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Cement Kiln Flue Gas Recovery Scrubber Project: A DOE Assessment

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Executive Summary

This document is a U.S. Department of Energy (DOE) post-project assessment (PPA) of the Cement Kiln Flue Gas Recovery Scrubber project, funded in Round II of the Clean Coal Technology (CCT) Program. In December 1989, the Participant, Passamaquoddy Technology, L.P. (Ptech), entered into an agreement to conduct this study with the host and co-sponsor, Dragon Products Company, at their cement plant in Thomaston, Maine. DOE provided 34 percent of the total project funding of $17.8 million. The demonstration was conducted between August 1991 and September 1993.

The technology involves removing sulfur dioxide (SO_2) from cement kiln flue gas, using available cement kiln dust (CKD) as the sorbent. No other reagents are required, and fertilizer-grade potassium salts are recovered as a saleable by-product. The process offers energy efficiency by using flue-gas waste heat to evaporate slipstream water from the scrubber in order to recover fertilizer-grade potassium sulfate (K_2SO_4).

The performance objectives of this project were the following:

- Remove SO_2 from the flue gas at efficiencies of 90 to 95 percent, using CKD as the sole reagent.
- Recycle CKD to the kiln after its potassium content had been reduced in the scrubber.
- Use waste heat for evaporation to concentrate and crystallize the by-product K_2SO_4.

The demonstration project met or exceeded these goals. At design flue-gas flow rates, SO_2 removal efficiencies ranged from 94 percent to over 98 percent. In addition, about 25 percent of the nitrogen oxides (NO_X), 98 percent of the hydrogen chloride (HCL), and over 70 percent of the volatile organic compounds (VOCs) in the flue gas were removed. Approximately 70 percent of the potassium in the CKD was removed in the scrubber. This allowed the treated CKD (which was previously landfilled) to be recycled to the kiln, thus eliminating a major solid-waste disposal problem. Although some problems were encountered with the evaporator/crystallizer system, by the end of the project it was concluded that fertilizer-grade K_2SO_4 could be recovered and that there was sufficient waste heat from the flue gas to accomplish the recovery.

The process shows an acceptable payout period for cement manufacture, provided a tipping fee can be obtained for utilizing ash from other sources. There is great potential for use of this technology. In the United States and Puerto Rico combined, there are over 100 Portland Cement plants, operating more than 200 kilns with an average size of almost 400,000 tons/yr (U.S. Environmental Protection Agency 1999c). The scrubber is also potentially useful for a variety of other applications, such as the pulp and paper industry and waste-to-energy plants.

I Introduction

The goal of the U.S. Department of Energy's (DOE) Clean Coal Technology (CCT) program is to furnish the energy marketplace with a number of advanced, more efficient, and environmentally responsive coal-utilization technologies through demonstration projects. These projects seek to establish the commercial feasibility of the most promising advanced coal technologies that have developed beyond the proof-of-concept stage.

This document serves as a DOE post-project assessment (PPA) of the Cement Kiln Flue Gas Recovery Scrubber project in CCT Round II, as described in a Report to Congress (U.S. Department of Energy 1989). In December 1989, Passamaquoddy Technology, L.P. (Ptech), the Participant, entered into a cooperative agreement with DOE to conduct this project. DOE funded 34 percent of the total project cost of $17.8 million. The independent evaluation contained herein is based primarily on information from the Final Report (Passamaquoddy Technology, L.P. 1994), as well as other references cited.

The Passamaquoddy Technology Recovery Scrubber™ (Recovery Scrubber™) removes sulfur dioxide (SO_2) from cement-kiln flue gas by reaction with alkaline solid wastes from the kiln. Disposal of these solids, known as cement-kiln dust (CKD), has been traditionally accomplished in a landfill. Under the Clean Air Act Amendments of 1990 (CAAA), regulations have been established for airborne emissions from the Portland Cement manufacturing industry. An expectation at the inception of this project was that CKD would be classified as a hazardous waste, thereby establishing a strong regulatory driver for the technology. The Recovery Scrubber™ provided a means of meeting federal and state air-quality requirements at the Passamaquoddy Cement Plant, using CKD as the SO_2 sorbent. After potassium removal, the reaction product (treated CKD) is recycled to the kiln, thereby eliminating a solid-waste disposal problem. In addition, potassium salts recovered from the CKD are usable as fertilizer-grade potassium sulfate (K_2SO_4).

The objectives of this project were the following:

- Remove SO_2 from the flue gas at efficiencies of 90 to 95 percent, using CKD as the sole reagent.
- Recycle CKD to the kiln after its potassium content had been reduced in the scrubber.
- Use waste heat for evaporation to concentrate and crystallize the by-product K_2SO_4.

II Project/Process Description

II.A Promise of the Technology

The promise of this technology was to demonstrate, at commercial scale, the technical and economic feasibility of using the Recovery Scrubber™ to reduce airborne emissions of SO_2 from cement plants. The Recovery Scrubber™ uses a slurry of CKD, a waste product of cement manufacture, as the only scrubbing reagent. No other reagents are required, and fertilizer-grade K_2SO_4 is recovered as a saleable by-product. After potassium removal, solids from the scrubber are suitable for recycle to the cement kiln, eliminating solid-waste products requiring disposal. The only other streams leaving the process are the scrubbed flue gas and pure water. The process offers high energy efficiency using the waste-heat content of the flue gas to evaporate the scrubber water and crystallize the by-product, K_2SO_4.

II.B Project Description

The host site chosen for this CCT demonstration project was the Dragon Products Company's cement plant at Thomaston, Maine. This plant is a commercial-scale operation rated at 450,000 tons/yr of cement. Demonstration-project operations started in August 1991 and were completed in September 1993.

