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1990 ANNUAL TECHNICAL REPORT
FOR THE
PASSAMAQUODDY TECHNOLOGY RECOVERY SCRUBBER™
AT THE DRAGON PRODUCTS, INC. CEMENT PLANT
LOCATED IN THOMASTON, MAINE

MASTER

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TREATMENT OF CEMENT KILN DUST AND EXHAUST GAS WITH THE
PASSAMAQUODDY TECHNOLOGY RECOVERY SCRUBBER TM

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ABSTRACT

The background and process of the Passamaquoddy Technology Recovery Scrubber TM are described. The Scrubber was developed for CDN USA's Dragon Cement Plant in Thomaston, Maine and facilitates a number of process improvements.

The exhaust gas is scrubbed of SO₂ with better than 90% efficiency. The kiln dust is cleaned of alkalies and so can be returned to kiln feed instead of dumped to landfill. Potassium sulfate in commercial quantity and purity can be recovered. Distilled water is recovered which also has commercial potential. Thus, various benefits are accrued and no waste streams remain for disposal.

The process is applicable to both wet and dry process cement kilns and appears to have potential in any industry which generates acidic gaseous exhausts and/or basic solid or liquid wastes.

TREATMENT OF CEMENT KILN DUST AND EXHAUST GAS WITH THE PASSAMAQUODDY TECHNOLOGY RECOVERY SCRUBBER

Philip A. Alsop *

INTRODUCTION

I would like to begin by giving you a brief history of the Company, Passamaquoddy Technology. The Dragon cement plant in Thomaston, Maine was bought in 1983 by the Passamaquoddy Indian Tribe employing funds derived from US Government compensation for lands lost some 200 years ago. In 1988 they agreed to sell the plant to Cementos del Norte (CDN USA) which is a major Spanish cement manufacturer with existing cement distribution operations based in Boston.

During the period of Passamaquoddy ownership, considerable improvements were made to the plant both in operating efficiency and in reduced environmental emissions. One particular problem which was addressed was the wasting of kiln cyclone and baghouse dust to mitigate the high alkalies which entered with the raw materials.

Alkali levels must be controlled in cement kilns. Due to their volatility, potassium and sodium oxides accumulate and cycle through the chain section of wet kilns and the lower cyclone vessels of preheater kilns causing build-ups and operating problems, though these tend to be far more severe in the case of preheater and precalciner kilns. Furthermore, alkalies cause destructive reaction with certain concrete aggregates and they are limited by most cement specifications; for example, ASTM C150 requires $\%Na_2O + 0.66\%K_2O$ to be less than 0.60% for low alkali cements. Dragon is a 1250MT/D wet kiln plant with, typically, 2.0% total alkalies in their raw materials. Alkalies become concentrated in kiln dust and control of alkali level in clinker requires that the dust from the kiln multicyclones and baghouse, some 10% of kiln feed, be discarded. The fuel is Pennsylvania coal with up to 3% sulfur content.

Dr. Garrett Morrison, then Director of Research and Development for Dragon, conceived a scrubbing system which achieves the following:

1. The kiln dust is converted to slurry and used to scrub the kiln exhaust gas.
2. Any calcined Ca is converted by CO_2 from the gas stream back to $CaCO_3$.

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3. SO_2 in the gas stream reacts with K (and Na) in solution to give K_2SO_4 which can be separated and crystallized after allowing the remaining kiln dust to settle.
4. The heat required for evaporation is waste heat from the kiln exhaust gas.

Thus:

1. The exhaust gas is scrubbed of SO_2 with better than 90% efficiency.
2. The kiln dust is cleaned of alkalies and so can be returned to the kiln as feed.
3. K_2SO_4 in commercial quantities and purity can be recovered.
4. Distilled water is recovered from the crystallizer and this also has potential for internal use or sale.

Both laboratory scale and pilot plant systems were constructed and tested successfully. When Passamaquoddy sold Dragon cement plant, this technology was retained by the Tribe, patented*, and is now being developed by Passamaquoddy Technology L.P. The Company is owned by the Tribe. However, the project was not significantly affected by the change in ownership of the plant, and the prototype Recovery Scrubber is presently under construction at Dragon. The project is being funded jointly by the Department of Energy under their Innovative Clean Coal Technology Program, and Cementos del Norte, the new owners of Dragon Cement. Both parties instigated exhaustive independent reviews of the process before proceeding. Construction began in April 1990 under the overall project management of Passamaquoddy Technology, and commissioning is expected to commence before the end of the year.

The original motivation for the project was the reduction of production costs at a plant which, being wet process, small, and exposed to competition from imported cement, had already been closed as uneconomic by its previous owners. It was also essential to meet ever more stringent regulation of gaseous emissions and landfilling of kiln dust, as well as trying to convince the local community that their real, if in some cases contentious, concerns were being seriously and effectively addressed.

Landfilling of kiln dust is an old established practice protected, in the United States, by the Bevill amendment to

* This technology is covered by one or more patents:
U.S. Patent Nos. 4,708,855, RE.33,031 and 4,915,914
together with patents in several foreign countries.

the Resource Conservation and Recovery Act which specifically excludes the dust from regulation. This exemption was intended to be temporary, allowing time for the EPA to complete studies and report to Congress; which report is now required by 1992. There have already been legal challenges to the exemption and it is reasonable to expect regulation of the practice within the near future. It should be noted that three dust dumps have already been designated "Superfund sites".

The Department of Energy Innovative Clean Coal Technology Program was created by Congress in December 1987 specifically to identify and encourage technologies which would minimize the acidic emissions from coal burning processes and which are capable of retrofitting to existing facilities. The Clean-Air Bill passed by the US Senate in April, and still being considered by the House of Representatives, contains provisions to reduce acid rain by halving the total emissions of both SO_2 , to 8.9 million tons per year, and NO_x to 2.5 million tons per year by 2001. The Edison Electric Institute estimates the annual cost of compliance to be \$5-7 billion and the Bush Administration has estimated a cost of \$4-5 billion annually by 2005 for utilities to install scrubbers or burn only higher cost, low sulfur fuel. The prospects are particularly disastrous for the eastern coalfields of West Virginia, Indiana, Illinois, Ohio and Pennsylvania which produce predominantly high sulfur coal.

The Department of Energy report on the project states that there are approximately 250 cement kilns in the United States and Canada emitting some 230,000 tons per year of SO_2 . They consider the Recovery Scrubber to be applicable on 75% of this capacity.

In Britain, Her Majesty's Inspectorate of Pollution is initiating "integrated pollution control", a policy which aims to ensure that elimination of one waste by regulation does not simply encourage disposal in an alternative, and equally polluting, form. The EC will start to implement this process on large combustion plants in April 1991.

PROCESS BENEFITS

Scrubbers for removing SO_2 , of course, are not new. However, of the scrubbers presently used by US coal burning facilities, 90% are wet scrubbers and of these, some two thirds use a lime or limestone slurry to absorb SO_2 . The absorbents, and the water required, constitute major costs while, in conventional systems, the used absorbent together with solid reaction products must themselves be disposed of as waste. Some scrubbers mitigate this problem by generating gypsum as product.

The Passamaquoddy Technology Recovery Scrubber TM is a dramatic improvement upon existing systems in that it is designed to use only existing waste materials and itself generate no waste streams. Ideally, this can be achieved internally by a single production process but an alternative is to incorporate wastes from two or more processes to achieve a balance.

As development has progressed, and as discussions have been held with engineers from various industries, it has become apparent that the basic concept allows of considerable versatility.

The fundamental requirements are the acidic gas stream and the basic absorbent, but various other processes can take place:

1. A system is available to handle high alkali raw materials in cement production. A by-pass would still be necessary on a preheater kiln, but landfilling is eliminated, together with the quarrying costs of the material which otherwise goes to landfill.
2. Depending upon the sulfur/alkali balance, the plant can be designed to recover dust from an existing landfill.
3. In other situations the alkali may come from an industrial waste stream, or from biomass ash which is always high in potassium.
4. SO₂ is removed from exhaust gases to better than 90%. There are indications that NO_x, chlorine, and unburned hydrocarbons are also extracted, but these cannot be quantified until the Dragon plant is in operation.
5. Heavy metals (from eg. waste fuels) can be removed by dissolution and selective precipitation.
6. Particulate emissions remaining in the feed gas stream will be effectively removed.
7. K₂SO₄ is removed and can be sold as fertilizer. If both sodium and potassium are involved, the two sulfates can be crystallized separately. Potassium sulfate commands a price of about \$300 per ton, with a world market for potassium based fertilizers of 22 million tons per year.
8. Distilled water is recovered from the crystallizer and can be sold.
9. Coloured effluents from caustic leaching in pulp mills could be decolourised by adsorption onto ash particulates, or oxidized in the Reaction Tank.

10. Reduction of manufacturing costs may also result from:
 - 1 Using cheaper raw materials with otherwise unacceptable levels of alkalies, sulfur and chloride.
 - 2 Using cheaper, high sulfur fuels.
 - 3 Burning waste fuels with otherwise unacceptable contents of volatiles, including heavy metals.
 - 4 Potential for providing disposal facilities for other industries; eg. biomass ash and various acidic and caustic sludges.

