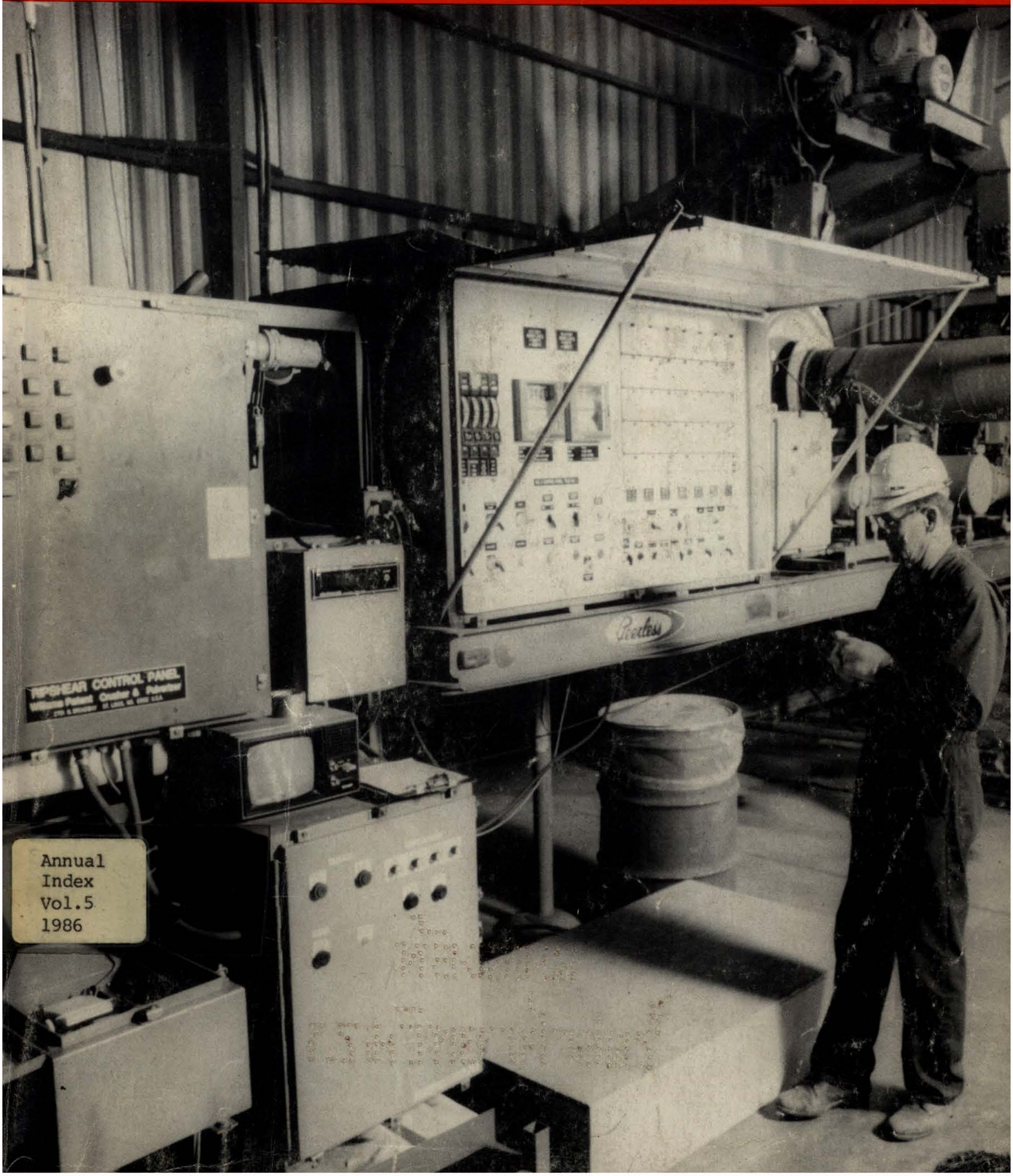
NOVEMBER 1986

ENVIRONMENTAL PROGRESS



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ENVIRONMENTAL PROGRESS

Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multi-faceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions within compliance standards. Papers will cover all aspects including water, air, liquid and solid wastes. Progress and technological advances vital to the environmental engineer will be reported.

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Publication Office, 215 Canal Street, Manchester, N.H. Published quarterly by the American Institute of Chemical Engineers, 345 East 47 St., New York, N.Y. 10017. (ISSN 0278-4491). Manuscripts should be submitted to the Manuscript Center, American Institute of Chemical Engineers, 345 East 47 St., New York, N.Y. 10017. Statements and opinions in *Environmental Progress* are those of the contributors, and the American Institute of Chemical Engineers assumes no responsibility for them. Subscription price per year: $50. Outside the U.S. please add $5 per subscription for postage and handling. Single copies $18. Outside the U.S. please add $2 for postage and handling. Payment must be made in U.S. dollars. Second-class postage paid at New York, N.Y. and additional mailing offices.

Volume 5 **Contents** Number 4

Cover: Toxic Waste Incinerator. ©1986 John Zonier/Poter Arnold Inc.

Environmental Progress fee code: 0278-4491/86 $2.00. Postmaster: Please send change of addresses to *Environmental Progress*, AIChE, 345 East 47 Street, New York, N.Y. 10017.

Offensive Environmental Chemical Engineering Education*

Louis J. Thibodeaux

The popular and image-saving excuse, used by members of the CPI when confronted with the legacy of the environmental problem, is: "We didn't think it was a problem or having an effect." Hindsight is perfect and it is now clear that we did not think. We did not do very much thinking about our chemical wastes nor our potentially harmful chemical products and their interaction with the natural environment. Although we do not like to admit we are non-thinkers in this regard, it is not the only root cause. I wish to explore in this editorial what I think are a few of the causes of the problem fostered by the education process chemical engineers undergo.

Chemistry is a very broad subject area. Chemical Engineering on the other hand is defined very narrowly. We have traditionally been associated with those aspects of chemistry that have to do with the bulk manufacturing and refinement of large quantities of chemical substances. Although the basic educational requirements for chemical engineers are broad, the focus of applied activities and values are very narrow. The traditional attitude has been to focus exclusively on the product and the process as though the chemical plant was disconnected from the natural environment. "As soon as a traditionally educated chemical engineer climbs over the factory fence or passes beyond the end of the effluent pipe, he finds himself in a world which is far removed from the ideal, deterministic world he is familiar with" [*1*].