The kiln was fired with about 10 tons/hr of Pennsylvania bituminous coal having a sulfur content that varied from about 2.1 to 2.7 percent. Typical coal properties are given in Table 1.

II.C Technology Description

II.C.1 Cement Manufacture

Cement is produced from a mixture of minerals, the main constituent being limestone (consisting mostly of calcium carbonate ($CaCO_3$)). Other minerals that may be used in the process are clay, sand, and iron ore. Figure 1 is a schematic diagram of a typical cement plant. After grinding and mixing, the feed mixture is heated to promote certain chemical reactions and to fuse the product into clinker, which is crushed, ground, and sold. Heating takes place in a kiln, which is an elongated, refractory-lined, cylindrical vessel, elevated at one end to create a modest slope. The entire vessel rotates slowly to mix the contents. Raw material is fed at the high end, and the clinker is removed at the low end.

Table 1. Typical Coal Properties

Coal Source and Type	Pennsylvania Bituminous
Proximate Analysis, wt% (as received)	
Fixed Carbon	49.57
Volatile Matter	35.74
Moisture	5.93
Ash	8.76
Total	**100.00**
Higher Heating Value, Btu/lb (MJ/kg)	
Wet	12,800 (29.8)
Dry	13,607 (31.6)
Ultimate Analysis, wt% (dry)	
Carbon	74.99
Hydrogen	5.05
Sulfur	2.32
Chlorine	0.16
Oxygen	6.45
Nitrogen	1.72
Ash	9.31
Total	**100.00**

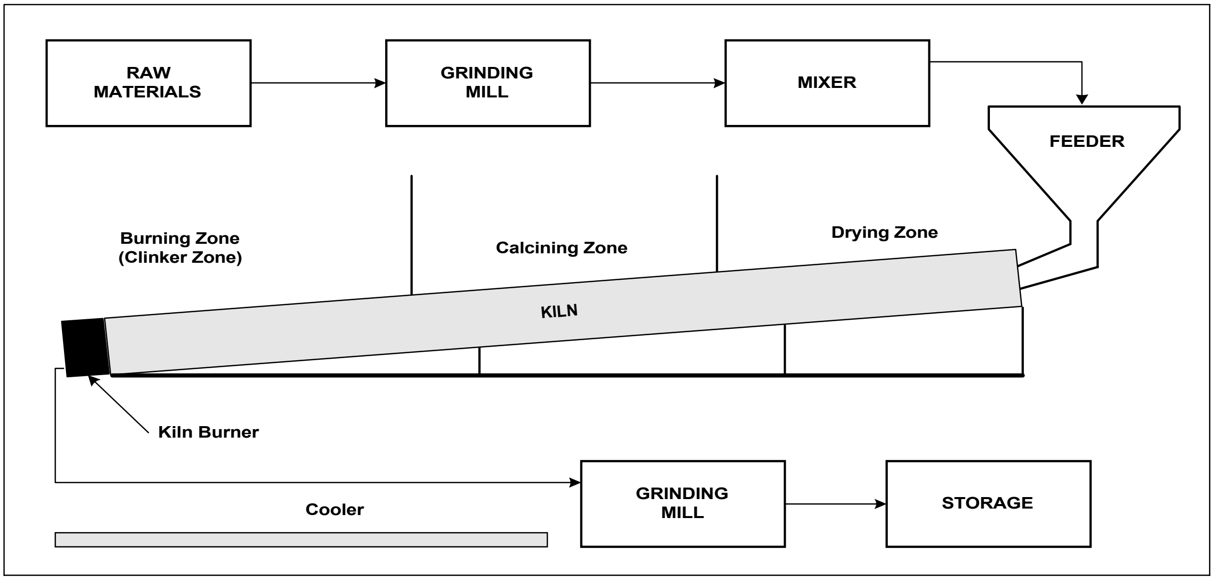

Figure 1. Schematic of a Typical Cement Plant

Cement plants are divided into two major categories, wet process and dry process, with some variations of these types, such as the semidry process. In the dry process, raw materials are milled and fed, already dry, to the kiln. In wet-process plants, water is added to the ball or tube mill during grinding to produce a pumpable slurry of about 65-percent solids, which is fed to the kiln. In the semidry process, water is added to the dry raw mix in a pelletizer to form moist pellets. They are conveyed on a moving-grate preheater, where they are dried and partially calcined before being fed to the rotary kiln.

The feed mixture, either dry or in the form of a dense aqueous slurry, is introduced into the elevated end of the kiln. Fuel for the process is combusted in a burner located at the opposite end. Fuel is typically coal or natural gas, but occasionally oil. Some kilns also fire other materials, such as solvents, waste tires, and hazardous wastes. Because of the high temperature in the kiln, fuel materials are essentially completely combusted, and any ash in these materials is incorporated into the clinker. However, kilns that burn hazardous wastes are classified as hazardous-waste burners by the Environmental Protection Agency (EPA), and are subject to more stringent regulatory requirements. (See section III.B.4.) In 1999, about 30 out of the 210 cement kilns in the United States burned hazardous waste as fuel (U.S. Environmental Protection Agency 1999a).

The combustion products pass upward through the kiln, heating the mineral feed. At the high operating temperature (about 3,000 °F) in the kiln, some of the potassium and sodium in the feed vaporizes as oxides, which then condense as a fine dust in the cooler parts of the kiln and mix with other mineral dusts. The exhaust gases exit the kiln, carrying along some of this mineral dust (CKD).