It should be born in mind that these benefits are based upon various levels of practical confirmation or intuitive probability and the technology is still in the demonstration stage.

I would particularly emphasize that we are seeking to justify the process on grounds of cost effectiveness alone while there is the further, and perhaps over-riding, benefit of reducing regulated emissions and improving public acceptance of an industrial facility. The Dragon installation is calculated to have a payback period of two to three years. Other systems should fall in the range of one to ten years and this, of course, must be determined when assessing feasibility

PROCESS DESCRIPTION (Dragon system)

The process flow for a wet-process cement plant is shown in figure 1.

The Recovery Scrubber process flow as designed for Dragon is shown in figure 2. Dry baghouse dust is mixed with water (in fact, this is partly water and partly a process solution from later in the system) in the Mix Tank to form a dilute slurry and this is pumped to the Reaction Tank. The solution reactions are exothermic which heat preconditions the slurry. The kiln exhaust gas at 90-150°C is passed through a water-spray Heat Exchanger where it is cooled to below its original dew point. The cooled exhaust gas is then blown upwards through a perforated-plate (sieve tray) in the Reaction Tank to contact the slurry. Reactions occurring in the Mix Tank and Reaction Tank include:

1. The alkalies, Na and K, are taken into solution.
2. Ca from CaO , Ca(OH)_2 , and dissolved CaSO_4 reacts with CO_2 from the kiln exhaust gas and is precipitated as CaCO_3 .
3. SO_2 from the exhaust gas and SO_4^{2-} from sulfates in the kiln feed react with, predominantly, potassium, under oxidizing conditions to produce K_2SO_4 which remains in solution.

The exhaust gas, scrubbed of SO_2 , is discharged to the stack.

The reacted slurry is pumped to the first Settling Tank where the K_2SO_4 solution is separated from the thickened slurry. This slurry is pumped to a second Settling Tank with dilution in the transfer line by distilled water (from the Condenser), and make-up water if necessary, to remove most of the residual alkali sulfate. From the second Settling Tank the thickened slurry, with approximately 45-50% water, and with composition similar to kiln feed, is returned to the cement plant slurry tanks for return to the kiln.

The solution taken from the first Settling Tank is split; part going to the Mixing Tank for initial slurry preparation, and part (at 3-4% K_2SO_4) being taken to the Centrate Tank. The solution from the second Settling Tank is all returned to the Mixing Tank.

From the Centrate Tank the K_2SO_4 solution is pumped to the Crystallizer, joining this system in a high velocity recirculation loop which also incorporates a heat exchanger which recovers heat from the kiln exhaust gas quenching water. The crystallizer operates at about 40°C under vacuum and the K_2SO_4 slurry produced is pumped to a centrifuge. The resulting moist cake is conveyed to a rotating-pin pelletizer and an oil-fired, fluidized-bed dryer and the granular product is then stored in a silo prior to shipment. The process vapour from the Crystalliser is conveyed by a vacuum pump to the Condenser and the condensate is collected; part to be recycled for washing the product of the first Settling Tank while the bulk is available for other use or for sale.

Material flows into the process, therefore, are kiln exhaust gas, kiln baghouse dust, and make-up water. Outflows are scrubbed exhaust gas, raw kiln feed, potassium sulfate and distilled water. No waste is generated and none remains.

The system controls are designed so that operation of the Scrubber does not affect operation of the kiln. The Scrubber entails a significant pressure drop but this is compensated by the system fan which is operated to keep the outlet pressure of the kiln fan constant. The only other interaction is the small effect upon kiln feed composition of returning the reacted kiln dust.

PILOT PLANT

The following numerical data were derived from the pilot scale test conducted at Dragon Plant. The pilot plant was approximately 1/100 scale and used kiln exhaust gas (3500AM³/H) and kiln dust (50-100Kg/H). The only process not incorporated in the pilot plant was the crystallizer, since neither the availability of sufficient heat for evaporation, nor the practicability of continuous crystallization of

potassium sulfate were in question. Solutions from the settling tank were evaporated in the laboratory.

Figure 3 shows the chemical analysis of the dust before and after reaction in the scrubber. These results came from the pilot plant and it can be seen that both sulfur and alkali levels in the dust as returned to the kiln are acceptable. Lower levels could be achieved if required but operation would normally be tuned to the most cost effective overall efficiency. Obviously mix design would normally be altered to compensate for the returned dust.

Figure 4 shows the effect upon scrubbing efficiency of varying levels of SO_2 . Monitoring of SO_2 was conducted continuously before and after the scrubber using pulsed fluorescence analysis.

Figure 5 shows the analysis of potassium sulfate recovered from the crystallizer. This composition will vary according to the alkali proportions in any given plant. Sodium sulfate commands a lower price than potassium sulfate and, depending on the specification required, differential crystallization of the two is possible. Chloride recovery is also possible as is differential precipitation of other leached components if return to the kiln is undesirable or if they would have separate value. Certain metals are not acceptable for fertilizer use. Heavy metals not already present as insoluble oxides generally precipitate as the insoluble sulfate or carbonate in the Recovery Scrubber process and are thereby returned with the dust to kiln feed.

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Fig. 1 Flow diagram for wet-process cement plant

Fig. 3

TYPICAL KILN FEED & DUST ANALYSES (ignited basis)

	<u>Kiln Feed</u>	<u>Kiln Dust</u>	<u>Reacted Kiln Dust</u>
SiO ₂	20.9%	19.0%	20.4%
Al ₂ O ₃	5.7	3.0	3.2
Fe ₂ O ₃	2.5	1.9	2.0
CaO	64.5	59.4	64.8
MgO	3.9	4.4	4.6
SO ₃	0.2	7.5	2.8
K ₂ O	1.7	4.4	1.6
Na ₂ O	0.6	0.4	0.6
Loss on ignition	34.7	27.0	34.7
C ₃ S	61	53	76
C ₃ A	11	5	5

Fig. 4

SO₂ SCRUBBING EFFICIENCY RELATED TO INITIAL CONCENTRATION

<u>Initial SO₂ concentration</u>	<u>SO₂ removal</u>
0-100 ppm	95.1%
100-200	94.5
200-300	95.2
300-400	95.0

Fig. 5

TYPICAL ANALYSIS OF POTASSIUM SULFATE BY-PRODUCT

Major constituents

Sulfate	54.1%
Potassium	25.9
Calcium	8.7
Magnesium	4.1
Sodium	3.6
Chloride	2.2

Minor constituents

Nitrate	600ppm
Iron	172
Zinc	49
Molybdenum	21
Nitrite	21
Manganese	11
Chromium	3
Copper	3
Phosphorous	L 1000ppm
Vanadium	L 10
Nickel	L 5
Cadmium	L 2
Mercury	L 0.1

Note: L = less than

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CKD and Flue Gas Scrubbing: The Demonstration at Dragon
Products Company

Garrett L. Morrison, September 16-18, 1990
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CKD and Flue Gas Scrubbing:
The Demonstration at Dragon Products Company

Dr. Garrett L. Morrison

INTRODUCTION

Dragon Products Company is installing a process** that will recover waste cement kiln dust (CKD) as kiln feed and also scrub exhaust emissions, produce marketable by-products, allow recovery of landfilled CKD, and produce income. Construction of the equipment is expected to be completed and will begin initial operation in October, 1990. The technology was selected by the U.S. Department of Energy as part of the Innovative Clean Coal Technology Program. Design and construction of the process is jointly funded by the U.S. Department of Energy and CDN USA, owners of the cement plant.

THE CKD AND STACK EMISSIONS PROBLEM

CKD may be an environmental problem or an economic problem, either because it has been generated and landfilled previously, or because it is currently being generated and is a disposal concern.

If CKD is not returned to the kiln it is always a cost, as lost raw material and the expense of handling and disposal. The environmental impact of CKD depends on disposal practices and dust composition. Concerns center around alkalinity, trace metal or organic content, and generation of fugitive emissions or leachate.

Cement plant stack emissions depend on fuel type and burning conditions. Sulfur dioxide, nitrogen oxides, unburned hydrocarbons, and particulate are the most likely to require monitoring and control. Control of carbon dioxide may be included in that list in the future.

PROCESS BENEFITS

Installation of a process designed to address these problems is underway at Dragon Products Company in Thomaston, Maine. The process was developed at the Dragon cement plant, by Dragon personnel, to solve both the waste CKD and sulfur dioxide emission problems at the plant. It is applicable to wet or dry process cement plants and to other industries including paper and waste to energy.

CKD Reuse. The CKD from a cement plant can be processed as it is produced. Previously landfilled material can also be processed. In either case the processed material may be returned to the kiln as raw material feed.

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** Patent #Re. 33,031

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Raw Material. Raw material requirements for the cement plant are reduced by the amount of CKD returned. Also, since sulfur and aklaki are removed by the process, the options of which raw materials may be used is greatly expanded. For example, an on-site, high alkali shale, clay or sand may be used instead of a high cost purchased material.