Our waste problem, and to a degree even pollution control, has been viewed as someone else's prime activity but not ours. (def. *pollution control:* Chemical engineering unit operations designed and controlled to remove chemical residues from air, water and solids before being placed back into the natural environment.) Our application of science has been two-tongued. We have been extremely clever and knowledgeable in manipulating physical and chemical principles to fashion useful substances in reactors and separation devices. Was it our conservatism and inward looking view of chemical engineering that caused us to not think about whether these same processes would occur in the natural environment? Specifically refer to the processes of fate and transport. (def. *fate and transport in the natural environment:* coupled processes that transform and mobilize chemicals in the air water and soil subsets of the ecosystem.) As a profession we have moved fairly easily into the area of pollution control since it was a natural extension of things we were comfortable in doing. Pollution control is essentially chemical separation processes aimed at removing residues. We are coming to grips with the fate and transport aspects of chemical engineering more cautiously. One reason for our reluctance is that we did not design, nor can we effectively control, this chemical processing system.

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*Extracted from Inaugural Lecture entitled "Offensive Environmental Chemical Engineering," on the occasion of appointment as Professor of Chemical Engineering, L.S.U. Baton Rouge, LA, Dec. 6, 1985.

The aspect of education and training of undergraduate and graduate students needs to be addressed. Undergraduate curricula changes in chemical engineering departments at U.S. universities have a time constant of at least 50 years. It is a conservative institution that reflects the narrow needs of the chemical process industries and is severely constrained by the professional organization (AIChE) and the accrediting agency (ABET). Students are still being produced with the old attitudes about what the profession entails and oftentimes without pollution control experiences, much less knowledge of fate and transport concepts concerning chemicals in the natural environment. "It is important to influence the way in which chemical engineers consider the environment, and it is often too late to do so after a conventional degree has hardened specific attitudes" [*1*].

The general lack of a good scientific/engineering data base and experienced professionals working in the area was a major contributor to our defensive stance. The CPI was not prepared to effectively counter many of the "sky is falling" predications about chemicals in the environment. An important contribution to this is the lack of data and knowledge. "In the absence of sufficient scientific data, decisions affecting environmental laws are based on socially perceived problems, rather than on the scientifically documented evidence" [*4*]. Apparently little progress has been made in this area since 1970. Jefcoat (1985) [3] has recently completed a survey of industry and university research in the environmental area. He finds that over the past decade there has been a dramatic decrease in environmental research activity involving chemical engineering principles as measured by the number of active projects reported.

Finally some attention must be devoted to placing limits on the nature of the involvement of the chemical engineer with chemicals in the natural environment. Knowing all things concerned with chemicals in the natural environment is beyond the capabilities of even the chemical engineer. The nature of this involvement should be in line with the existing and unique capabilities of the profession. Chemical engineers are unique in applying physicochemical principles to the transport and transformation of chemical species. These talents, when focused on the mechanisms of chemical fate and transport in the natural environment, will fill a void that presently exists. No other profession can bring such a high-level scientific and engineering know-how to this important area. No other profession has a vested interest to the degree we have in this area.

Daniels (1982) [2] notes that, with increasing concern for trace chemicals and their potential impact on human health and the environment, the chemical engineer must be acquainted with toxicology, industrial hygiene, and environmental science. Other important disciplines are: agronomy, geohydrology, hydrogeology, analytical chemistry, pesticide chemistry, civil (environmental) engineering, oceanography and biology.

Although Daniels and I are not necessarily suggesting additional formal coursework at the university level, some mechanism of indoctrination is needed to bring about an acquaintance with other disciplines that will raise the level of environmental consciousness of chemical engineers. I envy the good attitude nearly all civil engineering graduates have concerning the natural environment. As chemical engineers, we do work in a highly artificial niche and apparently a consciousness of and concern for the natural environment have been bred out. We need to stop doing something in the education process or start doing something else to correct this bad attitude. I obviously don't have a good answer on how to realistically correct this blind spot.

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__Louis J. Thibodeaux__ is currently professor of chemical engineering and director of the Hazardous Waste Research Center at Louisiana State University at Baton Rouge. He holds a Ph.D. in Chemical Engineering from Louisiana State University, and is the author of numerous articles dealing with the fate and transport of chemicals in the natural environment.

Environmental Shorts

Boston Harbor Cleanup Begun

The Massachusetts Water Resources Authority has selected the Boston-based team of Camp Dresser & McKee Inc. and Stone & Webster Engineering Corp. to prepare a facilities plan to restore the water quality of Boston Harbor. Plans call for scheduled completion in 1988 of the $1.1 billion engineering and construction program.

Facilities involved include a 500-million gal/day primary and secondary wastewater treatment plant, a five-mile tunnel under Boston Harbor, and an ocean outfall several miles in length.

Under the terms of the MWRA contract, Camp Dresser & McKee will serve as the plan manager and will direct the environmental engineering work, while subcontractor Stone & Webster will undertake geotechnical investigations, prepare engineering specifications for the tunnel, and outfall, and conduct environmental reviews.

Limestone Used to Control Acidity in New England Lakes, Ponds

Although the cause of acid rain still is controversial, the use of high calcium limestone to neutralize and restore acidified lakes and ponds has been used as a cost-effective remedy.

Continuing a program begun this summer at several lakes and ponds in Plymouth and Cape Cod, Mass. and in New York's Adirondack Mountains, Pfizer, Inc. recently delivered a shipment of limestone from its Adams, Mass. plant to Florida, Mass., where it was used to raise the pH level of North Pond in Berkshire County.

At the staging area, a dry powder form of calcium carbonate was slurried into a 70 percent solids suspension for transfer by tank truck to a helicopter at the 18-acre target pond.

Overseeing preparation of the neutralizing agent were the lime and limestone product manager for Pfizer and executives of International Science and Technology, Inc. IS&T, located in Reston, Va., is a contracting firm that designs and operates the treatment project in collaboration with Living Lakes, Inc., of Washington, D.C.

According to Pfizer's C.W. Kleckco, lime and limestone product manager, calcium carbonate is the neutralizing material in the United States, Canada, and Scandinavia because it is relatively inexpensive, non-caustic and easy-to-handle.

Liming to enhance fish production in acidified ponds and lakes began in the early 1940s, notably in Wisconsin and Michigan's upper peninsula, Kleczko said.

Depending on the size and state of the pond, its rate of flushing and the solubility of the calcium carbonate, the neutralizing effect is almost immediate. Normally, swimming and fishing can be resumed in a matter of hours.

LETTER

On "Retrofit SO_2 and NO_x Control Technologies for Coal-Fired Power Plants"

To the editor:

The article by Michael J. Miller [*Environmental Progress,* **5,** 171 (1986)] is an interesting survey of a very timely subject. We were surprised to note, however, the omission from consideration of one major technology that is being developed by several organizations and is at or near commercialization by a few of these. We refer to Advanced Staged Slagging Coal Combustors.

