical cement plant landfilled an average of 8 TPH of CKD and it operated 90% operating time (8,760 hours/year * 0.9 = 7,884 hours/year), it would landfill 63,072 tons of CKD per year. Therefore, the estimated annual operating expenses would be $4.12 per ton. When added to the estimated capital cost of $5.14 per ton and a conservative estimate of $1.00 per ton for CKD handling, the cost to landfill CKD would be about $10.26 per ton. This cost, $10.26 per ton or $647,100 if 63,072 tons were landfilled annually, could be saved if the need to landfill CKD were eliminated by installation of a Recovery Scrubber to renovated and recycle the waste CKD. These figures do not include the potential value of CKD as kiln feed (KF) when it is renovated by the Recovery Scrubber.

	Subtitle C	Monofill
Landfill capital cost	$5.14 per ton	$3.56 per ton
Annual landfill operating costs	$4.12 per ton	$4.12 per ton
Handling costs	$1.00 per ton	$1.00 per ton
TOTAL	**$10.26 per ton**	**$8.68 per ton**

*Although the PCA did find one sample of CKD that achieved 108 pounds/ft^3 under heavy compaction in the laboratory (PCA Research and Development Bulletin RD103T, page 8, Figure 8), 100 pounds/ft^3 is probably the maximum average achievable in the field.

In addition to the Recovery Scrubber's ability to renovate and recycle CKD as it is produced, the Recovery Scrubber may also be used to renovate and recycle CKD from existing landfills. CKD landfills may be mined by several methods, including hydraulic mining, that are more economical than typical "drill, blast, and haul" open pit mining. Depending upon site specific considerations, Passamaquoddy Technology estimates that the cost to recover and prepare CKD, from a landfill, for renovation in the Recovery Scrubber is between $2/ton and $5/ton. If CKD is valued at $5/ton as kiln feed, then a cement plant would recognize a raw material savings of from zero to $3/ton when reclaiming an existing landfill.

Dragon plans to begin mining previously landfilled CKD in the near future. They expect to reclaim this material at a rate of 5 tph at a net raw material savings of $3 per ton.

The above calculations do not consider the value of reducing and eventually eliminating a potential environmental liability. With three CKD landfills on the Superfund list, remediation of existing CKD landfills must be considered. Passamaquoddy Technology contacted an insurance company agent and explained the potential liability of owning an existing CKD landfill, then asked him to estimate what it would cost to provide coverage for the liability of remediating a 1,000,000 ton CKD landfill. He said the minimum premium to provide insurance to cover potential remediation would be about $300,000/year.

Since it began using the Recovery Scrubber, Dragon has experienced an increase in raw mill capacity of roughly 5% and a reduction in fuel consumption of about 7%. While these improvements may be the result of several factors, Dragon believes that they result in large measure from the quality of the material being returned from the Recovery Scrubber. Renovated CKD from the Recovery Scrubber contains more fines than normal kiln feed, which, among other things, aids fluxing action in a portland cement kiln and requires less grinding in the raw mills.

Dragon has investigated and expects to soon begin receiving, approximately 55,000 tons per year of biomass ash and mixed biomass ash and coal ash from area pulp and paper mills. It is anticipated that the net benefit to Dragon will be about $35 per ton of waste material used. Prior to installation and use of the Recovery Scrubber, Dragon would not have been able to tolerate the alkali content of this material. Passamaquoddy Technology believes that Dragon could accept and consume 200,000 tons of outside waste material annually and receive an average tipping fee of $20 per ton (for a total annual benefit of $4,000,000) simply by increasing its storage and handling equipment.

Savings from use of higher sulfur content fuel could produce an additional savings of at least $2 per ton of fuel used.

The actual and anticipated future benefits at the Dragon cement plant from the installation and use of the Recovery Scrubber are detailed in Table 18 - Revenue and Avoided Costs at Dragon.

If the estimated total cost of the Dragon Recovery Scrubber prototype is about $18,000,000, an annual net benefit of $5,235,000 would result in a simple payback period of:

$$\frac{\$18,000,000}{\$\ 5,235,000} = 3.4 \text{ years}$$

To compare the Dragon prototype to a second, or succeeding, installation of the same size and with the same benefits, additional costs of about :