Alkali Reduction. Soluble potassium or sodium is removed from the waste CKD as the sulfate or chloride salt. The solid alkali salts removed are recovered as salable by-product.

Sulfate. Calcium sulfate produced by the inherent scrubbing capacity of the kiln (when fuels containing sulfur are used) and present in CKD is partially dissolved and removed from the dust.

Acid Gas Scrubbing. A sulfur dioxide removal efficiency of 94+ percent was demonstrated in pilot plant operation at Dragon. Nitrogen oxides are also reduced, but the efficiency of removal will not be established until the Dragon installation is on line. Carbon dioxide is also scrubbed to some extent.

Unburned Hydrocarbons. Unburned condensible hydrocarbons are also scrubbed and made available for return to the kiln for disposal.

Heavy Metals. Heavy metals, that may build in concentration as circulating load because of reuse of all waste CKD, can be removed from the system by dissolution and selective precipitation.

Particulate Emissions. No particulate removal system is required downstream of the flue gas scrubbing. This process can be used in conjunction with existing particulate collectors to upgrade performance.

Operating Savings. Recovery of waste CKD as raw feed, avoidance of handling and environmental control expense, and production of marketable by-products produce significant savings which in most cases will exceed operation and maintenance expense.

Environmental Impact. Elimination of waste CKD handling and disposal as well as reduction of troublesome flue gas emissions are environmental benefits.

HOW THE PROCESS WORKS

Figure 1, Recovery Scrubber, Process Description, shows a schematic layout of the process components and flows.

Mix Tank. Dry CKD and water are mixed to form a dilute slurry. Make-up water is supplied, in part, from recirculated flows within the process and in part from plant water supply.

Heat Exchanger-Crystallizer. Hot flue gas is passed through a heat exchanger where heat is extracted to cool the gas and to make the heat available to the evaporator (crystallizer) for evaporation of water. The cooled and dehumidified gas is then passed to the reaction tank.

Reaction Tank. Cooled flue gas and CKD slurry are passed to the reaction tank where they are brought into contact and allowed to react. Scrubbed flue gas is then vented to the atmosphere. Reacted CKD is passed to the settling system.

Settlement System. Reacted CKD slurry is passed to the two stage settlement process where it is separated into liquid and settled solids fractions, washed with distilled water, and separated a second time. Recovered CKD is returned to the cement plant raw material preparation process. The liquid containing dissolved potassium sulfate is passed to the evaporator for recovery of the dissolved salts.

Evaporator (Crystallizer). Liquid containing dissolved alkali metal salts is passed from the first settlement stage to the crystallizer, where water is evaporated using heat recovered from the hot flue gas; alkali metal salts are precipitated. This liquid also is used as the coolant for the incoming flue gas. Water evaporated from the potassium sulfate salt solution (distilled water) is condensed for use in the dilution system.

Process Inputs and Outputs. Material flows into the process are waste CKD, exhaust gas, and make-up water. Process outputs are raw feed, alkali sulfate or chloride, distilled water, and scrubbed flue gas. There are no wastes generated.

CHEMICAL REACTIONS

Several chemical reactions, some of which are responsible for changes in the physical nature of CKD as well as the chemical nature, take place during treatment of CKD in the process.

In the mix tank basic metal oxides, created in the firing of the kiln, react with water to form hydroxides.

In the reaction tank carbon dioxide, sulfur dioxide or trioxide, and nitrogen oxides react with water to form their respective acids. Hydroxides (from the CKD) and acids (from the exhaust gas) react with each other to form a variety of soluble salts or insoluble precipitates.

Soluble salts, generally alkali sulfates and chlorides, are separated from insoluble precipitates, principally calcium carbonate, in the settlement system.

LABORATORY AND PILOT SCALE TESTING

Laboratory Tests. The process was first evaluated in a laboratory scale (1/100,000) setting. Tests were run using a slip stream from the kiln exhaust and CKD from the dust handling system. Analysis of the exit gas showed greater than 90 percent removal of sulfur dioxide. Analysis of the CKD showed that sufficient alkali and sulfate had been removed to allow the CKD to be recycled to the feed system. On the basis of the laboratory scale test results it was decided to proceed with pilot scale tests.

Pilot Scale Testing. The pilot plant (1/100 scale) was located where it could utilize both dust and flue gas from the cement plant as direct system

inputs. The intent of pilot plant testing was to verify the chemical reactions and the physical handling of the CKD, and to gather the necessary information to proceed with design of a full scale system.

The pilot plant provided for: mixing of dust with water to produce a slurry; pumping of the slurry to the reaction tank for reaction with exhaust gas; cooling of the exhaust gas and its delivery to the reaction tank for reaction with the slurry; settlement and recovery of the reacted dust; and recovery of the potassium sulfate solution for drying and analysis. The pilot plant was, therefore, a scale working model of the subsequently designed full scale system now being constructed at Dragon Products Co. in Thomaston, with one exception. Samples of the extracted potassium sulfate solution were dried in the laboratory rather than with heat derived from the exhaust gas. Since neither the availability of sufficient heat in the exhaust to perform the evaporation, nor the ability to crystallize potassium sulfate from solution on a continuous basis were in question (crystallizers are commercially available) it was decided not to undergo the significant expense to build a scale model crystallizer as part of the pilot system. Samples were extracted from the process on a regular basis and oven dried in the laboratory. In that way both quantitative and qualitative information on the efficacy of the process could be reliably obtained.

Dust Input. Dust for the pilot plant was obtained from the elevator carrying dust to the waste storage silo. In that way all cement plant process changes that could affect dust chemistry would be accurately reflected in the dust entering the scrubber process. Dust flow rate was controlled so that known levels of dilution could be obtained to evaluate a range of operating parameters for the process. Samples of input dust were taken on a regular basis for analysis and comparison with reacted material.

Input Exhaust Gas. Exhaust gas was extracted from the existing stack of the cement plant for input to the scrubbing process. A ten inch diameter pipe with three inch diameter holes every four inches along its length was placed in the stack, perpendicular to the gas flow, to extract a sample representative of the entire exhaust flow. The extracted gas flow was first cooled in a gas to liquid heat exchanger, passed through a blower to move the gas through the process, passed through a second heat exchanger to remove the heat of compression, passed through the reaction tank, and vented to the atmosphere.

The gas is cooled to below the dew point so moisture is collected in the heat exchanger. The liquid acid produced by that condensation was pumped to the mix tank where it was utilized as part of the process make-up water. The ducting in which gas moved through the process was fitted with an orifice plate for flow measurement and a manometer for measurement of the head loss imposed by the reaction tank. Gas composition is constantly monitored by the cement plant operating system. Therefore input parameters including temperature, oxygen content, sulfur dioxide and nitrogen oxide content, and flow volume were known. The output from the scrubber process was fitted with sulfur dioxide and temperature monitoring.

Pilot Plant Flow Parameters. Gas flow to the system was maintained as a constant throughout the test period. Flow of water and dust into the system were varied to produce a range of slurry concentrations,

throughput rates, and material flows. The range for each input and output parameter is listed below.

Material Input Flows

o	Gas Flow (as hot wet gas.)	2,000 CFM.
o	Dust Input, pounds per minute.	2.0 to 4.0
o	Slurry Input (Dust plus water).	1.5 to 3.7 GPM.
o	Dust, Wt. Percent in Slurry.	6.5% to 26%.

Separated Output Flows.

o	Reacted Dust Slurry (kiln Feed).	0.9 to 2.7 GPM.
o	Liquid Solution (Crystallizer feed)	0.3 to 2.8 GPM.

The amount of alkaline material present in the slurry far exceeds the stoichiometric requirement for scrubbing of sulfur dioxide, however, the scrubbing function of the process is only part of its value. It also functions to renovate CKD. Therefore, all CKD produced (and a steady feed of previously landfilled material, if desired) is fed to the process.

Material Analysis. Table 1, Solids Analysis, compares the composition of waste CKD with the composition of CKD that has been through the process and is suitable to be returned to the kiln feed system.

The potassium oxide content of reacted CKD was reduced to the level of normal raw feed (1.09%) so that return of dust will not add alkali to the total raw material mix. The sulfate content of reacted CKD has been significantly reduced, from 5.58 to 1.85. It is possible to further reduce the sulfate content in other applications, by appropriate system design, but for the Dragon installation no further reduction was necessary. Because reacted CKD is to be returned to the raw material preparation process of the cement plant, where it will be added to the flow of normal raw feed, and diluted by that flow, the resulting combination of materials is of acceptable sulfate content. Table 2, Combined Reacted CKD and Normal Raw Feed, compares the composition of normal raw material with the composition of combined reacted CKD plus normal raw material for the Dragon materials and process characteristics. Sulfate content is suitably low, and all other constituents are either the same as raw feed or easily adjusted in raw mix preparation.