We at TEDA have been performing a study on this active technology, and have reached the conclusion that it will have its place in the ultimate set of solutions. It has the advantages of not requiring significant modifications of the boiler envelope, and it may require little modification of downstream equipment. It requires little if any additional energy input. It can certainly be combined with coal cleaning and fuel switching for meeting the required reduction in the emission of acid rain precursors.

Our opinion that this is a viable technology is reinforced by the fact that the funds for development have come and continue to come not only from the DOE but also from many private sources.

Ronald F. Cascone and
Joel J. Kirwan
Technology Evaluation &
Development Associates Inc.
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Please take the time to fill out the Readership Questionnaire on page N6 of this issue.

Washington Environmental Newsletter

Hazardous Waste Rules For Small Quantity Generators

In November 1984, the Hazardous and Solid Waste Amendments to RCRA were signed into law. With these amendments, Congress directed EPA to establish new requirements that would bring small quantity generator (who generate between 100 and 1000 kilograms of hazardous waste in a calendar month) into the hazardous waste regulatory system. EPA issued final regulations for this category on March 24, 1986. Most of the requirements went into effect on September 22, 1986. Dates to take note of are:

September 22, 1986 Most of the new rules became effective. Noncompliance may lead to fines and legal action.
March 24, 1987 Small quantity generators that decide to store hazardous waste for longer than six months, perform certain kinds of waste treatment, or dispose of hazardous waste on their property must apply for a RCRA permit and comply with additional rules.

Categories

Generators of no more than 100 kg/mo.—are "conditionally exempt small quantity generators" and are required to: (1) Identify all hazardous wastes generated, (2) Send this waste to a hazardous waste facility, or a landfill or other facility approved by the state for industrial or municipal wastes. (3) Never accumulate more than 1000 kg of hazardous waste on their property. (If more is accumulated the generator becomes subject to all the requirements applicable to 100-1000 kg/mo. category.)

Generators of 100-1000 kg/mo.—If the business generates more than 100 and less than 1000 kg (between 220 and 2200 pounds or about 25 to under 300 gallons) of hazardous waste and no more than 1 kg of acutely hazardous waste in any month, the law requires the generator to comply with all the 1986 rules for managing hazardous waste, including the accumulation, treatment, storage and disposal requirements listed.

Generators of 1000 kg/mo. or more are required to comply with all applicable hazardous waste management rules.

Note: Under the federal hazardous waste management system, the generator may be regulated under different rules at different times depending on the amount of hazardous wastes generated in any given month. Many states have different generator categories and requirements. If there is a question concerning generator status call the state agency responsible.

These rules and regulations may be difficult for small businesses to understand, so toward that end, EPA has published an easy to read and understand handbook for small businesses entitled "*Understanding the Small Quantity Generator Hazardous Waste Rules*" that is available thru the Washington Office of AIChE. Distribution of this handbook to small businesses in your area can become an important function of your local section and a worthwhile community service.

Local Section Community Emergency Response Program

We are happy to report that to date, 44 of our 102 Local Sections and GIC's are beginning to participate in our program for community involvement. If your section is interested in participation call or write to:

Dr. Martin Siegel
AIChE — Washington Office
1707 L St., NW
Washington, DC 20036
(202) 223-0650

This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates, Inc.
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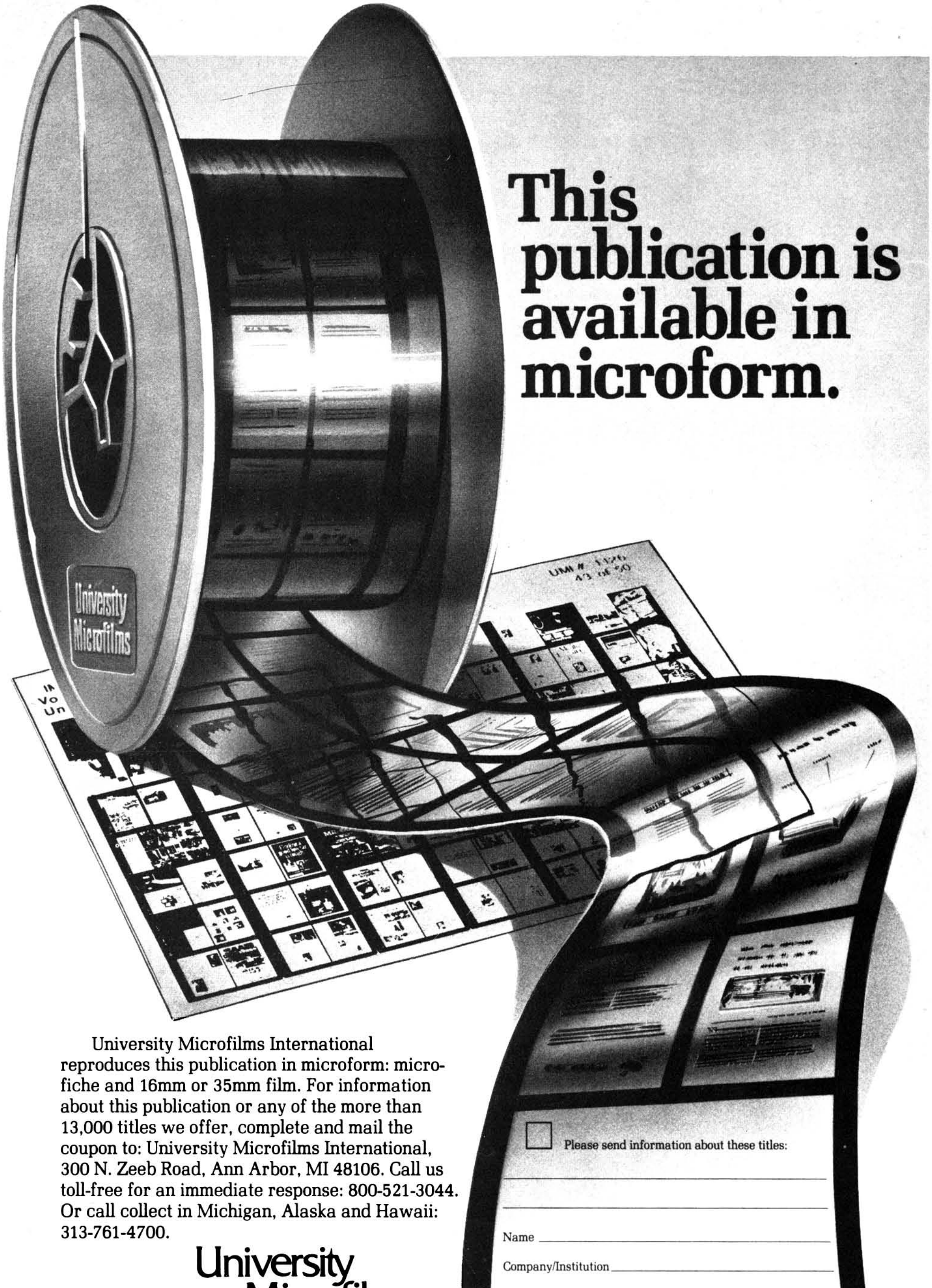
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Fly Ash Recycle in Dry Scrubbing