Because only limited quantities of potassium and sodium are acceptable in cement, the CKD cannot be recycled to the kiln nor incorporated into the final product. Current practice is to dispose of CKD by landfilling, frequently in an abandoned area of the limestone quarry associated with the cement plant. Annual production of CKD in 1993 in the United States was about 4.5 million tons (Abeln, et al. 1993). In 1995, the industry disposed of an estimated 3.3 million metric tons of CKD (U.S. Environmental Protection Agency 1999d). The EPA has established management standards for disposal of CKD, to be implemented at the state level. These standards require landfills to control releases of toxic metals to groundwater and to control releases of fugitive dust from the landfill and from the CKD handling and storage areas. When CKD is handled according to EPA's management standards, it is not classified as a hazardous waste. CKD is sometimes used as a soil amendment, and the standards identify concentration levels of various contaminants in the CKD used for this agricultural purpose.

Flue gas from the kiln represents another environmental problem because it contains sulfur dioxide (SO_2), nitrogen oxides (NO_X), hydrogen chloride (HCl), and volatile organic compounds (VOCs), all of which are subject to EPA regulations. The SO_2 content of the flue gas is a function of the sulfur content in the fuel and the mineral raw materials, as well as the design and operating conditions of the cement kiln. When medium- or high-sulfur coal is used as the fuel, the SO_2 content of the flue gas is likely to exceed air-quality-emission limitations. Where wet-limestone scrubbers are used to meet SO_2 emissions regulations, disposal of the resulting sludge poses another environmental problem. In addition, NO_X formed as a result of the combustion process in the kiln must meet today's more stringent emissions limitations.

II.C.2 Passamaquoddy Technology Recovery Scrubber™

The Recovery Scrubber™ was developed to meet the environmental requirements of cement kiln operation by providing a means of simultaneously removing pollutants from the flue gas and recycling CKD to the kiln, thereby eliminating the need for solid-waste disposal. Development of the Recovery Scrubber™ technology at PTech began with efforts by the Passamaquoddy Indian Tribe to solve a landfill problem at the Dragon Products Company cement plant, which the tribe owned at the time. The landfill used by Dragon was nearly full, and it was anticipated that securing permits for a new landfill would be extremely difficult. In addition, Dragon was faced with air-pollution-control regulations, promulgated by the State of Maine, that would have forced the plant to reduce its fuel sulfur content by about one-half. Lower-sulfur fuel would have been available only at a considerable premium in price.

To mitigate these problems, PTech undertook a test program to evaluate the Recovery Scrubber™ concept, beginning with laboratory-scale experiments. In these tests, a slipstream from the kiln exhaust gas was treated with CKD from the dust recovery system. The active ingredients of CKD are primarily the oxides of calcium, magnesium, and potassium. In addition, there are considerable amounts of inerts, such as silica, as well as traces of carbon resulting from incomplete fuel combustion.

Analysis of the exit gas from the laboratory-scale tests showed greater than 90-percent SO_2 removal. Based on this successful result, pilot-plant testing was conducted at a scale of about 1/100th of a commercial Recovery Scrubber™. The pilot plant simulated the proposed operation with the exception of the evaporation and crystallization steps, because the technology for these steps was thought to be well developed and would have been expensive to simulate. Performance results were sufficiently promising to justify a commercial-scale test under the CCT program.

A flowsheet of the Recovery Scrubber™ is shown in Figure 2. Flue gas from the kiln flows through the existing baghouse for removal of CKD, which is slurried with water to form a potassium-based sorbent for use in the scrubber. The hot gas exiting the baghouse is cooled from about 240 ^{o}F to 140 ^{o}F by a water quench and contacted with the CKD slurry in the scrubber (reaction tank). Potassium in the sorbent, in the form of potassium hydroxide (KOH), reacts with SO_2 to form potassium sulfite (K_2SO_3), which is then oxidized to K_2SO_4 by oxygen in the flue gas in the following reactions:

$$2KOH + SO_2 \text{ ----> } K_2SO_3 + H_2O \tag{1}$$

$$K_2SO_3 + \frac{1}{2} O_2 \text{ ----> } K_2SO_4 \tag{2}$$

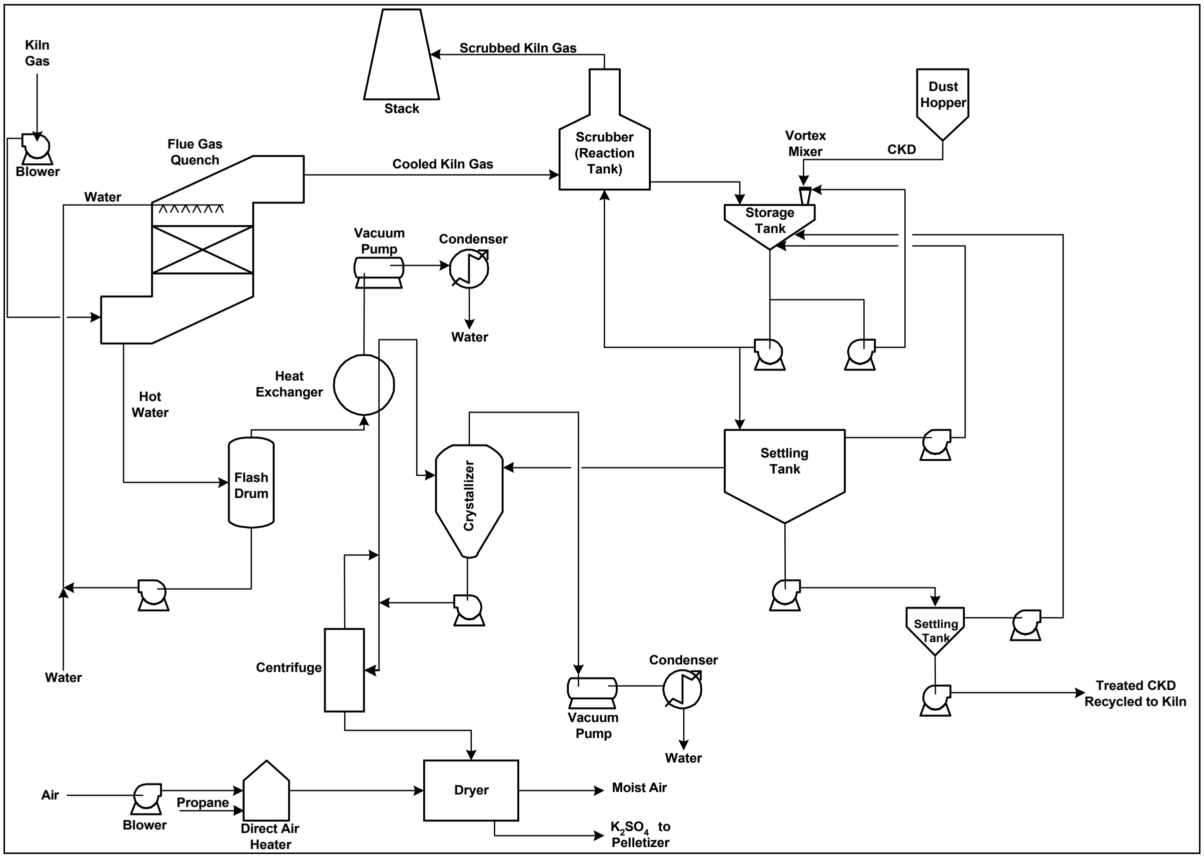

Figure 2. Passamaquoddy Technology Recovery Scrubber™

An advantage of using the potassium compounds in CKD to react with SO_2 is that K_2SO_4 is soluble in the aqueous reaction medium, thus permitting its recovery by crystallization. Removal of the potassium from the CKD as a soluble salt minimizes or eliminates the problem of potassium buildup and permits recycling the solid reaction products to the kiln, thus eliminating a solid-waste-disposal problem.

Other acid gases (HCl and carbon dioxide (CO_2)) in the flue gas are also removed in the scrubber. HCl is removed by the following reactions:

$$\mathrm{KOH} + \mathrm{HCl} \longrightarrow \mathrm{KCl} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{Ca(OH)_2} + 2\mathrm{HCl} \longrightarrow \mathrm{CaCl_2} + 2\mathrm{H_2O} \tag{4}$$

Calcium, in the form of calcium hydroxide ($Ca(OH)_2$), reacts with CO_2 to precipitate calcium carbonate ($CaCO_3$), which is recycled to the kiln along with the other solids.

$$\mathrm{Ca(OH)_2} + \mathrm{CO_2} \longrightarrow \mathrm{CaCO_3} + \mathrm{H_2O} \tag{5}$$

The slurry leaving the scrubber flows to a storage tank from which it is recycled to the scrubber. A slipstream of the recycled slurry is sent to settling tanks, where it is separated into liquid and solid fractions. The solids (treated CKD) are recycled to the kiln, and the liquid fraction is sent to the crystallizer. Hot quench water (resulting from cooling the flue gas) is flashed to produce subatmospheric-pressure 125 ^{o}F steam providing the heat required in the crystallizer. Slurry from the crystallizer is centrifuged to effect liquid/solids separation. The liquid is returned to the crystallizer, and the wet solids are sent to a dryer, where water is evaporated to recover dry alkali salts, consisting primarily of K_2SO_4. The potassium salt by-product is fertilizer-grade, suitable for sale. A vacuum pump maintains a vacuum on the crystallizer, and water vapor from the vessel is sent to a condenser. Steam from the crystallizer heat exchanger is also condensed. The recovered pure water is another by-product that can be disposed of easily or used in a variety of ways.

Under scrubber operating conditions, some kiln-gas NO_X is converted to nitric acid (HNO_3):

$$2NO_2 + \tfrac{1}{2}\ O_2 + H_2O \text{ ----> } 2HNO_3 \qquad (6)$$

Any HNO_3 formed is neutralized in the scrubber. Resulting nitrate salts end up in the fertilizer:

$$HNO_3 + KOH \text{ ----> } KNO_3 + H_2O \qquad (7)$$

$$2HNO_3 + Ca(OH)_2 \text{ ----> } Ca(NO_3)_2 + 2H_2O \qquad (8)$$

During the project's last year of operation, NO_X emissions decreased by 25 percent.

To summarize, the Recovery Scrubber™ process involves three major inputs: kiln exhaust gas, CKD, and makeup water. The outputs are scrubbed exhaust gas, treated CKD (which is recycled to the cement kiln), fertilizer-grade K_2SO_4, and pure water. There are no waste products that require disposal. Although intended primarily as an SO_2 scrubber, the Recovery Scrubber™ also serves to remove HCl and particulates, as well as part of the NO_X and VOCs.

II.D Project Objectives and Statement of Work

The objectives of this project, as stated in the cooperative agreement, were the following:

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

- Accomplish 90- to 95-percent sulfur control while firing high-sulfur bituminous coal.

- Demonstrate that a high percentage of the scrubber residue can be 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.

Thus, the goal of this project was to demonstrate the capabilities of the Recovery Scrubber™ to reduce gaseous and solid emissions from a coal-fired cement plant. The project was designed to confirm pilot-plant results and to develop scale-up procedures necessary for commercial application of the technology, as well as to resolve those technical issues that could not be adequately addressed in an engineering study or in pilot-scale tests.

The Scope of Work states that:

> *…the Participant will design, engineer, construct, operate, and test its patented Recovery Scrubber™. Major equipment and systems, other than the existing kiln facility and environmental controls, include a gas-slurry reaction tank, heat exchanger/crystallizer, waste dust and treated waste dust handling systems, mixing and settling tanks, and numerous pumps. The demonstration coal planned for testing is a high-sulfur (3.0 wt %) Pennsylvania coal. The predicted performance of the Recovery Scrubber™ is 0.2 lb of SO_2/million Btu [SO_2/MBtu], which will comply with State of Maine emissions permit limits of 0.41 lb of SO_2/million Btu [SO_2/MBtu].*

The project was conducted in three phases. Phase I: Design, Engineering, and Permitting; Phase II: Construction and Startup; and Phase III: Operation, Data Collection, and Reporting. This PPA is concerned mainly with Phase III and deals only minimally with Phases I and II. The Statement of Work for Phase III required the Participant to prepare and implement a test plan, collect and analyze data, and report both operating and environmental results. Specifically, the Participant was to do the following:

- Complete tests to determine emissions during normal operating conditions and during startup and shutdown.