Contingency	$1,000,000
Design/permitting	$2,000,000
Construction interest	$1,000,000
Licensing fees	$2,000,000
Total	$6,000,000

would be added to the $10,000,000 estimated "as built" cost

of the Dragon Recovery Scrubber prototype (see Section 9.1.1), resulting in a total cost of about $16,000,000. If the annual net benefits were the same as at Dragon, it would result in a simple payback period of:

$$\frac{\$16,000,000}{\$\ 5,235,000} = 3.1 \text{ years}$$

Table 18

Revenue and Avoided Costs at Dragon

	Dollars per year
Value of raw materials recovered (8 tph)(7,446 hr/yr)($5/t)	298,000
Avoided cost of CKD landfilling (8 tph)(7,446 hr/yr)($9/t)	536,000
Recovery of existing CKD landfill (5 tph)(7,446 hr/yr)($3/t)	112,000
High sulfur fuel cost savings (13 tph)(7,446 hr/yr)($2/t)	193,000
Revenue from sale of salt product (0.4 tph)(7,446 hr/yr)($200/t)	596,000
Revenue for accepting waste materials and value of waste as raw material (200,000 tons/yr)($20/t)	4,000,000
Total annual benefits =	$5,735,000
Less total annual costs (see Section 9.1.2)	- 500,000
Annual net benefit	**$5,235,000**

9.2 Potential Markets and Competition

9.2.1 Cement Industry

9.2.1.1 Background

Cement is made from a mixture of limestone, shale, and mineral additives which give a narrowly defined composition of calcium, silicon, aluminum and iron oxides. The raw materials are crushed, ground and burned to yield an intermediate product, clinker. All process chemistry occurs in a rotary kiln where the raw material is progressively heated up to approximately 2700°F; drying is followed by calcination of the limestone (evolution of CO_2), formation of various calcium silicates and aluminates and, finally, partial fusion to produce black nodules of clinker. Finished cement is made by intergrinding clinker with a small proportion of gypsum which acts to control the setting of hydrated cement. Cement is used, primarily, in concrete which is a mixture of cement, water and graded aggregate.

Cement manufacture is by two major processes, the wet and the dry, though there are also a few kilns using intermediate, semi-wet processes and some shaft kilns remain in less developed parts of the world. The wet process has greater fuel requirements and capacity limitations. Nearly 40% of operating kilns in the United States, however, are still wet process and their higher specific fuel consumption led them to pioneer the use of alternative fuels in order to remain competitive and continues to give them an advantage where hazardous waste is burned in return for a tipping fee. Plants in North America range in capacity from about 300,000 to 2 million tons per year while newer plants, almost exclusively in the Far East, range up to 12 million tons per year.

The burning process requires the blending of raw materials in precise proportions to give a eutectic mixture; the mixture which has the lowest possible melting point. Deviation from the mixture results in higher fuel consumption, reduced cement quality, and a number of kiln operating problems.

Raw materials also contain various minor volatile constituents which can give rise to process and quality problems if present in excess of certain limits. The objectionable materials are potassium, sodium, sulfur and chloride. Being volatile, these constituents tend to boil into a vapor, leave the hot zone of the kiln with exhaust gas, condense on fine dust particles in the cooler regions, and concentrate in the kiln dust collector catch of long kilns or the bypass dust of air suspension preheater kilns. Thus, by discarding dust, K, Na, S, and Cl can be removed from the process. To some extent, S and Cl will also remain in gaseous form and will be emitted with the flue gas. Quantitatively, the distribution of the volatile constituents between clinker, dust and flue gas depends upon many factors including the source of the volatile element, stoichiometric balance between the cations (K, Na) and anions (SO_3, Cl), and kiln type and operation. Coincidentally, the compounds formed between these ions are relatively soluble so that their removal from dust is most obviously effected by leaching, which is incorporated by the Recovery Scrubber.

9.2.1.2 Cement Industry Solid Waste

It is estimated that about 4,500,000 tons of CKD are generated annually, of which 756,200 tons are beneficially reused in some manner. The remainder, 3,700,000 tons, is landfilled[30]. CKD is generally the same composition as kiln feed and, if the volatile contaminants are removed, as is achieved in the Recovery Scrubber, the material can be returned to the process thereby avoiding both its disposal and its replacement by freshly mined material. In Western Europe the wastage is less due, partly, to less widespread occurrence of the volatile contaminants in raw materials, and partly, to different product specifications. In the Middle Eastern countries, dust wasting is ubiquitous and extreme, though the cause is more usually chloride contamination. In South East Asia almost no process dust is wasted. While some generalizations can be made, most cement plants need to be investigated individually to establish potential application and feasibility.

Where dust is wasted, it may be up to about 15% by weight of clinker production. Thus 100,000 tons per year of dust is

not unusual for a plant in North America and Passamaquoddy Technology has worked with the World Bank to investigate a group of three plants close to Cairo, Egypt which, between them, waste more than 2,000 tons per day.

Plants which waste dust usually dispose of the material by landfilling in old quarried areas of the plant. Some dust in the U.S. is sold for agricultural purposes, for construction uses, and to the waste treatment industry (for fixation or pH adjustment)[31] though this is a relatively small proportion and will probably decrease with tighter regulation, particularly as plants increase their use of alternative fuels.