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The University of Texas at Austin, Austin, TX 78712

Previous workers have shown that the recycle of product solids improves the utilization of slaked lime [$Ca(OH)_2$] for SO_2 removal by spray dryers with bag filters. In laboratory-scale experiments with a packed bed reactor, utilization was increased several-fold when the $Ca(OH)_2$ was first slurried with one of several different fly ashes. The enhancement increased with the higher loading of fly ash [g fly ash/g $Ca(OH)_2$]. Much higher $Ca(OH)_2$ utilization was achieved when silicic acid was used instead of fly ash. Scanning electron microscopy supports the explanation that $Ca(OH)_2$ and silica dissolve and reprecipitate as a more reactive calcium silicate. Other major constituents of fly ash have less or no effect at all on $Ca(OH)_2$ utilization. The amount of calcium in the fly ash did not affect the overall SO_2 removal after $Ca(OH)_2$ was added. Slurrying for longer than 2 hours at higher than 60°C can improve the utilization of $Ca(OH)_2$ slurried with fly ash.

INTRODUCTION

Flue gas desulfurization by the means of spray dryer and bag filter is an important new alternative to limestone slurry scrubbing. In the spray dryer/bag filter system, flue gas is contacted with a fine spray of an aqueous solution or slurry of a reactive alkali [typically $Ca(OH)_2$]· SO_2 removal and drying occur simultaneously. Since not all moisture is removed from the solids in the spray dryer, the remaining moisture promotes further removal of SO_2 in the duct joining the spray dryer and bag filter and in the bag filter itself. Therefore the total SO_2 removal in the system is a sum of removal in the spray dryer, the connecting duct, and bag filter.

Advantages of spray drying over the conventional slurry scrubbing methods are production of a dry solid waste and equipment construction from carbon steel. Economic studies have indicated that, for low and medium sulfur coals, dry scrubbing systems should compete economically with wet systems [*1*, *2*, *3*]. Numerous authors report that recycle of product solids and fly ash in $Ca(OH)_2$ spray dryer scrubbing results in substantial improvement of reagent utilization and SO_2 removal [*4*, *5*, *6*, *7*]. A spray dryer model based on gas/film mass transfer to liquid droplet overpredicts the performance of actual systems without recycle, but underpredicts the performance of the systems in which the recycle was used [8]. This suggests that there must be a substantial effect of gas/solid reactions enhanced by fly ash recycle. This paper explains this effect by studying the reaction of SO_2 with mixtures of $Ca(OH)_2$/fly ash, $Ca(OH)_2/SiO_2$, and $Ca(OH)_2/Al_2O_3$ at bag filter conditions.

FLY ASH RECYCLE IN PILOT PLANTS

Solids recycle from the spray dryer has been used to obtain better utilization of $Ca(OH)_2$. This option provides a higher $Ca(OH)_2$ concentration in the slurry feed at the same $Ca(OH)_2$ stoichiometric ratio [moles of $Ca(OH)_2$ fed to the system/moles of SO_2 in the feed gas]. In one pilot plant, increasing the recycle ratio [g solids recycled/g fresh $Ca(OH)_2$] from 6:1 to 12:1, increased SO_2 removal in the spray dryer from 70 to 80% at a stoichiometry of 1.0 [9]. In another installation, compared to once-through lime tests, recycle tests gave 10 to 15% more SO_2 removal at a stoichiometry of 1.5 [*10*].

Another option enhancing lime utilization uses the recycle of both solids collected in the spray dryer and solids from the baghouse. However, removal was not significantly different employing either spray dryer solids or fabric filter solids as a recycled material [*11*]. At a stoichiometry of 1.0 the removal increased from 53% when no recycle was employed to 62% with 0.5:1 recycle ratio. When ash content in the feed slurry increased from 5 to 20%, SO_2 removal in the spray dryer increased from 80 to 92% for a stoichiometry of 1.6 [*10*].

A/S Niro Atomizer ran several experiments investigating the effects of fly ash recycle and proved it to be beneficial for SO_2 removal in a spray dryer [*12*]. According to their results, substantially higher removal of SO_2 may be achieved when recycling the fly ash and $Ca(OH)_2$ than when recycling $Ca(OH)_2$ alone. Corresponding efficiencies for a stoichiometry of 1.4, 500 ppm inlet SO_2, and comparable solids concentration were 84 and 76%, respectively. For the same stoichiometry and SO_2 concentration, removal was only 67% for the simple once-through process. At low SO_2 concentration and high recycle ratios, over 90% removal was achieved even at extremely low stoichiometry. At 548 ppm SO_2, 25:1 recycle, 0.76 stoichiometry and at 170 ppm SO_2, 110:1 recycle, 0.39 stoichiometry, SO_2 removal was 93.8 and 97.8%, respectively.

Removal efficiencies up to 65% were reported with a slurry of highly alkaline (20% CaO) fly ash only [*13*]. In another experiment, 25% SO_2 removal was achieved when spraying slurried fly ash collected from a boiler burning 3.1% sulfur coal [*14*]. A weak trend found in a study of 22 samples of fly ash was that a slurry with a higher total slurry alkalinity tended to have a higher SO_2 capture [*15*]. A potentially significant hypothesis has been presented, which claimed that the fraction of available alkalinity which was utilized during a single pass through the scrubber was diminished as the alkalinity increased [*16*].

The results presented above show that there must be a substantial reaction between recycled $Ca(OH)_2$ and fly ash, promoting SO_2 removal in a spray dryer. The formation of hydrated calcium silicates during the recycle and their subsequent reaction with SO_2 may be the possible explanation of this phenomenon.

CaO-SiO_2-Al_2O_3-H_2O System

The nature of calcium silicate hydrate, calcium aluminate hydrate, and calcium aluminate silicate hydrate formation in CaO-SiO_2-Al_2O_3-H_2O systems is very complicated. It is usually impossible to assign a simple chemical formula to these products, especially at ordinary temperatures of interest in flue gas desulfurization [*17*]. At temperatures from 20 to about 100°C, two main calcium silicate hydrates are formed. Their ratio depends on the initial ratio of calcium to silica in the slurry [*18*]. Both monocalcium silicate hydrate [$CaO \times SiO_2 \times H_2O$] and dicalcium silicate hydrate [$(CaO)_2 \times SiO_2 \times H_2O$] are fibrous gels of specific surface areas in the range of 100-300 m^2/g [*19*]. At 20-100°C after eight hours of hydration, tobermorites (calcium silicate hydrates) may crystallize which are of high surface area [*20*]. However, below 100°C reactions yielding calcium silicate hydrate normally give poorly crystallized materials [*17*].