- Compile data on plant operation, maintenance, reliability, and environmental performance in accordance with the Test Plan.

- Provide necessary analysis of the collected data and correlation of relevant parameters to ensure meaningful use of all information.

- Monitor operating cost, operating income and savings for assessment of overall operating economics.

III Technical and Environmental Assessment

III.A Technical Results

III.A.1 Recovery Scrubber™ Operation

The Recovery Scrubber™ was initially operated in late December 1990 and, after typical startup problems, operated until the Dragon plant was shut down for winter overhaul in February 1991. During this period, several design deficiencies were corrected, including replacing the carbon steel shell on the heat exchanger in the crystallizer with an alloy shell, replacing the rubber-lined slurry mixing tank with a vortex mixer to prevent gypsum formation, adding baffles to the absorber reaction tank to improve gas flow, improving the flatness of the sieve tray in the absorber, adding a moving spray header to wash the bottom of the sieve tray to prevent solids buildup, installation of a mesh-type mist eliminator above the reaction tank, and modification of the pelletizer.

Most of the deficiencies mentioned above had been resolved by August 20, 1991, when Phase III operation and data collection began. Between August 20, 1991, and January 14, 1992, the Recovery Scrubber™ logged in excess of 1,400 hours of operation. Most of the scrubber downtime during this period was because the cement kiln was out of operation, rather than because of problems with the scrubber. After being shut down in January 1992, the kiln did not restart until May 1992.

Between May and October 1992, the scrubber was on stream for more than 1,300 hours. Again, most of the downtime was due to problems with the kiln, not with the scrubber. The scrubber was shut down on October 1, 1992, to install a Chevron mist-eliminator system to replace the mesh type de-mister, which had shown a tendency to plug. While the scrubber was down, the cement kiln shut down for winter turnaround and, because of the poor market for cement, remained down until April 1993.

The cement kiln restarted on April 13, 1993, and between that time and September 1993, plant performance improved significantly. During this period, the scrubber operated for a total of 2,600 hours. If kiln downtimes are excluded, the scrubber had an on-stream factor of 65 percent in April, 79 percent in May, 81 percent in June, and 99 percent in July. Performance in August and September was also good. During this period, virtually all of the CKD produced by the cement kiln was treated and recycled, and the SO_2 content of the exhaust gas met or exceeded the design value.

Feed to a cement kiln tends to vary with time, producing variability in the kiln exhaust gas. Table 2 provides typical or average values for operating parameters in both the kiln and scrubber during the test period.

Table 2. Typical Operating Parameters

Cement Kiln	
Raw Material	100 ton/hr
Water in Feed Slurry	52 ton/hr
Exhaust Gas	160,000 scf/hr
Gas Temperature	245 °F
Gas Composition	
CO_2	18.9%
O_2	7.7%
H_2O	12.8%
N_2	60.6%
SO_2	132 lb/hr
Recovery Scrubber™	
Slurry Flow Through Reaction Tank	9,000 gal/min
CKD Feed Rate	10 tons/hr
Recycled CKD Flow Rate	11 tons/hr
Reaction Tank Temperature	141°F
Makeup Water Flow Rate	48 gal/min

Because it involved only post-combustion treatment of the flue gas, scrubber operation had no adverse effect on cement kiln performance. Recycling the CKD sorbent from which the potassium had been leached produced no adverse effects on kiln operation. Table 3 shows that approximately two-thirds of the potassium was removed from the CKD in the scrubber, making the material leaving the scrubber suitable for recycle to the kiln.

Table 3. Analyses of CKD Entering and Leaving the Scrubber

Component, wt%	Entering	Leaving
SiO_2	14.1	12.9
Al_2O_3	2.3	2.1
Fe_2O_3	1.4	1.3
CaO	44.1	40.0
MgO	3.3	3.0
K_2O	3.3	1.0
Na_2O	0.3	0.2
SO_3	5.6	3.7
CO_2	25.6	35.8

Operating parameters did not vary significantly from the values in Tables 2 and 3 during the test period. It was not possible, with one exception, to correlate cement kiln operating parameters, such as CKD composition or exhaust-gas rate, with scrubber performance. The one exception was SO_2 concentration in the exhaust gas, which affected scrubber SO_2 removal efficiency. (See section III.B.1.)

After some initial problems were corrected, the Recovery Scrubber™ proved to be a reliable and efficient method for removing sulfur dioxide from cement-kiln exhaust gas and for treating CKD so that it could be recycled to the kiln. This eliminates a waste-disposal problem and reduces the requirement for raw materials by almost 10 percent. Through the lessons learned from this demonstration, a new unit could be designed to be more reliable by increasing corrosion resistance through additional use of fiberglass or alloys.

III.A.2 Fertilizer Production

One major objective of this project was the removal of SO_2 from the kiln gas stream. A second objective was the recovery of fertilizer-grade potassium sulfate crystals, which was achieved in an evaporator/crystallizer system. Crystals produced in the crystallizer are recovered by removing a slipstream from the crystallizer for dewatering. Following dewatering, the crystals are pelletized for use as a fertilizer. Initially, problems were encountered because the centrifuge provided insufficient dewatering to permit pellet formation. This was a result of the presence of small amounts of syngenite (potassium calcium sulfate) and gypsum, both of which retained water. After several unsuccessful attempts to solve this problem, a hydroclone was added to the crystallizer circuit to separate the very fine gypsum and syngenite crystals from the much coarser potassium sulfate crystals.