The alkali sulfate salts produced by the process are potentially salable materials. In the case of potassium sulfate the value, which on the retail market is seven to eight times the value of cement on a per ton basis, will, for Dragon, exceed the combined operating and maintenance cost of system.

The world market for potassium based fertilizer is currently at about 22 million tons per year, or more than 6,000 times the expected fertilizer production from Dragon. It is, therefore, reasonable to expect to be able to effectively market all potassium production from any cement plant that could benefit by use of the process.

If CKD has a high chloride content the potassium product will be potassium chloride, rather than the sulfate, or a mixture of the two salts. The chloride salt has a value of approximately half that of the sulfate

salt. Of the 22 million ton per year market for potassium based fertilizers potassium chloride currently accounts for approximately 20 million tons.

CKD which may be rich in sodium, if processed in this system, will produce sodium sulfate or sodium chloride. Both salts are marketable at a lower value than potassium salts. If CKD contains a mixture of potassium and sodium as soluble cations it is possible to separate them, by selective crystallization, in order to maximize process economics.

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 be considered. Heavy metals, not already present as insoluble oxides, precipitate as the insoluble sulfate or the carbonate. As insoluble materials the heavy metals are separated from the liquid fraction which feeds the crystallizer to move with the bulk of reacted CKD to be returned to the cement plant as raw feed. Therefore, the crystallized solid potassium sulfate salt contains only low levels of heavy metals. Table 3, Potassium Sulfate Analyses, presents major and minor element analyses of the salts produced at Dragon.

Heavy metals returned to kiln feed will either become trace quantities in the clinker or, if sufficiently volatile, will again end up as part of the CKD. If all CKD is continually returned to the kiln there will be a circulating load of volatile materials. Recovery of volatile alkalis has been described here. Other volatile heavy metals can be similarly recovered by a process of dissolution and precipitation, and should in most cases be recovered as marketable salts.

Exhaust Gas Scrubbing. Scrubbing of flue gas allows use of higher sulfur fuels or hazardous waste fuels without the problems of emission of either gaseous or particulate wastes. The Dragon plant burns only coal or oil. There is no use of hazardous waste liquids or solids, and no use of tires. Some petroleum coke is used with coal. There is no limit on the sulfur content of coal or oil used in the kiln, only an emission limit of 103 pounds per hour of sulfur dioxide. Further, it should be noted that Dragon does not have a problem meeting the emission limit. Their current average emission of sulfur dioxide is 70 to 80 pounds per hour. Addition of the process described here is based on its return on investment not a regulatory requirement to reduce emissions.

Operation of the pilot plant included EPA Method 5 and Method 6 stack testing to measure sulfur dioxide and particulate released from the process. The kiln baghouse has a demonstrated particulate removal efficiency of 99.97 percent. The particulate emissions from the scrubber process are less than the rate from the baghouse.

Stack monitoring of sulfur dioxide was done with continuous extraction of a sample and pulsed fluorescence analysis. Monitors were used to sample the gas before and after the scrubbing step. Average scrubbing efficiency calculated by:

$$100 - \frac{\text{output SO}_2 \text{ concentration in ppm}}{\text{input SO}_2 \text{ concentration in ppm}} \times 100 = \% \text{ removed}$$

was 94.81 percent.

Data analysis was done to determine whether the initial SO₂ concentration in unscrubbed flue gas influenced the removal efficiency or if the scrubbing efficiency was independent of initial SO₂ concentration. The monitoring results were divided, by input SO₂ concentration, into 100 ppm increment groups of those having an initial SO₂ concentration of 0-100 ppm, 100-200 ppm, 200-300 ppm, etc. and the scrubbing efficiencies of each group was calculated. The results, shown in Table 4, Scrubbing Efficiency, indicate that scrubbing efficiency of the process is independent of initial SO₂ concentration over the range of concentrations evaluated.

APPLICATIONS

The process described here is applicable to wet or dry process cement plants. In dry process applications the system output slurry must be reduced in water content before it is added to kiln feed or raw mill feed.

Almost any other system, kiln or boiler, that burns fossil fuel or waste may use the process beneficially. Many of those possible applications relate to cement plants because process solids from those applications may be suitable as kiln raw material. Paper industry boilers, for example, are frequently fired by biomass fuels. Biomass ash composition may be high in potassium, calcium, and silica. If a paper mill were to use this process to scrub flue gas and recover potassium salts the remainder of the ash solids could be useful as a constituent of kiln feed.

ECONOMICS

The Dragon installation will have a short payback period. It is expected to be between two and three years. After that payback period it will generate process savings and income from sale of by-product.

Benefit is derived from avoided costs that are now paid but will not be incurred when the process is functioning.

Avoided costs include:

- Lost raw material.
- Dust handling and transport cost.
- Dust landfill cost.
- Fugitive emissions control.
- Leachate collection and treatment.
- Low sulfur fuel.

Benefit is also derived by process related income. Sale of by-product potassium sulfate and distilled water has been mentioned. Dragon may now become a disposer of wastes generated by others and charge a tipping fee for the service. Wastes that can be accommodated include acids or bases and ash from other burners. Those materials may now include alkali rich materials.

Process income includes:

- Marketing of potassium sulfate.
- Marketing of distilled water.
- Consumption of waste acids.

Consumption of waste caustic (including alkalis).
Consumption of ash residues.

There are other less quantifiable benefits that may be important at some plants. One is public awareness and public opinion of the plant. If there is concern on the part of the public about dust release or landfilling, or exhaust emissions, then elimination of the dust and scrubbing of the exhaust may be important.

Future environmental regulation may make landfilled CKD a significant liability and scrubbing of flue gas mandatory. In some cases the CKD wasted by a plant is a large quantity in relation to a plants useful quarry lifetime. Recovery of dust can, therefore, extend a plants life.

In some regulatory jurisdictions allowable levels of particulate emissions are sufficiently restrictive that no added activity or production increase is allowed. Control of not only particulate emissions from the stack, but elimination of fugitive emissions related to waste CKD may allow significant added plant activity.

Figure 1.

RECOVERY SCRUBBER - PROCESS DESCRIPTION

Table 1.

SOLIDS ANALYSIS
(Reacted Dust compared to Normal Raw Material Feed)

<u>Oxide</u>	<u>Unreacted</u> <u>Waste Kiln</u> <u>Dust</u>	<u>Reacted</u> <u>Waste Kiln</u> <u>Dust</u>
SiO ₂	14.1	11.53
Al ₂ O ₃	2.25	3.56
Fe ₂ O ₃	1.42	1.96
CaO	44.1	41.52
MgO	3.28	3.03
SO ₃	5.58	1.85
K ₂ O	3.28	1.08
Na ₂ O	0.3	0.37
Ignit.	—	—
Loss-	27.0	34.7

Table 2.

COMBINED REACTED CKD AND NORMAL RAW FEED

Oxide	Raw Material Feed	Reacted Dust Plus Raw Material
SiO ₂	13.75	13.53
Al ₂ O ₃	3.75	3.73
Fe ₂ O ₃	1.63	1.66
CaO	42.38	42.29
MgO	2.59	2.63
SO ₃	0.11	0.28
K ₂ O	1.09	1.09
Na ₂ O	0.37	0.37
Ignition Loss	34.7	34.7

Table 3.

POTASSIUM SULFATE ANALYSES
(By-Product Material)

Element	1	2	3
Calcium	10%	6.0%	4.5%
Magnesium	0.75%	6.0%	3.8%
Sulfate	38.2%	47.4%	46.6%
Potassium	19.4%	22.6%	21.2%
Sodium	2.5%	3.8%	2.4%
Phosphorous	L 0.1%	L 0.1%	L 0.1%
Chloride	0.82%	2.0%	3.8%
Nitrate	950 mg/kg	212 mg/kg	312 mg/kg
Nitrite	21 "	9 "	34 "
Iron	344 "	84 "	87 "
Vanadium	L10 "	L10 "	L10 "
Manganese	19 "	8 "	6 "
Copper	3.2 "	3.0 "	2.4 "
Zinc	140 "	4.8 "	3.2 "
Molybdenum	20 "	22 "	20 "
Cadmium	L 2 "	L 2 "	L 2 "
Chromium	3.6 "	4.0 "	2.0 "
Nickel	L 5 "	L 5 "	L 5 "
Lead	3.2 "	L 5 "	L 5 "
Mercury	L 0.1 mg/kg	L 0.1 mg/k	g L 0.1 mg/kg
Insol. Ash	30%	11%	14.3%

L = less than

Table 4.

SCRUBBING EFFICIENCY
(Percent SO₂ Removed as a Function of Initial Concentration)

Initial SO ₂ Concentration	0-100ppm	100-200ppm	200-300ppm	300-400ppm
Percent of SO ₂ Removed	95.08	94.45	95.22	95.00

EXHAUST GAS SCRUBBING AND WASTE ELIMINATION,
AN APPLICATION OF THE RECOVERY SCRUBBER TO A CEMENT KILN

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ABSTRACT

The Recovery Scrubber is an SO₂ scrubbing and waste reduction - elimination process which has been selected for demonstration under round two of the U.S. Department of Energy Innovative Clean Coal Technology Program. The process, which is expected to reduce SO₂ emissions by greater than 90%, will: utilize, and completely recover for reuse, waste cement kiln dust; produce a high valued potassium sulfate by-product, plus distilled water; and produce no solid or liquid scrubber residue. By-product income and process savings will exceed operating costs. The process will be demonstrated on a coal fired cement kiln at Dragon Products Co. Inc. in Thomaston, Maine.