The reaction of fly ash and $Ca(OH)_2$ in the presence of water is called the pozzolanic reaction. A pozzolan is a siliceous or siliceous and aluminous material which in itself possesses little or no cementitous value but will, in finely divided form and in the presence of moisture, chemically react with $Ca(OH)_2$ at ordinary temperatures to form compounds possessing cementitous properties [*21*]. Due to small particle size and generally noncrystalline character, fly ash usually shows pozzolanic properties, or pozzolanic and cementitous properties in the case of high-calcium ashes [*22*]. High-calcium fly ash contains tricalcium aluminate hydrate, which is the most reactive mineral present in portland cement [*23*]. Pozzolanic reactions give products with cementitous properties and high surface areas that can enhance SO_2 removal.

During fly ash recycle in dry flue gas desulfurization systems, reaction of fly ash with makeup $Ca(OH)_2$ or unreacted, recycled $Ca(OH)_2$ probably takes place in several steps. First, $Ca(OH)_2$ dissolves in water. Then silica and alumina are digested from the fly ash. Finally calcium aluminum silicate hydrates are formed and reprecipitate on the surface of the fly ash.

EXPERIMENTAL

Apparatus

Experiments were conducted in the apparatus [*24*] shown in Figure 1. The glass reactor (40 mm in diameter, 120 mm in height) was packed with a powdered reagent mixed with 40 g of 100 mesh silica sand to prevent channelling of $Ca(OH)_2$ [*25*]. The reactor was immersed in a water bath controlled by a thermostat to within 0.1°C. Simulated flue gas was obtained by mixing nitrogen and sulfur dioxide from gas cylinders. The flow of gas was monitored using rotameters. Water was metered by a syringe pump, evaporated, and injected into the dry gas. Reactor tubing upstream of the water injection was heated to prevent condensation of the moisture.

Before entering the analyzer, the gas was cooled and water condensed by an ice bath. The SO_2 concentration was measured with a pulsed fluorescent SO_2 analyzer (ThermoElectron Model 40). A bypass of the reactor allowed preconditioning of the bed and stabilization of gas flow at the desired SO_2 concentration. Prior to each run the bed was humidified by pure nitrogen at a relative humidity of about 98% for six minutes and then pure nitrogen at a relative humidity at which the experiment was to be performed for ten minutes.

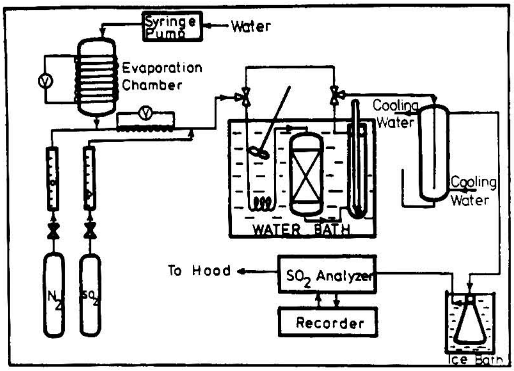

Figure 1. Experimental apparatus.

Most of the experiments were performed at a relative humidity of 54% with some experiments at 17 and 74%. At typical flue gas conditions, 17, 54, and 74% relative humidities correspond to 38, 9.5, and 4.7°C approaches to saturation, respectively. Reactor temperatures were 95, 66, and 64.4°C for 17, 54, and 74% relative humidities, respectively. Common purity (99.5%) nitrogen at 4.6 l/min (0°C, 1 atm) was used as a carrier gas. The nominal concentration of SO_2 was 500 ppm, and exposure time of the sample to the sulfurized gas was one hour.

Sample Preparation

The sample preparation consisted of two essential steps: slurrying and drying. In every experiment, 0.4 g of reagent grade $Ca(OH)_2$ was used. This amount of $Ca(OH)_2$ was slurried with fly ash or other additive at the desired loading. The water-to-solids ratio was between 10:1 and 20:1, most often 15:1. A propeller stirrer at 350 rpm was used to agitate the slurry. Slurrying time varied from two to 24 hours, and the temperature of the slurry was set at 25 to 92°C. The samples used for the investigation of the effect of slurrying conditions were vacuum filtered (about five minutes) and subsequently vacuum dried (about ten minutes) at 95°C. All other samples were dried overnight in an atmospheric oven without filtering; it took several hours to evaporate the water. The new drying procedure (vacuum filter and oven) was introduced to minimize the additional reaction time of a wet sample in high oven temperature (95-90°C).

Sample Characterization

Four different fly ashes were slurried with $Ca(OH)_2$. The characterization of the fly ashes is given in Table 1. During the experiments on slurrying conditions, a new batch of fly ash IV was used. It was obtained from the same vendor and was produced by burning coal from, reportedly, the same source. These samples were characterized by scanning electron microscopy (SEM). The composition of the particles was found using a Kevex Micro-X 7000 X-ray Energy Spectrometer (XES). Mean particle size was determined using a Hiac-Royco particle counter.

RESULTS

The Effect of Fly Ash Type and Ratio

Four samples of fly ash were slurried with $Ca(OH)_2$ at a loading of 4 [4 g fly ash/g $Ca(OH)_2$] for four hours at 65°C and reacted at a relative humidity of 54% (54% RH). The

TABLE 1. FLY ASH CHARACTERIZATION

	I	II	III	IV	
Power Plant	Bull Run Plant TVA	Gibson Plant Plant Service of Indiana	Seminole Electric Coop. Palatka, FL	San Miguel Electric Coop. San Miguel, TX	
Coal Type	bituminous	bituminous	bituminous	lignite	
XES Analysis [weight %]					
Ca	34	5	4	11[1]	15[2]
Si	42	41	59	66	68
Fe	6	31	15	4	2
Al	16	20	20	18	14
Mass Mean Particle Size [μm]	19	9	14	10	10

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[1] Old Batch
[2] New Batch

samples having the best and the worst performance at 54% RH were also tested at the extreme humidities of 17 and 74%. The results are presented in Figure 2. Also shown in Figure 2 are the conversions when $Ca(OH)_2$ only was exposed to the sulfurized gas. With 0.4 g $Ca(OH)_2$ the average SO_2 removal would be 83% with 100% utilization of $Ca(OH)_2$. As can be seen, all fly ashes improved the utilization at every RH investigated. Samples with 16 g fly ash/g $Ca(OH)_2$ (slurried at the same conditions as above) enhanced utilization at 54% RH to a greater extent than was the case for 4 g fly ash/g $Ca(OH)_2$. The $Ca(OH)_2$ utilization was 67, 79, 65, and 71% when fly ashes I, II, III, and IV were used, respectively. These values are much higher than the ones presented in Figure 2. Based on these two series of experiments, no correlation was found between SO_2 removed and calcium content of the fly ash sample.