Although landfilling of CKD is not currently prohibited by environmental laws, CKD landfills have become a source of serious environmental concern. Alkaline leachate from CKD landfills can contaminate groundwater and CKD landfills can produce significant fugitive dust. Cement producers remain liable for contamination caused by CKD landfills even though the landfilling itself was properly licensed and conducted. As a result of groundwater contamination, CKD disposal sites of Lonestar Cement Company in Salt Lake City, Utah, and of Northwestern States Cement Company in Mason City, Iowa, have been placed on EPA's National Priorities List, or Superfund list as it is more commonly known.

Waste CKD disposal is of especial concern for plants which burn hazardous waste as a substitute fuel because of the potential for toxic heavy metal contamination of the waste CKD. Some 29 cement plants in the United States derive significant benefit from accepting and burning liquid and, increasingly, solid hazardous waste. Both disposal fees and the risk of heavy metal contamination would be increased by burning solid hazardous waste.

The U.S. EPA has recently instituted a moratorium on the permitting of new hazardous waste incinerators and a review of existing facilities. This review is primarily aimed at non-dedicated industrial furnaces such as cement kilns. In a recent draft strategy, the U.S. Environmental Protection Agency indicated its intention, in the short term, to use its omnibus permit authority to "impose upgraded particulate matter standards and, if necessary, additional metal emission

controls, and to impose limits on dioxin/furan emissions" for these facilities. Over the longer term the Agency intends to use its rule making authority to upgrade combustion rules still further (see Appendix M).

The U.S. Congress has also designated CKD as a special study waste under the Resource Conservation and Recovery Act. EPA's study of CKD is scheduled for completion by the end of 1993 and the industry expects the study to result in more aggressive regulation of CKD disposal.

In addition to the environmental concerns about CKD, landfilling CKD is becoming untenable from an operating cost standpoint. Estimates of direct costs for landfilling CKD range from over $8 per ton to more than $10 per ton (see Section 9.1.3). When the $3 to $14 per ton value of CKD as kiln feed[32] is added to the cost to landfill CKD, a cement plant's cost to dispose of CKD can range from $11 per ton as a low estimate to over $24 per ton.

9.2.1.3 Cement Industry Air Emissions

Cement kilns also generate acidic air emissions which, in common with many other industries, contain SO_2 and NOx. Most cement plants meet current SO_2 emission standards because the limestone used in cement manufacturing provides inherent scrubbing. However, some do not, and new or significantly modified U.S. plants are required to install BACT emission controls for SO_2 under New Source Performance Standards. Several states impose additional air emission standards on existing U.S. plants, and many European and Japanese facilities, both existing and new, are required to meet strict SO_2 standards.

Of significance is a recent unsolicited approach by EPA who, during the week of September 9, 1993, had Entropy, Inc. perform testing on the Dragon Recovery Scrubber for the express purpose of designating the technology "Maximum Achievable Control Technology" (MACT).

Also, Passamaquoddy Technology, L.P. was asked by Research Triangle Institute (P.O. Box 12194, Research Triangle Park, NC, 27709-2194) to prepare a report on the anticipated environmental and economic performance of a Recovery Scrubber

when applied model cement plants at different HCl emissions levels (see Appendix K). RTI is operating under contract to the U.S. EPA to provide technical support for development of MACT standards for HCl control from portland cement kilns.

9.2.1.4 Competition

There are few alternatives for SO_2 control for cement plants which need it. Passamaquoddy Technology knows of only two cement plants, other than Dragon, which have an SO_2 scrubber. Both are special situations and their solutions are not considered generally applicable. An earlier system installed at Dragon in 1986 involves a low cost spray dryer which injects a slurry (made from the high alkali runoff from the waste CKD landfill) into the discharge end of the kiln. This reduced SO_2 emissions by 50-60% but provides no other benefits. The system is applicable only to wet process cement plants, and was invented by Dr. Morrison. The patent rights are owned by Passamaquoddy Technology.

In the past, some cement plants have leached out the offending components (K, Na, S, Cl) from CKD. Such leaching requires large quantities of water due to the low solubility of the compounds of interest, and this method of CKD recovery has only been viable while the leaching solution could be discharged to a water course. This is no longer an environmentally acceptable procedure.

Passamaquoddy Technology has studied two systems for reclamation of CKD in Egypt, where CKD wasting can be extreme. One system, which is nearing completion, is at National Cement Company's plant at Helwan where a full-scale dust leaching system is combined with an upgrading program on two old long kilns. The technology was developed by National jointly with a German company, BKMI. Bypass dust from two precalciner kilns is washed, filtered, dried, and returned, with the long kiln ESP dust to the latter kilns. The installation has been under construction since 1985 and is due for completion mid-1993. The system will probably work satisfactorily, but the task of treating the 18,000 NM^3/day of leachate and washings from CKD renovation had not been addressed. Cost of the installation was estimated at US$45 million exclusive of water treatment.