Waste cement kiln dust and water are mixed in a slurry and reacted with kiln exhaust gas to provide efficient gas scrubbing. Dissolved solids and suspended solids in the reacted slurry are separated into two process streams. The dissolved solids are crystallized by using waste heat from the exhaust as the energy source for evaporation. The suspended solids, minus soluble alkali, chloride, and sulfate, are returned to the cement kiln raw material feed system for reuse in the production of cement. No waste is created or disposed by the process.

The Dragon cement plant expects to recover the total project cost in under three years. Process savings accrue due to elimination of lost raw material, and environmental control costs. Fuel savings are available by use of higher sulfur content coal. By-product income and cement plant process savings exceed scrubber process operating cost. Pilot plant operating results and the demonstration project equipment and process flows are described. Waste to energy and boiler applications are discussed briefly.

EXHAUST GAS SCRUBBING AND WASTE ELIMINATION, AN APPLICATION OF THE RECOVERY SCRUBBER TO A CEMENT KILN

INTRODUCTION

The Recovery Scrubber application discussed in this paper relates to pollution control in a cement manufacturing plant. The scrubbing process, with appropriate modifications, is applicable to virtually any fossil fuel or waste fired facility. Those applications will be discussed briefly.

This paper will present information on the operation of a cement plant as it relates to production of pollutants, followed by chemical and physical characterization of the cement plant's two major pollution streams and the reactions those materials undergo within the scrubbing process. A discussion of pilot plant operation as conducted at the Dragon Cement Co. Inc. plant in Thomaston, Maine, and results obtained utilizing those materials in the pilot plant are presented. The design of the full scale Recovery Scrubber (which is under construction at the Dragon Cement Plant) component parts and their function is discussed in light of the material characterization and the pilot plant test results.

CEMENT KILN OPERATION - BACKGROUND INFORMATION

Portland cement, the very fine, gray, powdery material used to prepare concrete as used in foundations, buildings, bridges, and roads, is manufactured from calcium and silicon compounds available in the natural environment. It is formed at high temperature in a horizontal rotary kiln.

A cement kiln is a long steel cylinder, usually about 200 to 500 feet in length, and about 14 feet in diameter. Raw material is fed into one end and ignited fuel is fed into the other. The two materials travel counter current to each other so that the raw material becomes progressively hotter and the exhaust gas becomes progressively cooler.

Manufacture of cement begins when limestone (CaCO_3) and silica sand, or clay, are mixed in proper proportions and finely ground. The mixture is then heated in the kiln, first to drive the carbon dioxide from the limestone, and then, in the hottest zone of the kiln, to cause the resulting calcium oxide and silica, from the sand or clay, to fuse. The heating of the raw material within the kiln is accomplished by allowing the coal flame to come in contact with the raw material. New chemical compounds, a variety of hydraulically active calcium silicates, are formed. The new compounds formed are termed clinker. Clinker is ground to finer than 44 microns to produce cement.

Firing of cement kilns in the United States is done primarily with coal, although oil, hazardous waste, or natural gas may be used. There is, therefore, emission of sulfur dioxide and other acid gases. The emissions, in pounds per million BTU, are somewhat lower for a cement kiln than for a boiler because the limestone raw material within the kiln acts to scrub a portion of the acid gases. The sulfur dioxide emission rate from a kiln is also highly variable, ranging from 100 ppm to over 1,500 ppm as process conditions change.

Because the coal flame and combustion gases are allowed to be in contact with the raw materials within the kiln, finely ground raw material feed is entrained in the exhaust gas stream. Particulate in the exhaust gas is removed by a bag house or electrostatic precipitator. The quantity of particulate produced may be large. In a few cases the collected fine particulate, kiln dust, may be returned to the kiln. However, in most cases the dust is not reusable because of contamination by alkali metals. The temperature in the burning zone of the kiln is high enough, around $3,000^\circ\text{F.}$, to volatilize the alkalis sodium and potassium during firing of the cement raw materials. Those metals, if present in the raw material, are carried along with the exhaust gas to the particulate collection device. In that lower temperature environment the alkalis condense on the collected particulate and cause it to be enriched in alkali metal oxides. High alkali content cannot be tolerated in the finished cement product; and so, the collected kiln dust becomes a waste and must be discarded. A cement plant, therefore, has two significant waste streams: a caustic alkali rich dust, and acidic exhaust gas. The Recovery Scrubber uses the caustic waste kiln dust and the acidic

exhaust gas as chemical reactants to provide for mutual beneficiation and production of high value by-products. In addition, waste heat contained in the exhaust gas stream is recovered and used to reduce the energy requirements of the process.

Before going into the description of the process in detail it is necessary to discuss the nature of the reactants used in the process, namely waste kiln dust, and exhaust gas from the kiln. These reactants undergo a variety of chemical reactions. Knowledge of their chemical composition and physical properties is important to understanding the Recovery Scrubber.

WASTE STREAM CHARACTERIZATION

Exhaust Gas Characterization

Exhaust gas from a cement kiln contains the normal combustion products expected from burning of coal plus additional carbon dioxide produced from calcining of the limestone present in the raw material feed to the kiln. The exhaust, therefore, has a higher CO₂ content than other fossil fuel fired systems. If the cement plant is a wet process plant, water vapor, produced by drying the raw material input, is also included in the exhaust. The composition of the flue gas generated at the Dragon plant, a wet process plant, is shown in Table 1. Exhaust temperature may exceed 3,000°F. in the burning zone of the kiln where the kiln contents are brought to the fusion point. As the gas travels the length of the kiln, its thermal energy is utilized. Calcining ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) the limestone in the feed consumes exhaust heat in the mid regions of the kiln. Similarly, gradual warming of the raw material to the calcining temperature consumes heat in the "back end" of the kiln. Drying of the raw material feed slurry at the raw material input end of the kiln consumes much of the remaining energy. Slurry is pumped into the kiln at a water content of about 30 percent by weight. All of that water is evaporated within the kiln and added to the exhaust gas stream. The gas, now cooler, passes through a cyclone dust collector where approximately 50 percent of the entrained particulate is removed and the gas is further cooled through heat loss to the outside environment. Downstream from the cyclones is the bag house where the remaining dust is separated from the exhaust. Because the entire kiln exhaust gas handling system operates at a slight negative pressure, parasitic air leaks into the bag house diluting and further

cooling the gas. The gas exiting the stack has an average temperature of 250°F.

The amount of exhaust produced is variable and dependant on a number of process related variables including temperature, fuel moisture, and process feed variation. During normal operation the gas flow rate will be 754,000 pounds per hour. The volume will be 200,000 to 225,000 cubic feet per minute.

Waste Dust Characterization

The chemical composition of waste cement kiln dust is dependant on raw feed composition, fuel sulfur and ash content, and kiln operation.

Because the dust is generated from raw material within the kiln, it consists of kiln feed in a variety of stages along the way to becoming cement. It may be fresh, unchanged feed, or material that has been calcined, or material that has been fused into cement compounds (calcium silicates). It also includes calcium sulfate or sulfite formed when limestone in the raw material feed and sulfur dioxide or sulfur trioxide in the exhaust react. One other important material is potassium. Alkali metals, which are vaporized from the raw feed in the burning zone of the kiln, and subsequently condensed in the cooler environment of the bag house, form either potassium (alkali) oxide or potassium (alkali) sulfate and are collected with the waste dust. The average composition for kiln dust from the Dragon cement plant is given in Table 2.

The average particle size of waste dust is about 9 microns. Because all raw material feed to the kiln is ground to less than 75 microns before it enters the kiln, essentially all dust generated within the kiln is initially a small size. Additionally, only the finer particle sizes are entrained in the exhaust stream and carried to the dust collection system. The production rate of kiln dust is dependant on kiln operation. When the exhaust gas volume, and therefore gas velocity, increases, dust production increases. For the Dragon kiln average production is 250 tons per day. The scrubbing system is designed to accommodate low production of zero tons per day and high production of 500 tons per day for a period of three days.

PROCESS CHEMICAL REACTIONS

There are a number of chemical reactions, and accompanying changes in form by dissolution or precipitation, occurring in the process. For purposes of this discussion the reactions are grouped into the following: exhaust gas reactions, dust reactions, and reactions between products of the former two reactions.

Exhaust Gas Reactions

Reactants	Products	Location in Process*
$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ (soluble)		Reaction Tank
$\text{H}_2\text{SO}_3 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{SO}_4$ (soluble)		Reaction Tank
$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ (soluble)		Reaction tank
*See Figure 2.		