Fly ash I was selected to test the effect of fly ash loading on $Ca(OH)_2$ utilization. The results of experiments at 54% RH are presented in Figure 3. Increasing fly ash loading from 0.5 to 20 g/g $Ca(OH)_2$ increased $Ca(OH)_2$ utilization from 17 to 78%.

Additives Other Than Fly Ash

The other main components of fly ash were also investigated. Reagent grade Al_2O_3, Fe_2O_3, and silicic acid were used as sources of alumina, iron, and silica, respectively. Fly ash was simulated as a mixture of three substances: 49% H_2SiO_3, 29% Al_2O_3, and 22% Fe_2O_3 (weight %). Figure 4 shows that this mixture models the performance of fly ash at a loading of 4 (30 and 27%, respectively). This again implies that calcium content of fly ash is not of primary importance, since the utilization of added $Ca(OH)_2$ was higher when no fly-ash-bound calcium was present.

The addition of silicic acid had the most significant effect on the $Ca(OH)_2$ utilization. No SO_2 removal was observed when silicic acid alone was exposed to simulated flue gas. Figure 5 gives the effect of silica loading on conversion at 17 and 54% RH. Silicic acid was used for most of these experiments. Some experiments were performed with Zeothix 265 and Zeofree 80, synthetic precipitated

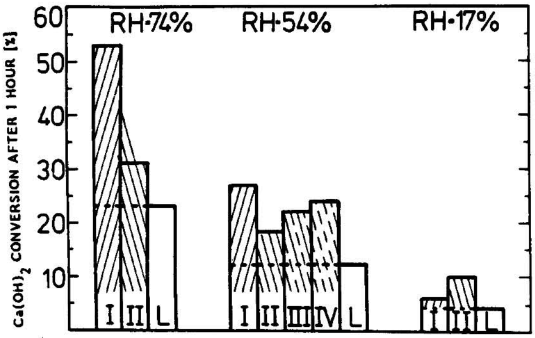

Figure 2. The effect of fly ashes I, II, III and IV and relative humidity on $Ca(OH)_2$ utilization, L = $Ca(OH)_2$ alone.

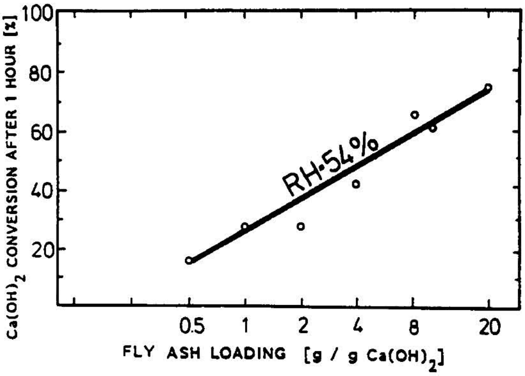

Figure 3. The effect of fly ash I loading on $Ca(OH)_2$ utilization.

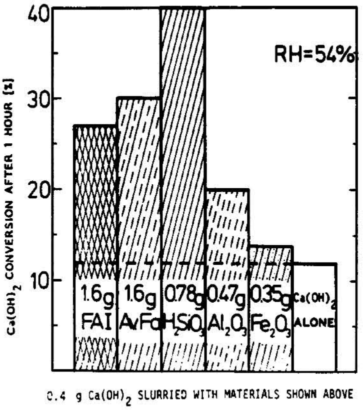

Figure 4. The fly ash simulation experiment at 54% RH. Simulated fly ash (Av. Fa.) and reagent grade mixtures slurried with 0.4 g of $Ca(OH)_2$ for four hours at 65°C.

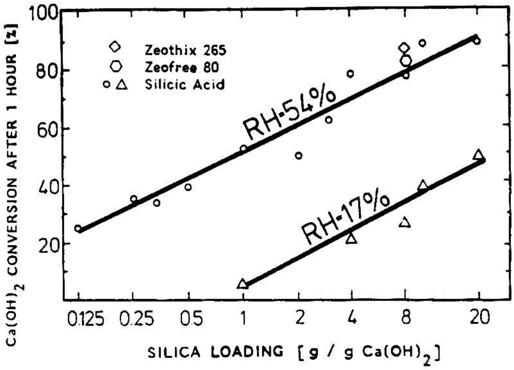

Figure 5. The effect of silica loading on $Ca(OH)_2$ utilization.

silicas of surface area 250 m^2/g and 140 m^2/g, respectively (samples and data obtained courtesy of Huber Corp.). However, these substances did not enhance $Ca(OH)_2$ utilization significantly better than silicic acid (Figure 5). As can be seen from Figure 5, $Ca(OH)_2$ conversion increased with silicic acid loading. The comparison of the results presented in Figures 3 and 5 shows that silicic acid promotes $Ca(OH)_2$ utilization better than fly ash. For example, at 54% RH and 8 g silicic acid/g $Ca(OH)_2$ the conversion of lime was 78%. At 8 g fly ash I/g $Ca(OH)_2$, the conversion was 65%.

Reactivities of fly ash and silicic acid should be compared on the basis of silica content. Assuming that fly ash I is 50% silica, 8 g silicic acid/g $Ca(OH)_2$ should be compared to 16 g fly ash I/g $Ca(OH)_2$ (conversions of 78 and 68%, respectively). The difference between silicic acid and fly ash is more apparent at lower loadings. For 1 g silicic acid/g $Ca(OH)_2$, conversion was 53%, and for 2 g fly ash I/g $Ca(OH)_2$, it was 32%.

The effect of alumina loading was tested at 54% RH using two sources of alumina (Figure 6). When reagent grade Al_2O_3 was used, increasing loading did not change SO_2 removal. No SO_2 removal was observed for Al_2O_3 alone. However, the removal increased with increasing loading of activated alumina (chromatographic grade, 80-200 mesh). Activated alumina alone removed SO_2. The adsorptive capacity of activated alumina was calculated as 0.023 g of SO_2 per g of alumina. Based on this value, the corrected SO_2 removal has been determined due to the possible formation of calcium aluminates. These corrected values are lower than the ones observed for the same additive loading when silicic acid was used instead of alumina. Therefore, the silica content of fly ash is mainly responsible for the enhancement of $Ca(OH)_2$ utilization.