Because of the problems with the pelletizer, bulk quantities of commercial-grade pelletized potassium sulfate were not produced during the life of this project. However, chemical analysis of by-product fertilizer produced near the end of the project indicated that the product (see Table 4) would be fully acceptable as a commercial fertilizer.

An important economic aspect of this project was that all the heat required to produce fertilizer-grade crystals should be supplied from exhaust-gas-stream waste heat. In the Recovery Scrubber™ project, about 420 lbs of water per minute needed to be evaporated. The exhaust gas stream proved to be more than adequate to supply the required heat. Excess heat was released to the atmosphere or dissipated in a cooling pond.

Table 4. Chemical Analysis of By-product Fertilizer

Analysis as Oxides	wt%
K_2O	48.5
Na_2O	0.8
CaO	1.0
SO_3	43.5
Cl	0.2
Insolubles	3.0
Water of hydration	3.0
Analysis as Compounds	
K_2SO_4	89.6
$Na_2SO_4 + 10H_2O$	4.1
$CaSO_4 + 2H_2O$	3.0
NaCl	0.3
Insolubles	3.0

III.B Environmental Performance

III.B.1 Air Emissions

The demonstration project had a beneficial impact on the environment by removing over 90 percent of theSO_2, nearly 25 percent of the NO_X, more than 95-percent of the HCl, and over 70 percent of the VOCs. These reductions enabled the cement plant to meet environmental regulations in effect at the time and, thus, continue operating.

The efficiency of SO_2 removal in the Recovery Scrubber™ depends in part on the SO_2 content of the gas exiting the kiln. The demonstration project efficiencies are summarized in Table 5.

Table 5. Sulfur Dioxide Removal Efficiency as a Function of Inlet Concentration

Scrubber Inlet SO_2, lb/hr	SO_2 Emissions, lb/hr*	Removal Efficiency, %
<100	4.0	82.0
100-200	7.7	94.1
>200	3.6	98.5

*Uncontrolled emissions were about 3.4 lb SO_2/MBtu

These data indicate that the target SO_2 removal efficiency of 90 to 95 percent was met or exceeded at inlet SO_2 flow rates above 100 lbs/hr, a rate typical of normal kiln operation. As noted in Table 5, the exit SO_2 emissions remained fairly steady regardless of the inlet concentration. This indicates that the gas leaving the scrubber reached equilibrium with the CKD slurry at all inlet SO_2 concentrations.

Some NO_X reduction resulted from conversion of NO_X to nitric acid, which was neutralized by reaction with potassium hydroxide to form potassium nitrate in the fertilizer by-product. (See section II.C.2.) NO_X emissions were reduced by an average of 18.8 percent over the entire demonstration period. NO_X removal increased to about 25 percent during the final months of operation.

Particulates emissions were very low, in the range of 0.005 to 0.007 grains/standard cubic foot. This was about 10 percent of the emissions rate allowed under EPA regulations for cement kilns at the time the project was conducted.

III.B.2 Hazardous Air Pollutants

Hazardous air pollutants (HAPs) removal efficiencies of about 98 percent for HCl and over 70 percent for VOCs were achieved in the demonstration project.

III.B.3 Pollution Prevention/Recycling

Pollution prevention minimizes environmental impacts and improves efficiency by re-engineering processes to reuse by-products. This project reduced CKD waste by recycling it to the kiln, thus providing an improved waste-management strategy. Recycling the treated CKD to the kiln eliminated about 250 tons/day of CKD landfill. Therefore, a more efficient use of natural resources was accomplished. Reuse of CKD provided economic and environmental benefits by reducing waste at its source rather than managing it at the landfill.

Another environmental benefit of the process demonstrated by this project is that the technology can be employed to reuse previously landfilled CKD by recycling it to the kiln after treatment in the Recovery Scrubber™.

III.B.4 Regulatory Developments

New regulations have been implemented or proposed since completion of the project. These new regulations will need to be considered before replication of the Recovery Scrubber™ technology.

Cement producers may include nonhazardous by-products from other industries in the raw ingredients fed to cement kilns. Examples include electric-utility fly ash, mill scale from steel making, and foundry sand from glass manufacturing. In 1999, EPA addressed emissions of HAPs from cement kilns by promulgating National Emissions Standards for Hazardous Air Pollutants (NESHAPs) for the Portland Cement manufacturing industry. The new rule is applicable for both new and existing nonhazardous waste (NHW) kilns. Under the new rule, stringent limits are set for particulate matter (a surrogate for HAPs metals), total hydrocarbons (a surrogate for organic HAPs), dioxins, furans, and opacity (U.S. Environmental Protection Agency 1999b).

The EPA also developed regulations, implemented at the state level, that provide management standards for CKD. CKD will be classified as a nonhazardous waste so long as the waste is managed according to the requirements. However, CKD becomes a regulated hazardous waste if significant violations of the management standards occur. Under the standards, CKD is to be managed in landfills designed to meet performance requirements that protect groundwater from toxic metals. A performance standard requiring facility owners and operators to take measures to prevent CKD releases from landfills, storage areas, or handling conveyances was also developed. EPA further initiated technology-based standards requiring compacting and periodic wetting of CKD in landfills; on-site handling of CKD in closed, covered vehicles; and keeping CKD in enclosed tanks, containers, and buildings prior to disposal or sale (U.S. Environmental Protection Agency 1999c).