Dust Reactions

Reactants	Products	
$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$ (soluble)		Mix Tank
$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ (insoluble)		Reaction Tank
CaSO_4 in water $\rightarrow \text{Ca}^{++} + \text{SO}_4^{=}$ (in solution)		Reaction Tank
$\text{K}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow 2\text{K}^+ + \text{SO}_4^{=}$ (in solution)		Mix Tank
$\text{K}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{KOH}$ (soluble)		Mix Tank

Reactions Between Products of

Dust Reactions and Exhaust Gas reactions

Reactants	Products	
$2 \text{KOH} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$ (soluble)		Reaction tank
$\text{Ca(OH)}_2 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O}$ (insoluble)		Reaction Tank
$\text{Ca}^{++} + \text{CO}_3^{=}$ $\rightarrow \text{CaCO}_3$ (insoluble)		Reaction tank
$2\text{K}^+ + \text{SO}_4^{=}$ $\rightarrow \text{K}_2\text{SO}_4$ (soluble)		Reaction Tank

LABORATORY AND PILOT SCALE TESTING

Lab Scale Testing

The scrubbing process was first evaluated in a laboratory scale (1/100,000) setting. The tests were run using a slip stream from the kiln exhaust and waste kiln dust from the cement plant dust handling system. Analysis of the exit gas showed greater than 90 percent scrubbing of SO_2 . Analysis of the dust composition before and after reaction showed that sufficient alkali and sulfate had been removed to allow the dust to be reused in the cement making process. On the basis of the laboratory scale test results it was decided to proceed with pilot scale tests.

Pilot Scale Testing

The pilot plant was constructed adjacent to the cement plant exhaust gas and waste dust handling systems. It was built at 1/100 scale. Figure 1., Pilot Plant, shows the pilot facility flow diagram and components.

The pilot facility provided for mixing dust, in the mixing tank, with condensate from the cooled gas plus make up water as needed. The slurry was then pumped to the reaction tank for contact with the gas to be scrubbed. Reacted material was delivered to a settling tank for separation of the solid and liquid phases. In the pilot plant the solid phase was not returned to the cement plant for use because of the small amount of material and high equipment cost to do so. It was, however, sampled for material analysis and production rate. Liquid was similarly sampled, the remainder being sent to waste rather than to a crystallizer.

Exhaust gas was extracted from the existing cement plant stack. A ten inch diameter pipe with three inch diameter holes every four inches along its length was placed in the stack, perpendicular to the gas flow, to extract a sample representative of the exhaust. The gas was cooled in a water cooled heat exchanger, compressed by a blower, passed through an additional heat exchanger, and conducted to the reaction tank. Condensate recovered from the exhaust gas in both heat exchangers was collected and pumped to the slurry mix tank for reaction with the dust feed. The gas duct was fitted with an orifice plate for flow measurement and a manometer for measurement of the head loss in the reaction tank.

The composition of the exhaust gas is constantly monitored by the cement plant for process control and environmental compliance. An additional monitor was added to the scrubber output stack to monitor the SO_2 content of the scrubbed exhaust.

Pilot Plant Flow Parameters. Gas flow to the system was maintained constant throughout the test period. Flow of water and dust into the system were varied to produce a range of slurry concentrations, throughput rates, and material flows. The range for each input and output parameter is listed below.

Material Input Flows.

o	Gas Flow (as hot, wet gas)	2,000 CFM.
o	Dust Input, pounds per minute	2.0 to 4.0
o	Slurry Input (Dust plus Water)	1.5 to 3.7 GPM.
o	Dust, Wt. Percent in Slurry	6.5% to 26%.

Separated Output Flows.

o	Reacted Dust Slurry (kiln feed)	0.9 to 2.7 GPM.
o	Liquid Solution (crystallizer feed)	0.3 to 2.8 GPM.

It should be noted that the solids content of the scrubbing slurry far exceeds the limestone solids required, on a stoichiometric basis, to accomplish scrubbing of SO_2 . However, the process provides for both scrubbing of exhaust gas and renovation of waste dust to kiln feed, and will accommodate a large excess of dust.

Material Analysis. Dust, to be used as part of cement plant raw feed, must be modified so it will not introduce excess alkali or sulfate to the normal raw feed. The intent of the process, in addition to scrubbing, is to chemically change the dust. Table 3., Solids Analysis, compares the composition of waste kiln dust produced by the cement plant, reacted waste kiln dust as produced from the Recovery Scrubber, and normal raw material feed to the cement plant.

Column (a) of Table 3. shows the increased proportion of potassium and sulfate in waste dust, compared to cement plant raw material in column (c). It is the potassium and sulfate that prevents waste dust from being reused in the kiln.

Comparing column (a), unreacted dust, with (b), reacted dust, indicates the compositional changes that occur during reaction of the dust. Silica is somewhat lower in waste dust than in kiln feed because it tends to be a larger particle size than limestone, so that less is lost from the kiln as dust. Silica also decreases because some silica is lost as finely divided particulate with the liquid fraction during solid-liquid separation. Silica serves to increase the ash content of the recovered potassium sulfate, as will be seen in the analyses of that material. In the full scale process under construction at Dragon, silica will be recovered with the settled solids because of more effective separation, and the ash content of the potassium sulfate will, therefore, be lower. Calcium is lower in the reacted material because some calcium is dissolved in the liquid

fraction containing the potassium sulfate. Magnesium, as the sulfate, is also dissolved and removed to a minor extent. Potassium undergoes a major change. It is reduced by 67 percent. The potassium remaining in the reacted material is present in insoluble silicates that are found in the raw material feed. Sulfate also undergoes a large change. It is reduced by almost 67 percent. For both potassium and sulfate the change is sufficient to allow the reacted dust to be used as raw material. It should be noted here that the removal of SO_4 from the unreacted dust is by dissolution of the calcium sulfate present and precipitation of calcium carbonate in its place.

Comparison of column (b), reacted waste kiln dust, with column (c), cement plant raw material feed, yields column (d), the difference between the two materials. Column (d) is, therefore, indicative of the suitability of reacted material for use as kiln feed. The decrease in silica content will not be present in the full scale system material. If it were, it would not be a problem because additional silica could be added to the feed material to compensate for the difference. Similarly, the decrease in CaO content can be readily compensated for by increasing the Calcium carbonate content of newly prepared raw material that is mixed with reacted waste kiln dust. The SO_3 increase is higher than desirable; however, it does not result in a problem. Because reacted dust will be added to the normal raw material feed stream, it will be diluted by about ten to one by that material. The impact of treated dust, as added to the total raw material feed is shown in Table 4, Combined Reacted Waste Dust and Raw Feed. The decrease in potassium is large enough to bring the level in the reacted material below that of the initial raw material. Alkali will, therefore, not be a problem.

Column 4 of Table 4. shows that there is no significant difference between normal raw feed and raw feed with added reacted waste kiln dust. The dust will, therefore, not cause operational or quality problems when incorporated in kiln feed.

To assure the scrubber product will not have adverse effect on clinker or cement quality a sample of the by-product kiln feed was evaluated after being burned to form clinker. It was determined to provide a better quality clinker than normal raw feed because of the small particle size and intimate mixing of lime and silica in

particles formed by agglomeration of reacted material.

Potassium Sulfate By-Product. The solution containing the soluble fraction of the reacted waste kiln dust was evaporated to dryness in order to recover the dissolved solids for analysis. Three samples of solution were collected.

Material flow rates were different for each sampling period resulting in differences in the suspended solids content of the resulting samples. Table 5., Potassium Sulfate Analyses, lists the analytical results and the average composition on an ash free basis.

Scrubbing of Sulfur Dioxide. Scrubbing of SO_2 in the reaction tank is highly efficient. The contacting of the gas and liquid phases is enhanced by bubbling the gas through the liquid rather than spraying the liquid through the gas. There is, of course an energy penalty for this method of contact. The cost is, however, more than compensated for in the overall process economics.

Stack monitoring was done with continuous extraction of a sample and pulsed fluorescence analysis of the flue gas prior to scrubbing and as the scrubbed gas exited the scrubber. The monitors were calibrated with a standard SO_2 .

Average scrubbing efficiency calculated by

$$100 - \frac{\text{output } \text{SO}_2 \text{ concentration in ppm}}{\text{input } \text{SO}_2 \text{ concentration in ppm}} \times 100 = \% \text{ removed,}$$

was 94.81 %. Data analysis was done to determine whether the initial SO_2 concentration in unscrubbed flue gas influenced the removal efficiency or if the scrubbing process was independent of initial SO_2 concentration. The monitoring results were divided, by input SO_2 concentration, into 100 ppm increment groups of those having an initial SO_2 concentration of 0-100 ppm, 100-200 ppm, 200-300 ppm, etc., and the scrubbing efficiencies calculated. The results, shown in Table 6., Scrubbing Efficiency, indicate that scrubbing efficiency of the process is independent of initial SO_2 concentration over the range of concentrations evaluated.