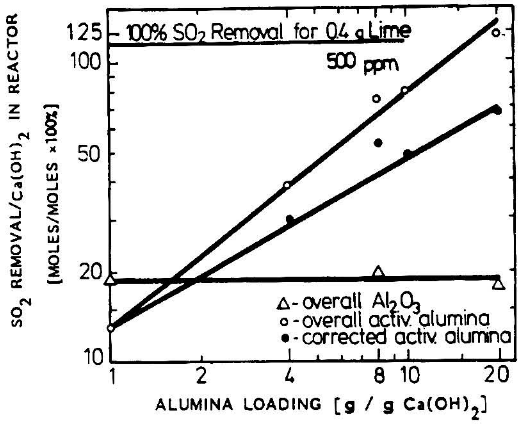

Figure 6. The effect of alumina loading on $Ca(OH)_2$ utilization at 54% RH and at SO_2 concentration of 500 ppm.

Slurrying Conditions

Slurrying tests were performed at 25, 45, 55, 65, and 92°C, and time was varied from two to 24 hours. The samples for these tests were prepared by vacuum filtration and vacuum drying. Both old and new batches of fly ash IV were used as a source of silica at 16 g fly ash/g $Ca(OH)_2$. Reactor relative humidity during exposure was 54%. $Ca(OH)_2$ conversion is given in Figure 7.

As can be seen, the slurrying temperature was the decisive parameter affecting the process. The results show that there is a critical slurrying time for every temperature tested, for which $Ca(OH)_2$ conversion reaches a maximum value. The time needed to reach this maximum shortens with increasing temperature. $Ca(OH)_2$ conversion converged on 40% after 16 hours of slurrying at 25°C and 80% after five hours at 92°C. Compared with 12% utilization of $Ca(OH)_2$ alone at 54% RH, the utilization of fly ash/$Ca(OH)_2$ slurried at 65°C improved dramatically.

SEM photographs (Figures 8 and 9) show the development of the surface area of the samples. Figure 8 shows the sample slurried for zero time. Separate fly ash spheres with smooth surfaces (as in an unslurried fly ash) and irregular particles of $Ca(OH)_2$ can be seen. Increasing the temperature of slurrying to 92°C resulted in a well developed surface area of the deposit as depicted in Figure 9.

The maximum utilization of $Ca(OH)_2$ is not a uniform function of the temperature of slurrying (40, 50, 55, 80, and 80% for 25, 45, 55, 65, and 92°C, respectively). There ap-

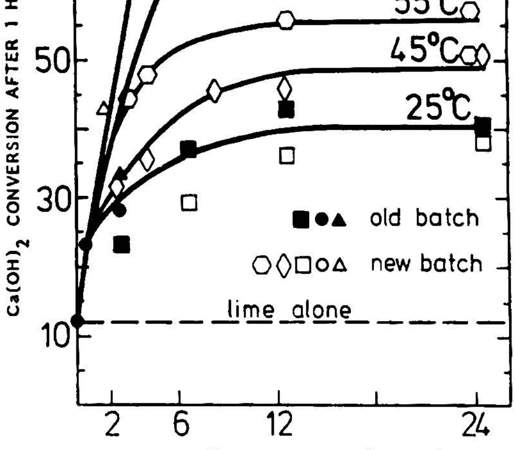

Figure 7. The effect of fly ash IV on $Ca(OH)_2$ reactivity, 16 g fly ash IV/g $Ca(OH)_2$.

Figure 8. SEM photograph of 16 g fly ash IV/g $Ca(OH)_2$ sample slurried for zero hours.

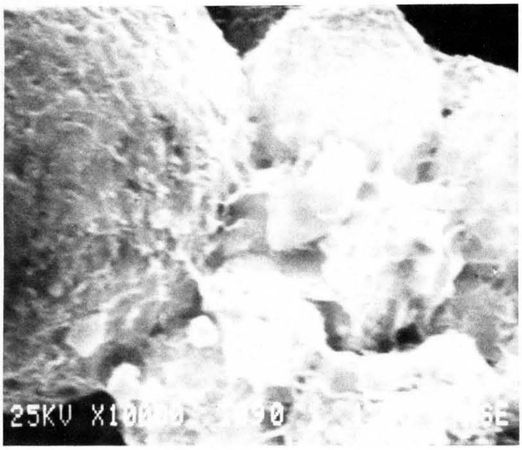

Figure 9. SEM photograph of 16 g fly ash IV/g $Ca(OH)_2$ sample slurried for 12 hours at 92°C.

pears to be a discontinuity between 55 and 65°C that may indicate a change in the hydration of the calcium aluminum silicate. The resulting solids have better reactivity for SO_2 removal than those formed below 55°C. When tested by Differential Scanning Calorimetry (DSC), the solids formed at 65 and 92°C have an additional endothermic peak between 416 and 465K (143 and 192°C). No peak was observed for samples slurried at 25, 45, and 55°C. The DSC scans of the samples of 16 g fly ash IV/g $Ca(OH)_2$ slurried at 65 and 55°C are shown in Figures 10 and 11, respectively.

CONCLUSIONS

1. Enhanced performance of spray dryer/bag filter systems with recycle of fly ash and calcium solids is probably due to reaction of $Ca(OH)_2$ with fly ash to produce calcium silicates. The calcium silicate solids have greater surface area than the unreacted $Ca(OH)_2$ and are more effective for gas/solid reactions.

2. Calcium silicates are more reactive than aluminates or ferrites. The available silica content of the fly ash is most important.

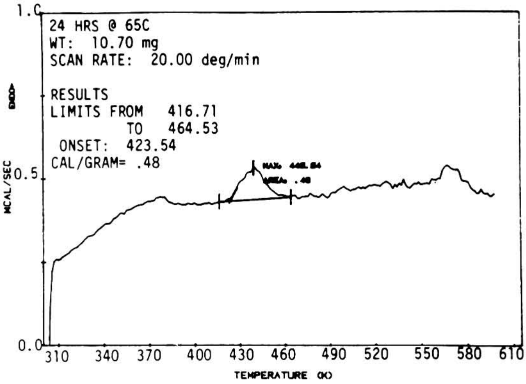

Figure 10. DSC scan of a sample of 16 g fly ash IV/g $Ca(OH)_2$ slurried for 24 hours at 65°C.