Untreated CKD has also been used as an agricultural soil amendment to raise the pH of acid soils to a level that is appropriate for crops. It is assumed to be applied only to soils that are acidic. However, there may be an incremental risk associated with the use of CKD as a soil amendment due to some of its constituents (U.S. Environmental Protection Agency 1999e). Therefore, EPA proposed concentration limits for arsenic, cadmium, lead, thallium, dioxins, and furans when CKD is used for beneficial agricultural purposes (U.S. Environmental Protection Agency 1999c). CKD waste-management regulations regarding use of CKD on soils were developed at the state level in response to EPA's proposal. A strong environmental benefit of the Passamaquoddy Project is that potassium sulfate, a product that can easily be used as a commercial fertilizer, can be readily made as a by-product of the technology and applied to both acidic and nonacidic agricultural soils.

Cement kilns that burn hazardous waste are regulated under a separate EPA rule that covers hazardous waste generators. These kilns receive liquid hazardous wastes to burn as fuel to run their cement processes. EPA's Revised Technical Standards for Hazardous Waste Combustion Facilities (U.S. Environmental Protection Agency 1999c) are based on the maximum achievable control technology (MACT) approach required by the CAAA. MACT reflects the maximum degree of hazardous air-pollution reduction that can be achieved, considering the availability, current use, and non-air environmental impacts of emissions of dioxins, furans, mercury, semi-volatile metals (cadmium and lead), low-volatile metals (arsenic, beryllium, chromium, and antimony), particulate matter, acid gas emissions (hydrochloric acid and chlorine), hydrocarbons, and carbon monoxide.

IV Market Analysis

IV.A Market Size/Commercialization

Although the technology demonstrated in this project was applied to a wet-process cement plant, the Recovery Scrubber™ emissions control system is potentially applicable to any cement plant. To apply the technology to a dry-process cement plant, equipment would need to be added to dewater the treated CKD from the scrubber before it is recycled to the cement kiln. Incorporating the Recovery Scrubber™ technology into cement manufacture would permit use of medium- or high-sulfur coal as fuel for the kiln while eliminating a CKD solid-waste disposal problem and conserving natural resources. Many existing plants could be potential users of the Recovery Scrubber™ technology.

The technology is also potentially applicable in a number of other areas, including municipal solid-waste incinerators and the pulp and paper industry. The ash from these operations is frequently high in potassium and could be used to scrub the flue gas, recovering potassium salts for sale as fertilizer, and producing solids which could be used in cement manufacture. Some pulp and paper facilities burn biomass as a means of lowering fuel costs, meeting emission limitations, and reducing waste volume. Typical biomass ash properties are shown in Table 6. The composition of this material is such that considerable quantities could be included in the kiln feed. Of course, it would be necessary for a cement plant to be located reasonably close to the waste incinerator or paper mill to minimize transportation costs.

Table 6. Chemistry of Biomass Ash

Typical Biomass Ash	
Constituent	**Analysis, wt%**
SiO_2	54.0
Al_2O_3	7.0
Fe_2O_3	2.0
CaO	21.0
MgO	2.5
SO_3	1.5
K_2O	8.0
Na_2O	2.0
Others	2.0
Total	**100.0**

Export of the Recovery Scrubber™ technology presents another marketing opportunity, with about 100 cement plants operating in Canada and Mexico as well as about 500 plants in non-North American countries. However, to date, attempts to commercialize the Recovery Scrubber™ technology beyond the Dragon Products application have been unsuccessful. In the past, this lack of success was attributed, at least in part, to uncertainty regarding EPA's position on disposal of solid wastes from cement plants. Recent EPA regulations categorize CKD as nonhazardous, so it can be landfilled under certain conditions. Therefore, trying to meet hazardous waste-disposal regulations under the Resource Conservation and Recovery Act will not be a driving force in the application of this technology.

The Recovery Scrubber™ technology performs a needed function in removing SO_2 from kiln exhaust gas, and it achieves this goal in a cost-effective way by utilizing a waste product as the sorbent rather than requiring purchase of additional reagents. Another advantage of the Recovery Scrubber™ is the capability of reclaiming previously landfilled CKD. This provides additional benefits including:

- Savings on the cost of mining, crushing, and grinding kiln feed.
- Eliminating the cost of permitting and constructing new landfills.
- Making land previously used for CKD disposal available for other uses.
- Eliminating future environmental problems associated with landfilling.
- Extending the life of existing limestone quarries.

The scrubber used in this demonstration project has become a permanent part of the Dragon Products cement plant, where it continues to operate successfully. However, PTech is no longer in business, and efforts are underway to sell the Recovery Scrubber™ technology. PTech actively pursued marketing the Recovery Scrubber™ in cement plant applications, both in the United States and in other countries, without success. Other flue-gas-scrubbing applications were investigated, including pulp and paper manufacture and waste-to-energy plants. Another application of the Recovery Scrubber™ principle would involve reaction of acid gases with alkaline solids. In view of the many benefits resulting from use of the Recovery Scrubber™, it is difficult to see why efforts to promote this technology have been unsuccessful.

IV.B Capital Costs

The estimated capital cost for a Recovery Scrubber™, installed at a wet-process cement plant having a design capacity of 450,000 tons/yr, is $10.1 million in1990 dollars (Delta Engineering 1991). In terms of 1996 dollars, this figure becomes about $10.5 million. This is the cost to essentially duplicate the facility installed at the Dragon Products plant, but with the incorporation of all the lessons learned from the demonstration project.

IV.C Operating Costs

Operating costs consist of operating and maintenance (O&M) expenses and capital charges. The Participant estimated that the maintenance costs would be $150,000/yr. The only significant variable operating cost is electricity at $350,000/yr. The process does not use any purchased materials and does not have any waste-disposal costs. No additional operators are required to operate the scrubber. Therefore, total O&M expenses are $500,000/yr. The only other operating costs are property taxes and insurance, estimated to be 3 percent of the total capital on an annual basis, or $315,000/yr. Depreciation for a 15-year life is $700,000 per year. Total expenses, including depreciation are $1,515,000/yr.