Helwan Cement Company has been working since 1988 with Lurgi on a pilot-plant scale fluidized bed roasting system for treating bypass dust. Passamaquoddy Technology was skeptical of the system's feasibility and, indeed, it appears to have been abandoned.

Fuller Company has developed a fluidized bed technology which they have been offering to the cement industry for two or three years. To Passamaquoddy Technology's knowledge, no industrial facility has been built or is contemplated.

The only existing alternatives to landfilling CKD are its use as a neutralization agent for mine tailings, as a liming agent for agricultural land or as a stabilization agent for municipal sludge or other wastes. These disposal methods, however, cannot economically consume enough CKD either to be complete CKD disposal solutions or, effectively, to compete with the Recovery Scrubber.

The Recovery Scrubber is the only known system for CKD recovery which is in successful full-scale operation. Certainly there is no competitive technology which simultaneously and synergistically addresses both flue gas emission and process waste dust disposal while generally operating at a profit.

9.2.1.5 Status of the Recovery Scrubber in the Cement Industry

The Recovery Scrubber is expected to solve the waste CKD problem through recycling, and SO_2, HCl, particulate, and other emission problems through scrubbing. System economics are enhanced by the ability to sell potassium by-products, the potential for obtaining tipping fees for accepting waste from outside sources, and the possible avoidance of expenses for upgrading particulate collection equipment. The Dragon installation has been observed to reduce NOx nearly 19%. Tests conducted by an EPA contractor, Acurex, on a pilot-scale Recovery Scrubber indicated total removal of dioxins and furans as well as HCl from flue gas. This ability to effectively remove dioxins and furans is important for cement producers who burn, or wish to burn, waste fuels.

The Recovery Scrubber is applicable to both wet and dry

process cement plants. Wet process plants tend to produce more waste CKD and thus should see greater potential savings from reuse of the raw material. Ignoring the many environmental benefits, at wet process plants wasting CKD, a Recovery Scrubber will generally operate at a substantial profit. The smaller amount of waste CKD from dry process plants have higher concentrations of volatile contaminants and, thus, should produce more salt product from a relatively smaller installation.

There is no device available that can simultaneously recover CKD (both freshly generated and previously landfilled), scrub SO_2, HCl, NOx, particulates, and other exhaust gas pollutants, and do so at an operating profit.

9.2.2 Pulp and Paper

9.2.2.1 Background

The manufacture of paper involves the separation of wood fibers from raw wood to make pulp, followed by the heating and compression of the wood fibers to make paper. Separation of the wood fibers is accomplished either mechanically (the "groundwood" process), or chemically (generally through the "kraft" process). Most pulp mills employ the kraft process. Kraft plants include a lime kiln which produces a caustic used to reprocess sodium hydroxide as part of the pulping process.

Pulp and paper mills generally produce large volumes of acidic exhaust gases and alkaline ash. The production process also gives rise to significant amounts of total reduced sulfur ("TRS") and colored water. Kraft mills using older technology (roughly half of the total) often produce sulfuric acid.

9.2.2.2 Pulp and Paper Industry Emissions

Pulp and paper sludge constitutes 30% of all of the solid waste produced in the State of Maine each year, which is probably typical of areas with high concentrations of pulp and paper mills. While most of this volume is currently landfilled on site, existing capacity is declining and licensing of new landfills is becoming increasingly more

expensive and difficult.

During the last decade many pulp and paper producers have installed biomass boilers as a means of lowering fuel cost, meeting SO_2 emission limitations, and reducing waste volume. Such boilers are fueled with wood waste, bark, and sludge (high in wood fibers) from their water treatment plants to reduce the need for purchased energy and to reduce the volume of solid waste to be landfilled. This in turn has resulted in the production of high alkali ash.

If the mill is burning bark, the silica content of the ash may be high because of the dirt or sand accumulated by the bark as the log was dragged out of the forest. If whole trees (including leaves) are being burned, the MgO content of the ash may be elevated. Different species of trees produce ashes with different chemistry. Table 19 presents typical analyses of biomass ash in the Northeast U.S.

Table 19

Chemistry of Biomass Ash
(all figures are in weight percent)

	Typical Biomass Ash	No.1 Ash Sample	No.2 Ash Sample
SiO_2	54.0		
Al_2O_3	7.0		
Fe_2O_3	2.0		
CaO	21.0	31.7	25.0
MgO	2.5		
SO_3	1.5		
K_2O	8.0	3.0	7.3
Na_2O	2.0	0.9	2.3
Total	98.0		

The typical analysis contains a substantial percentage of silica with lesser amounts of calcium, alumina, iron, and alkalis. The two individual analyses show higher proportions of calcium and lesser amounts of alkali. A typical cement plant could use substantial quantities of this type of material if the alkali content were reduced. If this

material is slurried with CKD and renovated in the Recovery Scrubber, the soluble alkali will be removed and the resulting material will be suitable for use as a portion of cement raw materials. Dragon Products Company has been approached by several generators of ash and is currently investigating the possibilities for use of this type of material.