PROCESS DESCRIPTION

Figure 2., Recovery Scrubber- Process Description, shows the generalized layout of the process components and flows. The following discussion refers to Figure 2 and the labeled components.

Mix Tank

Dry dust from the cement plant storage silo is mixed with water in the mix tank to form a dilute slurry having 20 to 25 percent solids. The reaction is exothermic. Water is supplied from several sources. They include condensed exhaust gas moisture, rinse water from the second settling tank, distilled water condensed from the crystallizer output, and make-up water from plant water supply.

Wetted kiln dust is pozzolonic and will react and harden in much the same way as cement if allowed to do so. Therefore, the slurry is mixed in a small volume, high shear agitation tank and immediately delivered to the reaction tank. Slurry pH is 12.5. Slurry from the mix tank is pumped to the reaction tank where it is brought in contact with the cooled exhaust gas.

Reaction Tank

Several chemical reactions take place in the reaction tank. Those reactions are discussed in the previous section on "Process Chemical Reactions". One important chemical reaction is carbonation of the reactive sites on the dust so that, for example, CaO is converted to CaCO_3 . The dust is rapidly converted by carbonation from a pozzolonic to a non-pozzolonic material.

Acidic gases, including sulfur dioxide, are brought into contact with the slurry and scrubbed from the gas stream. Carbon dioxide is reacted with the dust and is dissolved in the water of the slurry. The slurry maintains an acidic pH of about 6.7. Soluble compounds in the dust are dissolved. Potassium sulfate is removed from the solid phase. Calcium sulfate, whether present as gypsum or anhydrite, is dissolved and reacted with carbon dioxide. The products formed are calcium carbonate and sulfate ion in solution. Calcium sulfate has low solubility; however, the dilute slurry and 14 hour residence time of the slurry in the reaction tank system serve to provide for solution and reaction of much of the calcium sulfate present. Calcium carbonate is more than 100 times less soluble than gypsum. Therefore, maintaining a solution which is saturated with CO_2 will assure precipitation of calcium as the carbonate if gypsum dissolves to provide calcium ion in solution. The result is that the liquid phase of the dust slurry cannot become saturated with respect to gypsum and, therefore, gypsum scaling cannot occur.

The net results of the reactions occurring in the reaction tank are:

1. Waste kiln dust is renovated. Calcium compounds are converted to original raw feed. Alkali metals are dissolved and removed. Sulfate is dissolved and removed.
2. Exhaust gas is scrubbed. The slurry of alkali and alkaline earth metal compounds is effective at removal of acid gas compounds. Those compounds become available to combine with alkali metals extracted from the waste kiln dust.

Settling Tank

From the reaction tank the slurry is pumped to the settling tank. The reacted slurry settles quickly and almost quantitatively. As calcium carbonate is formed by the reaction between dissolved calcium and CO_2 it tends to act as a cement to agglomerate smaller particles of limestone and silica into particles in the 70 to 75 micron range. Settling, therefore, provides an effective means of separating suspended solids, which are to be returned to the cement plant as raw material, from dissolved solids which are to be crystallized. As an added benefit to the cement plant, the agglomeration of calcium carbonate with silica from the dust produces a higher quality raw feed material, with more intimately mixed calcite and silica, than produced by the cement plant raw material preparation system.

Rinse And Settle

The settled solids are rinsed with distilled water to enhance removal of dissolved salts. They are then sent to another separation system for removal of water (to 70 a percent solids slurry) before returning the material to the cement plant for drying or for use as slurry.

The liquid carrying the dissolved solids, principally potassium sulfate, is pumped to the crystallizer for evaporation and recovery of the solid salts.

Heat Exchanger-Crystallizer System

The crystallizer system consists of two loops, a heat recovery loop and an evaporation loop. The heat recovery loop is a direct contact heat exchanger using water spray in the exhaust gas stream to both cool the gas before it enters the reaction tank and to recover heat for process use. The heated water output from the heat exchanger is pumped to a second non-contact heat exchanger where the recovered heat is used to provide energy to the potassium sulfate solution

process stream in the evaporation loop.

Heated water in the evaporation loop is circulated from the heat exchanger to an evaporation tank which operates at less than atmospheric pressure. Water from the process solution is evaporated to yield a salt solution sufficiently concentrated to cause formation of potassium sulfate salt crystals. The slurry of solution and crystals is constantly recirculated through the heat exchanger. A purge stream of that slurry is passed through a continuous flow centrifuge where the salt crystals are removed. The recovered crystals are then processed into pellets for sale as fertilizer. Water evaporated from the salt solution is condensed, using recirculated quarry water from the cement plant as cooling agent, and made available as distilled water for use in the process.

Process Output

The process has four output streams: kiln feed, potassium sulfate, scrubbed exhaust gas, and distilled water.

Kiln Feed. Quality control for the cement plant raw material feed is critical to cement quality. Because the kiln dust receiving treatment in the scrubber has an initial composition close to that of normal raw feed there are only two problems relating to chemical quality. The first is the presence of potassium. Alkali in cement may react with aggregate used in making concrete to produce a deleterious product. Therefore alkali is to be minimized. The second is sulfate. Sulfate is added to cement during its manufacture to provide control over the rate of setting. There is, however, a limit on the total sulfate content of the final product.

The use of kiln dust for scrubbing solves both of these concerns. Potassium is dissolved from the dust and separated from the material returned to the kiln. Sulfate is dissolved and converted to calcite (CaCO_3) to an extent sufficient to allow the combined reacted dust and normal kiln feed composition to remain below the upper limit for sulfate in the final product.

Potassium Sulfate. Potassium sulfate produced from the process may be used as an ingredient in commercial fertilizer or it may be used as raw material for the chemical industry. Product purity from the Dragon plant will be sufficient for either use. Analyses are shown in Table 5.

Scrubbed Exhaust Gas. The gas exiting the Recovery Scrubber will contain very low levels of sulfur dioxide and particulate emissions. Scrubbing is efficient, and coupled with the inherent scrubbing within the kiln, where limestone raw feed comes in contact with exhaust gas, will provide between 97 and 99 percent sulfur dioxide removal.

Distilled Water. All water used in the process is eventually passed to the evaporator for extraction of the dissolved salts. The water vapor produced is condensed and returned to the process for reuse, or made available for sale. The quality of the distilled water will be high. Total dissolved salts will be under 50 parts per million, with potassium and sulfate constituting most of that quantity. If a higher quality, laboratory grade distilled water is desired, either double distillation or use of an ion exchange column can easily upgrade this high quality starting material.

PROCESS ECONOMIC EVALUATION

The Dragon cement plant currently disposes of an average 250 tons per day of waste dust that cannot be reused in the cement making process. The 250 tons per day of waste is equivalent to 20 percent of quarry production and carries with it the materials, equipment, manpower, and energy cost for drilling, blasting, hauling, crushing, and the fine grinding necessary for use as raw feed. In addition, disposal of the waste entails additional handling, trucking, landfill operation, leachate collection, and treatment of leachate prior to discharge.

The Recovery Scrubber will reclaim all of the waste dust as raw feed. The 20 percent of kiln ready material now contaminated with alkali and lost as waste will be returned to the cement plant as kiln ready material. In addition, the effective exhaust gas scrubbing will allow use of higher sulfur content, lower cost fuel. The process will produce a valuable, marketable by-product, and eliminate the need for operation of a waste dust landfill. Savings attributable to the Recovery Scrubber will depend on price fluctuations in both the fertilizer and fuel markets, but are expected to provide Dragon a net benefit (income and savings) of between \$1.5 and \$2 million per year after deduction of operating costs.

NON-CEMENT PLANT APPLICATIONS

Sodium or potassium, present as the oxide or hydroxide, in a variety of low cost waste materials may be used to advantage in the Recovery scrubber. Two principal non-cement plant applications will be briefly discussed. They are: fossil fuel fired boilers; and waste, or waste to energy incinerators.

Fossil Fuel Fired Boilers

Flue gas from boilers fired by either coal or oil may be scrubbed by use of the process substantially as described for a cement kiln. In a boiler application boiler fly ash and biomass ash (from another source) can be mixed and substituted for kiln dust as the scrubbing reagent. Ash is available in the U.S. for scrubbing of approximately 50,000 MW of generating capacity. There may, or may not, be scrubber residue generated which will require landfill disposal, depending on the nature of the biomass ash used and the mode of scrubber operation. In many cases scrubber residue can be utilized as cement kiln feed. In most cases process income (from sale of alkali sulfate) and operating savings (by elimination or reduction of fly ash disposal costs and use of higher sulfur coal) will be greater than operating expenses.

Waste Incinerators

Waste to energy plants or waste incinerators generally require scrubbers for control of particulate and gaseous emissions. Use of waste to energy ash, or that ash in conjunction with biomass ash, can provide effective scrubbing of acid gas emissions and control of volatile organic compounds.

An added advantage of the process is treatment of waste to energy ash to render it insoluble. Waste to energy ash processed (used as scrubbing reagent) in the Recovery Scrubber will be free of soluble materials to the extent that the ash, including toxic heavy metals present, after processing, will pass the EP Toxicity test.