IV.D Economics

An economic evaluation of the technology is given in Table 7. Because of the many benefits of the Recovery Scrubber™, income comes from a combination of by-product sales and operating-cost savings, as follows:

- Income of $4,000,000/yr in tipping fees. PTech estimated that up to 200,000 tons/yr of waste materials from sources such as ash (from area pulp and paper mills) could be accommodated at the Dragon Products plant, which would receive a tipping fee estimated at $20/ton. However, it needs to be noted that adding any hazardous waste materials in a cement kiln can change its regulatory category to that of a hazardous waste incinerator, with different pollution emissions requirements.

- Income of $600,000/yr from sale of fertilizer-grade K_2SO_4 at $200/ton.

- Savings of $300,000/yr from use of recycled CKD, based on fresh kiln feed valued at $5/ton and a usage rate of about 60,000 tons/yr.

- Savings of $540,000/yr from avoided cost of landfilling 60,000 tons/yr of CKD at $9/ton.

- Savings of $110,000/yr from the use of previously landfilled CKD, based on use of about 37,000 tons/yr at a credit of $3/ton.

- Savings of $190,000/yr from use of high-sulfur coal (made possible by installation of the Recovery Scrubber™) based on kiln fuel usage of 95,000 tons/yr and savings of $2/ton.

Table 7. Economics of Recovery Scrubber™ Process

Cement Plant Capacity, tons/yr	450,000		
Capacity Factor, %	85		
Capital Cost, $\$10^6$ (1996 dollars)	10.5		
Revenues and Credits	**Tons/yr**	**$/ton**	**$/yr**
Tipping fees for waste materials processed	200,000	20	4,000,000
Sale of fertilizer grade K_2SO_4	3,000	200	600,000
Recycled CKD	60,000	5	300,000
Avoided cost of landfilling CKD	60,000	9	540,000
Recovery of previously landfilled CKD	37,000	3	111,000
Fuel cost savings through use of high-sulfur coal	96,800	2	194,000
Total Income			**5,745,000**
Expenses			
Taxes and insurance @ 3%/yr			315,000
O&M costs			
Power	787 kW	$0.06/kWh	350,000
Maintenance			150,000
Depreciation			700,000
Total Expenses			**1,515,000**
Profit Before Taxes			4,230,000
Taxes @ 38%			1,607,000
Profit After Taxes			**2,623,000**
Payout Period After Taxes	3.2 years		

Based on these values, total revenues and credits are $5,745,000/yr. Then, profit before income taxes is $4,230,000/yr, and profit after taxes is $2,623,000/yr, at an assumed tax rate of 38 percent. On this basis, the simple payout period after taxes on the $10.5 million investment is 3.2 years. This represents an acceptable level of profitability. Potential users of the technology would need to compare these economics with the cost of alternatives, such as continuing existing operations while paying increased costs for landfilling CKD (based on more recent EPA requirements), burning low-sulfur coal, etc.

Another point to keep in mind when considering these economics is that many of the factors involved may vary considerably from one location to another. The major source of income in this analysis is tipping fees (nearly 70 percent of total revenues and credits), which may not be available to all plants. Also, the possibility of using reclaimed CKD and the cost differential between high- and low-sulfur coal will vary from site to site. If the tipping fee is removed, then the economics look much less favorable, with the payout period increasing to 12.5 years.

V Conclusions

The Cement Kiln Flue Gas Recovery Scrubber Project was a technical success and demonstrated the following:

- CKD can be used successfully as the sole reagent for removing SO_2 from cement kiln flue gas, with removal efficiencies of 90 percent or greater.
- Removal efficiencies for HCl and VOCs were approximately 98 percent and 70 percent, respectively.
- Particulate emissions were low, in the range of 0.005 to 0.007 grains/standard cubic foot.
- The treated CKD sorbent can be recycled to the kiln after its potassium content has been reduced in the scrubber, thereby avoiding the need for landfilling.
- The process can yield fertilizer-grade K_2SO_4, a saleable by-product.
- Waste heat in the flue gas can provide the energy required for evaporation and crystallization in the by-product recovery operation.

The demonstration program established the feasibility of using the Recovery Scrubber™ for desulfurization of flue gas from cement kilns, with generally favorable economics, assuming tipping fees are available for disposal of ash from biomass combustion. The process appears to be suitable for commercial use on any type of cement kiln. EPA has ruled that CKD is a nonhazardous waste, provided the facility meets Performance Standards for the Management of CKD (U.S. Environmental Protection Agency 1999d). Therefore, regulatory drivers for the technology focus more on reduction of air pollutants and pollution prevention, rather than on treating CKD as a hazardous waste. Application of the Recovery Scrubber™ concept to other waste-disposal operations, where pollution and waste reductions are needed, appears promising.

Abbreviations

$CaCO_3$	calcium carbonate
CO_2	carbon dioxide
$Ca(OH)_2$	calcium hydroxide
CAAA	Clean Air Act Amendments of 1990
CCT	Clean Coal Technology
CKD	cement kiln dust
DOE	Department of Energy
EPA	Environmental Protection Agency
HAPs	hazardous air pollutants
HCl	hydrogen chloride
HNO_3	nitric acid
KOH	potassium hydroxide
K_2SO_3	potassium sulfite
K_2SO_4	potassium sulfate
MACT	maximum achievable control technology
NESHAPs	National Emissions Standards for Hazardous Air Pollutants
NHW	nonhazardous waste
NO_X	nitrogen oxides
O&M	operating and maintenance
Ptech	Passamaquoddy Technology, L.P.
Recovery Scrubber™	Passamaquoddy Technology Recovery Scrubber™
PPA	post-project assessment
SO_2	sulfur dioxide
VOCs	volatile organic compounds

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