Some generators of biomass ash pay more per ton to dispose of biomass ash than cement companies charge for a ton of cement. In other words, in some situations, a cement plant may be paid more to take non-hazardous biomass ash as a raw material substitute than they get paid for the product (cement) that they produce, providing that the material is first processed through a Recovery Scrubber.

In the event that landfill disposal of the biomass ash is the desired option, the spent ash would be essentially free of soluble materials and of no more environmental concern than landfill disposal of limestone or sand.

9.2.2.3 Competition

Pulp and paper mills in the past have tended to use conventional lime or limestone scrubbers in instances where scrubbing is installed. While these systems are effective for SO_2 control, they simply convert gaseous pollution into solid pollution. Pulp mills usually also generate biomass ash.

9.2.2.4 Status of the Recovery Scrubber in the Pulp and Paper Industry

The Recovery Scrubber alone addresses both gaseous and solid pollution and produces an inert solid material which can be conveyed to a cement plant and consumed as raw material, or can be landfilled without the special precautions and expense attaching to special wastes. As a total solution there are no alternative technologies presently available.

9.2.3 Waste Incineration

9.2.3.1 Background

In a waste-to-energy (WTE) facility, municipal solid waste is incinerated and heat given off in the combustion process is used to produce steam which drives electric generators or is sold as process steam to an adjacent industrial consumer. Waste volume is reduced by 90% and weight by approximately 70%. Entrained particulates are collected in a baghouse or electrostatic precipitator and SO_2, HCl, and NOx when required is typically controlled with spray dryer scrubbers. A typical WTE plant costs $35-500 million to build, of which 15-25% is for pollution control equipment (excluding landfills).

9.2.3.2 WTE Industry Solid Waste

Incinerator ash is considered a special or hazardous waste depending on its chemical composition and local regulatory definitions. Currently, the primary causes of concern are alkalinity and heavy metals. Heavy metals in municipal solid waste (MSW) are concentrated in the ash and rendered more soluble by incineration. For these reasons, WTE ash must normally be disposed of in licensed, double lined, under-drained landfills, with leachate collection and treatment, and long-term monitoring. The federal government is considering new regulations concerning incinerator ash which may further increase the long-term cost of WTE ash disposal. Also, landfill capacity in some parts of the country is in critically short supply. The Recovery Scrubber is believed to have the ability to alleviate this solid waste problem.

In tests conducted by Acurex Corporation using the facilities of the Air and Energy Engineering Research Laboratory of the U.S. EPA, the supernatent solution of reacted slurry from a pilot scale Recovery Scrubber met regulatory limits for disposal and the residual solids exceeded requirements for Toxicity Characteristic Leaching Procedure (TCLP) tests. By reducing WTE ash alkalinity and heavy metal solubility, the Recovery Scrubber can potentially convert incinerator ash into benign material for landfill or, perhaps, useful products such as cement kiln feed.

Incinerator ash tends to be high in silica, iron, and alumina with CaO ranging between 0.5 and 38 percent[33]. However, potassium is between 1 and 6.6 percent, sodium is from 1 to 5 percent, and chloride is 0.1 to 1.1 percent in flyash[34]. Also, lead concentrations range from 200 ppm to over 36,600 ppm, zinc ranges from 100 ppm to over 15 percent, and cadmium, mercury, and several other heavy metals may pose problems for cement plants considering incinerator ash as a portion of their raw materials[35].

The Recovery Scrubber will remove the sulfate, potassium, and sodium contaminants in the MSW ash and capture low boiling point metals such as mercury. In addition, it is now possible to selectively remove heavy metals and chlorides by proprietary processes being developed by Passamaquoddy Technology, L.P. The metals thus removed would then be sent to a smelter as feedstock in a metals refining process, while the chlorides would be removed as by-product chlorine gas or other marketable chlorine compounds.

The "Bangor Daily News" featured an article on a local incinerator, the Penobscot Energy Recovery Company or "PERC". After spending $3 million on an application for an ash landfill, two state agencies denied the permits for the proposed landfill. A contract was eventually signed with a private landfill to dispose of the ash for $26 per ton. However, the private landfill just opened a new phase and the disposal cost for incinerator ash has increased from $26 per ton to $50 per ton[36].

Although the disposal fees for ash, both incinerator ash and biomass ash, in other areas may not be as high as the $50 per ton cited above, landfill disposal fees are increasing rapidly nationwide as landfill space becomes an ever shrinking resource. Cement kilns, with Recovery Scrubbers, can provide much needed capacity for the safe, environmentally responsible, and economical disposal of biomass ash, MSW incinerator ash, and other waste acids and/or caustics.