Use of incinerator ash as scrubbing reagent results in both lower scrubber reagent costs and lower scrubber residue and toxic ash disposal costs, so that overall operating costs are significantly decreased.

Figure 1, Pilot Plant Flow Diagram, shows the blower, heat exchangers, mix tank, reaction tank, and settling tank, with process flows as used in the pilot plant.

Figure 2, Recovery Scrubber-Process Description, shows system components and flows from kiln dust and exhaust input to kiln feed, K_2SO_4 , and scrubbed exhaust output.

Table 1

EXHAUST GAS COMPOSITION
(Dragon Cement Plant)

<u>Component</u>	<u>Percent</u>	<u>Component</u>	<u>Percent</u>
H ₂ O	13	O ₂	8
CO ₂	19	N ₂	60
SO ₂ ave. = 200 ppm		NO _x ave. = 500 ppm	

Source: Compliance testing gas analyses.

Note: Gas composition is variable, values shown are representative of testing averages or long term operating averages.

Table 2

AVERAGE KILN DUST COMPOSITION
(Dragon Cement Plant)

<u>Constituent</u>	<u>Percent</u>	<u>Constituent</u>	<u>Percent</u>
SiO ₂	14.1	MgO	3.28
Al ₂ O ₃	2.25	SO ₃	5.58
Fe ₂ O ₃	1.42	K ₂ O	3.28
CaO	44.1	Na ₂ O	0.30

Loss on Ignition* 27.0

* Loss on ignition is principally evolution of CO₂ from limestone which has not been calcined.
Source: Dragon Products Co. Inc.

Table 3.

SOLIDS ANALYSIS (Reacted Dust compared to Normal Raw Material Feed)				
<u>Oxide</u>	(a) <u>Unreacted</u> <u>Waste Kiln</u> <u>Dust</u>	(b) <u>Reacted</u> <u>Waste Kiln</u> <u>Dust</u>	(c) <u>Cement Plant</u> <u>Raw Material</u> <u>Feed</u>	(d) <u>Difference</u> <u>Between</u> <u>b & c</u>
SiO ₂	14.1	11.53	13.75	-2.22
Al ₂ O ₃	2.25	3.56	3.75	-0.19
Fe ₂ O ₃	1.42	1.96	1.63	+0.33
CaO	44.1	41.52	42.38	-0.86
MgO	3.28	3.03	2.59	+0.44
SO ₃	5.58	1.85	0.11	+1.74
K ₂ O	3.28	1.08	1.09	-0.01
Na ₂ O	0.3	0.37	0.37	0.00
Ignit.				
Loss*	27.0	34.7	34.7	0.00

* Loss on Ignition is principally evolution of CO₂ from uncalcined limestone present in the waste dust.

Table 4

COMBINED REACTED WASTE DUST AND RAW FEED
(Comparison with Normal Raw Feed)

Oxide	1 Reacted Waste Kiln Dust	2 Cement Plant Raw Material Feed	3 Combination- Reacted Dust+ Raw Material	4 Diff. Between 2 & 3
SiO ₂	11.53	13.75	13.53	-0.22
Al ₂ O ₃	3.56	3.75	3.73	-0.02
Fe ₂ O ₃	1.96	1.63	1.66	+0.03
CaO	41.52	42.38	42.29	-0.09
MgO	3.03	2.59	2.63	+0.04
SO ₃	1.85	0.11	0.28	+0.17
K ₂ O	1.08	1.09	1.09	0.00
Na ₂ O	0.37	0.37	0.37	0.00
Ignit. Loss	34.7	34.7	34.7	0.00

Table 5
POTASSIUM SULFATE ANALYSES
(By-Product Material)

Element	1	2	3	Ash Free Basis (Ave.)
Calcium	10%	6.0%	4.5%	8.8%
Magnesium	0.75%	6.0%	3.8%	4.2%
Sulfate	38.2%	47.4%	46.6%	54.6%
Potassium	19.4%	22.6%	21.2%	26.2%
Sodium	2.5%	3.8%	2.4%	3.5%
Phosphorous	L 0.1%	L 0.1%	L 0.1%	L 0.1%
Chloride	0.82%	2.0%	3.8%	2.7%
Nitrate	950 mg/kg	212 mg/kg	312 mg/kg	649 mg/kg
Nitrite	21 "	9 "	34 "	27 "
Iron	344 "	84 "	87 "	217 "
Vanadium	L10 "	L10 "	L10 "	L10 "
Manganese	19 "	8 "	6 "	14 "
Copper	3.2 "	3.0 "	2.4 "	3.6 "
Zinc	140 "	4.8 "	3.2 "	68.4 "
Molybdenum	20 "	22 "	20 "	25 "
Cadmium	L 2 "	L 2 "	L 2 "	L 2 "
Chromium	3.6 "	4.0 "	2.0 "	3.9 "
Nickel	L 5 "	L 5 "	L 5 "	L 5 "
Lead	3.2 "	L 5 "	L 5 "	L 5 "
Mercury	L 0.1 mg/kg	L 0.1 mg/kg	L 0.1 mg/kg	L 0.1mg/kg
Insol. Ash	30%	11%	14.3%	0.0%

Table 6

SCRUBBING EFFICIENCY

(Percent SO₂ Removed as a Function of Initial Concentration)

Initial SO ₂ Concentration	0-100 ppm	100-200 ppm	200-300 ppm	300-400 ppm
Percent of SO ₂ Removed	95.08	94.45	95.22	95.00

The Recovery Scrubber

a system that uses
SO₂ and CO₂ emissions
to produce sulfur and dust

Recovery Scrubber

Passamaquoddy Technology's Recovery Scrubber uses waste emissions (CO_2 and SO_2) and waste heat from a waste cement kiln dust (CKD). In the course of doing so the Recovery Scrubber is expected to:

- Convert CKD to kiln feed
- Minimize CKD disposal costs
- Produce saleable potassium
- Reduce SO_2 emissions by over 90%
- Make it easier to burn hazardous waste or high sulfur fuel
- Extend quarry and plant life
- Increase net income

The Recovery Scrubber should also yield positive public relations. Unlike other scrubbers which produce sludge that adds to landfills and CO_2 that contributes to the greenhouse effect, the Recovery Scrubber consumes CO_2 and produces no liquid or solid waste other than distilled water. An operator should thus be able to gain credit from regulatory agencies and the public not only for reducing airborne, liquid and solid pollution, but for doing so in a manner which does not create new environmental problems.

Dragon demonstration

CDN-USA, the Spanish cement consortium which is building the first full-scale Recovery Scrubber at its Dragon Products Company cement plant in Thomaston, Maine, commissioned studies by Krupp Koppers AG, the Instituto Espanol Del Cemento y Sus Aplicaciones (the Spanish Cement Institute, IECA), and the Massachusetts Institute of Technology before committing \$4.8 million for this project. The U.S. Department of Energy subjected the Scrubber to exhaustive independent review before agreeing to provide the balance of the financing for the Dragon installation under its Innovative Clean Coal Technology Program. The Recovery Scrubber was one of sixteen projects nationwide selected for such funding and the only one specifically designed for the cement industry.

The Dragon installation is expected to be operational by the fall of 1990 and performance data will be available shortly thereafter. Interested parties are invited to visit the construction site, contact the U.S. and foreign experts who have reviewed the system, and discuss with Passamaquoddy Technology staff how the Recovery Scrubber can be applied to their operations.

How the Scrubber works

The Recovery Scrubber* was invented by Dr. Garrett Morrison, a geochemist, who realized that potassium contaminants can be reacted out of CKD without risk of setting if the dust is first reconverted to limestone.

Conversion is accomplished in the Recovery Scrubber by reintroducing into CKD the CO_2 that was released during calcining. Exhaust gas from

the kiln is cooled in a heat exchanger (A) and bubbled through a reaction tank (B) containing a slurry of CKD and water. CO_2 in the gas reacts with CKD in the slurry to reclaim CKD for kiln feed, while SO_2 reacts with potassium in the CKD to form potassium sulfate in solution. Reclaimed CKD is separated in a settling tank (C), rinsed in a secondary settling tank (D) to remove potassium sulfate remnants, and returned to the cement plant as raw feed. Potassium sulfate solution is pumped to the crystallizer (E) for recovery as dry potassium sulfate. Heat for the crystallizer is obtained from the exhaust gas heat exchanger (F).

*This technology is covered by one or more patents:
U.S. Patent Nos. 4,708,855, RE.33,031 and 4,915,914.

Passamaquoddy Technology

Passamaquoddy Technology is dedicated to providing effective solutions for the environmental problems that confront heavy industry.

Our products are designed for the treatment of waste water and the control of air emissions. Our advanced air pollution control systems for the waste-to-energy, pulp, paper and chemical processing industries. Applications in these industries are designed to scrub atmospheric pollutants, eliminate the toxicity of waste ash, and produce saleable by-products without generating new wastes.

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