9.2.3.3 WTE Industry Air Emissions

In the tests conducted by Acurex, SO_2 removals in excess of 70% were obtained when using incinerator ash alone as the

scrubbing reagent. Removal efficiency increased proportionally with addition of wood ash or commercial alkali. HCl removal was greater than 98%.

Other testing conducted at the University of Maine showed 98% efficiency in SO_2 control using WTE ash alone as the scrubbing reagent and suggests some scrubbing of NOx. Particulate control should be equal to that provided in a cement kiln installation (i.e., 0.005 - 0.007 gr/SCF).

9.2.3.4 Competition

As with pulp and paper mills, the WTE industry typically uses conventional lime or limestone scrubbers in instances where scrubbing is installed. Waste incinerators have to consider the disposal of combustion ash that is either hazardous or carries a special waste designation.

The Recovery Scrubber alone addresses both gaseous and solid pollution and produces an inert solid material which will pass TCLP requirements. The ash can be conveyed to a cement plant and consumed as raw material or can be landfilled without the special precautions and expense attaching to special wastes. As a total solution there are no alternative technologies presently available.

9.2.3.5 Status of the Recovery Scrubber in the WTE Industry

Passamaquoddy Technology believes that the Recovery Scrubber can be designed to function efficiently using WTE ash as the scrubbing reagent, notwithstanding the chemical and physical differences between WTE ash, CKD, and biomass ash.

9.2.4 Other Applications

Oil-fired power generators offer a variety of opportunities. These plants are frequently used for providing peaking capacity. If such a plant has access to waste alkali such as biomass ash, there is a potential for switching to high sulfur fuel and, by reducing unit costs, for increasing the plant hours connected to load. Similar benefits could be achieved at base-load facilities from fuel cost savings.

Manufacturing processes which use wood particles (e.g., oriented strand board, medium density fiber board, and particle board) might offer substantial additional opportunities. There may be as many as 100 such plants in the U.S. Louisiana Pacific recently paid an $11 million fine (the second highest recorded) for excessive particulate emissions. The industry is also coming under pressure to control the release of volatile organic compounds (VOC). The Recovery Scrubber might prove to be the most cost-effective means of solving both the particulate and organic emission problems of these producers. In recent testing at the Dragon installation, VOC (as represented by α-pinene) removal efficiency of the Recovery Scrubber exceeded 70% (see Section 6.3.5).

It is also considered probable that specific applications will be found within the chemical industry where appropriate alkaline solid or liquid wastes occur on the same process as, or adjacent to, acidic gaseous emissions.

9.3 Current Marketing Efforts

It is anticipated that the Recovery Scrubber will be a more economical way of dealing with SO_2 emission and alkaline solid waste than methods currently employed, and that this will be a primary component of the demand for the Recovery Scrubber. Passamaquoddy Technology intends to remain focused upon marketing and process design. Employees will be added as required either to cover certain specialties such as contract management or instrumentation, or to increase our in-house knowledge of host industry process technology.

9.3.1 Cement Industry

The Recovery Scrubber, in many preliminary feasibility studies conducted for numerous cement companies, generally operates at a net annual profit. That is, the value of the products produced or expenses that may be avoided when using the Recovery Scrubber exceeds the costs of maintenance and operation of the Recovery Scrubber.

Passamaquoddy Technology has begun preliminary design (the feasibility study indicated exceptional benefits to the client) for a second Recovery Scrubber in the cement

industry. It is anticipated that this preliminary design will lead to a contract for installation in early 1994.

9.3.2 Pulp and Paper Industry

Preliminary feasibility studies for two pulp and paper mills have been completed and one application in Maine appears to have favorable economics. Discussions have also been held with five other major pulp and paper companies in the United States.

9.3.3 Waste Incineration Industry

Several feasibility studies have been completed for WTE plants and contact with several other companies involved in the waste incineration industry has been made. One waste incineration company has been working with a cement company on the possibility of using WTE ash as a component of the raw material feed to the cement company's kilns. The cement company involved suggested that a Passamaquoddy Technology Recovery Scrubber™ would probably be required to treat the WTE ash prior to use in the cement plant's kiln. The waste incineration company has made preliminary contact with Passamaquoddy Technology to investigate the possibilities of combining waste incineration, cement manufacturing, and the Recovery Scrubber in an environmentally and economically appropriate manner.

9.3.4 Other Potential Applications

Passamaquoddy Technology continues to investigate other opportunities to market the Recovery Scrubber. Preliminary discussions have been held with several utilities operating fossil fuel fired boilers and indications from recent meetings have been favorable.

The Recovery Scrubber has demonstrated great flexibility in beneficially using both solid and liquid wastes and acidic exhaust gas emissions to produce saleable by-products. Additional applications are considered quite likely in the chemical process industry and possibly in the petroleum industry.

10.0 SUMMARY AND CONCLUSIONS

10.1 Background

The U.S. DOE, Office of Fossil Energy issued a Program Opportunity Notice (PON), DE-PS01-88FE61530, in response to Pub. L. No. 100-202, "An Act Making Appropriations for the Department of the Interior and Related Agencies for the Fiscal Year Ending September 30, 1988, and for Other Purposes." This Act provided funds to conduct cost-shared Innovative Clean Coal Technology (CCT) projects to demonstrate emerging clean coal technologies that were capable of being retrofitted on existing coal burning facilities. The stated purpose of the PON was to solicit proposals to demonstrate technologies that would be capable of being commercialized in the 1990's, that would be more cost effective than current technologies, and would be capable of achieving significant reductions of SO_2 and/or NOx emissions from existing coal burning facilities.

10.2 The Passamaquoddy Tribe's Proposal

Pursuant to that PON, the Passamaquoddy Tribe, a Federally recognized Indian Tribe (which later formed Passamaquoddy Technology, L.P. to develop and market the Recovery Scrubber technology), submitted a proposal for partial funding of an exhaust gas scrubbing device to be installed at the Dragon Products Cement plant located in Thomaston, Maine.

In that proposal, the process was described as being based on the concept that waste kiln dust collected from the cement kiln contains both usable cement manufacturing raw material and unusable material (alkali metal compounds). If the alkali metals could be removed from the dust, the previously wasted CKD would be a source of kiln feedstock, and the dust disposal problem would be eliminated. Further, it was stated that by reacting a slurry of water and CKD with the acidic oxides in exhaust gas, the exhaust could be efficiently scrubbed and a potassium sulfate leachate would be preferentially generated and could be separated from the CKD slurry. This would result in reducing the alkali content of the insoluble CKD solids sufficiently to be acceptable for kiln feedstock and the exhaust gas would be scrubbed of most

of its SO_2 and some of its NOx. It was asserted that the process would provide high efficiency scrubbing, consume all of the scrubber waste solid as feedstock to the kiln, and produce highly valued by-products.

The claimed advantages the proposed process had over other scrubbing technologies were:

- The sulfur removal efficiency, at >90 percent is as good as, or better, than other scrubbers.

- The process does not require purchase of any material as scrubber reactant. CKD would be more than sufficient.

- There would be no scrubber waste sludge for disposal. All of the scrubber reactants would be reclaimed for use. The CKD solids would be used as feedstock in the cement kiln. The liquid carrying the dissolved alkali sulfates would be recovered as distilled water while the alkali sulfates would be recovered as fertilizer.

- The system could be retrofitted to existing cement plants.

- Operation of the system would provide income resulting in no net cost of operation.

The scrubbing efficiency expected, based on pilot plant testing, was over 90 percent. Also, an interesting aspect of the scrubbing was noted in that, during pilot plant testing, the SO_2 removal efficiency did not appear to decrease with increased SO_2 content of the untreated exhaust (i.e., the removal efficiency was 90.7% with 100 ppm SO_2 in the untreated inlet gas and was 90.7% with 300 ppm SO_2 in the untreated inlet gas). The expected SO_2 emissions (based on 24 hours per day and 330 operating days) after treatment in a Recovery Scrubber would be 75.86 tons per year.

10.3 Cooperative Agreement No. DE-AC22-90PC89657

The Passamaquoddy Tribe's proposal was accepted and a Cooperative Agreement was negotiate and issued December 20, 1989.

In Article I--Statement of Joint Objectives of that agreement, the technical benefits of this Cooperative Agreement were to:

- Retrofit and demonstrate a full-scale industrial scrubber and waste recovery system for a coal-burning wet process cement kiln using waste dust as the reagent.

- Accomplish a 90 to 95 percent sulfur control on high-sulfur eastern bituminous coals.

- Demonstrate that a substantial percentage of the scrubber residue is consumed as kiln feedstock.

- Produce a potentially significant commercial by-product (potassium based fertilizer).

- Demonstrate the overall technical, economic and environmental viability of the patented technology with respect to coal-burning wet process cement facilities.

10.4 Passamaquoddy Technology Recovery Scrubber™

Subsequent to the Cooperative Agreement, Passamaquoddy Technology designed and had built a Recovery Scrubber at the Dragon Products cement plant in Thomaston, Maine.

Operation during Phase III has demonstrated that the Recovery Scrubber has conclusively and successfully demonstrated all of the initial claims made in the Passamaquoddy Tribe's proposal and has also demonstrated all of the technical benefits described or anticipated in Cooperative Agreement No. DE-AC22-90PC89657.

10.4.1 Claims Made in the Tribe's Proposal

In the proposal, a claim was made that if CKD were renovated in the Recovery Scrubber it would be suitable for use as feedstock in the cement plant kiln and that CKD disposal would be eliminated. Phase III operation has demonstrated that CKD is renovated in the Recovery Scrubber may be

recycled as a portion of the cement kiln feedstock. During operation of the Recovery Scrubber, no CKD is wasted.

In the proposal, a claim was made that most of the SO_2 and some of the NOx would be removed from the exhaust gas by reactions in the Recovery Scrubber. Ensuing operation of the Recovery Scrubber during Phase III has demonstrated an average SO_2 removal efficiency of 89.2 percent and a NOx removal efficiency of nearly 19 percent.

In the proposal it was also claimed that the process would produce highly valued by-products by reacting CKD with the acidic oxides in exhaust gas and that the resultant potassium sulfate could be separated from the CKD slurry. Phase III operation has demonstrated this.

In addition, the proposal contained a list of advantages that the proposed process had over other scrubbing technologies. One advantage listed was that the SO_2 removal efficiency would be >90 percent. After some fine tuning during the latter stages of Phase III, the average SO_2 removal efficiency was demonstrated to be 94.6 percent.

Another listed advantage was that CKD would be more than sufficient as the scrubbing reagent and that no additional material would be required as a reactant. Phase III operation has demonstrated that CKD is the only reactant required for scrubbing in this process.

No generation of scrubber sludge requiring disposal was a claimed advantage. The Recovery Scrubber does not generate any waste material (or other material) requiring disposal.

An anticipated advantage of the Recovery Scrubber was that it could be retrofitted to an existing cement plant. The Recovery Scrubber was, in fact, retrofitted to the Dragon cement plant.

A final advantage claimed was that the system would provide income which would result in no net cost of operation. Phase III operation has demonstrated this (see Section 9.1).

In the proposal, an interesting aspect of pilot scale testing was noted. During pilot plant testing, the SO_2 removal

efficiency did not appear to decrease with increased SO_2 content of the untreated exhaust. During Phase III, the following information was collected:

Inlet SO_2 Range (in pounds/hour)	Average SO_2 Emissions (in pounds/hour)	Calculated Removal Efficiency (in percent)
<100	4.0	82.0
100 - 200	7.7	94.1
>200	3.6	98.5

Finally, it was claimed that, after installation of a Recovery Scrubber, the annual emissions of SO_2 (based on 24 hours per day and 330 days per year operation) would be 75.86 tons per year. Based upon the average SO_2 emissions during Phase III of 12 pounds per hour (see Table 11) and assuming the same operating time, the annual SO_2 emissions from the Dragon cement kiln would be:

$$\frac{(12 \text{ lb } SO_2/\text{Hr.})(24 \text{ hr/d})(330 \text{ d/yr})}{2{,}000 \text{ lb/T}} = \underline{\underline{47.52 \text{ tons per year}}}$$

10.4.2 Cooperative Agreement - Statement of Joint Objectives

In the Statement of Joint Objectives in the Cooperative Agreement, five technical benefits were to accrue from a successful completion of this demonstration project.

First would be to retrofit and demonstrate a full-scale industrial scrubber and waste recovery system for a coal-burning wet process cement kiln using waste dust as the reagent. Installation and operation of the Recovery Scrubber at Dragon has successfully demonstrated this benefit.

The second benefit would be to accomplish a 90 to 95 percent sulfur control on high-sulfur eastern bituminous coals. Operation has demonstrated an average SO_2 removal efficiency of 94.6 percent in the latter stages of Phase III. Frequently, during Phase III SO_2 inlet values were so low that an emission rate of 2 to 5 pounds of SO_2 resulted in calculated removal efficiencies of less than 90 percent.

When SO_2 at the inlet to the Recovery Scrubber was greater than 200 pounds per hour, the Recovery Scrubber demonstrated a removal efficiency of 98.5 percent.

Another technical benefit would be the demonstration that a substantial percentage of the scrubber residue would be consumed as kiln feedstock. During Phase III operation, substantially all of the CKD generated was renovated by the Recovery Scrubber and recycled as feedstock by the Dragon cement kiln.

The fourth technical benefit would be that the process would demonstrate the ability to produce a potentially significant commercial by-product (potassium based fertilizer). The Recovery Scrubber has consistently produced crystalline potassium sulfate that meets specifications for fertilizer. Bulk potassium sulfate fertilizer is worth about $200 per ton wholesale. Although production of pellets of potassium sulfate remains a goal of Passamaquoddy Technology, pelletized potassium sulfate fertilizer is only worth about $5 per ton more than the crystalline product consistently produced during Phase III operation.

The final technical benefit would be the demonstration of the overall technical, economic and environmental viability of the patented technology with respect to coal-burning wet process cement facilities. This technical benefit has accrued to the project as evidenced by the continued and growing interest by other cement companies (and companies in other industries) in the potential application of the Recovery Scrubber technology to their plants and processes.

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