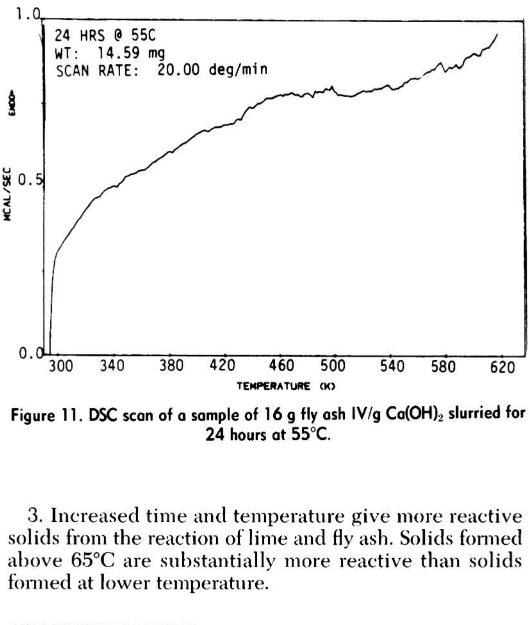

Figure 11. DSC scan of a sample of 16 g fly ash IV/g $Ca(OH)_2$ slurried for 24 hours at 55°C.

3. Increased time and temperature give more reactive solids from the reaction of lime and fly ash. Solids formed above 65°C are substantially more reactive than solids formed at lower temperature.

ACKNOWLEDGEMENTS

This work was performed under EPA Cooperative Agreement CR-811531. The EPA project officer was Theodore G. Brna.

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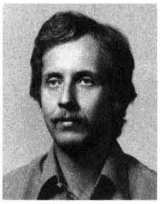

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Pilot Testing of Sodium Thiosulfate

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Pilot plant tests have been conducted to evaluate sodium thiosulfate as an oxidation inhibition additive in five lime/limestone slurry flue gas desulfurization processes. It was found that the oxidation rate of absorbed sulfur dioxide (SO_2) was reduced by more than 50 percent in the presence of 100 to 200 ppm of thiosulfate ion in the scrubbing slurry. Calcium sulfate dihydrate (gypsum) scaling was eliminated and the unsaturated (with respect to gypsum) operation mode was maintained by the addition of sodium thiosulfate. Other benefits of sodium thiosulfate addition observed at the pilot plant included improvement in solids dewatering properties for limestone processes and improvement in SO_2 removal efficiency for magnesium-enhanced lime/limestone processes.

INTRODUCTION

Due to the oxidation reaction between absorbed sulfur dioxide (SO_2) and dissolved oxygen, calcium sulfate dihydrate (gypsum) scaling in scrubber internals and associated equipment has been an operation and maintenance problem for lime/limestone slurry flue gas desulfurization (FGD) processes. A contributing factor to this problem is that older boilers tend to operate at higher levels of excess air. Scrubbers with induced-draft fans also have the potential of air leakage which enhances the oxidation.

Laboratory experiments have demonstrated that sodium thiosulfate is an effective oxidation inhibitor [1, 2]. It was reported that sodium thiosulfate, as an additive in the regenerable citrate FGD process, reduced the sulfur oxidation rate [3]. Pilot plant tests, conducted to evaluate the effectiveness of sodium thiosulfate in a limestone-regenerated dual alkali system, showed that sodium thiosulfate inhibits oxidation in the sodium sulfite/bisulfite clear-solution scrubber [4]. However, the effective level of thiosulfate needed to inhibit oxidation was proportional to the sulfite concentration. Therefore, large quantities of sodium thiosulfate would be needed for concentrated solution scrubbing processes.

The effects of thiosulfate on lime/limestone slurry processes are less consistent. The study of the retrofit scrubber system at Louisville Gas & Electric (LG&E) Paddy's Run Plant, which experienced little sulfate scaling, suggested that the presence of thiosulfate as an impurity in the carbide lime used might have inhibited oxidation and relieved gypsum scaling [1]. However, pilot plant tests, simulating this scrubber's operation by adding sodium thiosulfate to a conventional lime scrubber, did not show any oxidation reduction with thiosulfate addition [5]. The first successful application of commercial grade sodium thiosulfate to slurry FGD processes was at the Phillips Station of Duquesne Light which has a magnesium-enhanced lime system [6]. Gypsum scaling problems were caused by a combination of high excess air, low scrubber liquid-to-gas (L/G) ratio, low slurry solids content, and no hold tank to provide retention time for dissipating the sulfate saturation. The addition of sodium thiosulfate eliminated the scaling and substantially reduced maintenance requirements. In addition, a slight improvement of SO_2 removal was experienced. Noting this success, sodium thiosulfate was applied at Elrama Station, which also has a magnesium-enhanced lime scrubber, and similar benefits were obtained [6].

TVA Shawnee Station tested sodium thiosulfate in a prototype spray tower simulating limestone FGD processes [7]. Dramatic descaling effects were observed with the addition of sodium thiosulfate. Only 100 ppm of thiosulfate was needed to reduce the sulfate saturation and sustain scale-free operation. An unexpected benefit discovered was the improvement of solids dewatering properties as reflected by the increase of filter cake solids content. However, material balances showed that the sodium thiosulfate consumption was more than 10 times the estimated loss with filter cake moisture. Significant amounts of polythionates, ranging from dithionate to pentathionate, were found by chemical analyses of the scrubbing liquor [7].

Under the sponsorship of U.S. Environmental Protection Agency's (EPA) Industrial Environmental Research Laboratory (now Air and Energy Engineering Research

Laboratory, AEERL) at Research Triangle Park, NC, pilot plant tests were conducted to evaluate the effect of sodium thiosulfate as an additive to wet FGD systems. The objectives were to verify the oxidation reduction effect of sodium thiosulfate and to evaluate the effectiveness of thiosulfate in five lime/limestone slurry FGD processes. This paper summarizes the test results and compares them with previous data.

TEST FACILITIES

The test facility, located at EPA/AEERL's laboratories in Research Triangle Park, NC, is a three-stage mobile bed with 7.5-m³/min (approximately 0.1 MW) flue gas capacity (Figure 1). No flyash is present in the flue gas which is drawn from a gas-fired boiler and injected with pure SO_2. Typical operating conditions for the sodium thiosulfate evaluation tests are listed in Table 1. Adjustment of the lime or limestone slurry feed rate via feedback control was used to maintain constant hold tank pH.

High calcium limestone, quarried in Fredonia, Kentucky, and ground to 80% less than 325-mesh, was used as the reagent for the limestone tests. Hydrated lime, $Ca(OH)_2$, was mixed with water to make 30 wt.% solids slurries for the lime tests. Five FGD processes (limestone, lime, magnesium-enhanced lime, magnesium-enhanced limestone, and adipic-acid-enhanced limestone) were evaluated. In order to simulate magnesium-enhanced processes, epsom salt ($MgSO_4 \cdot 7H_2O$) was added to the hold tank to maintain the desired magnesium concentrations. Commercial grade adipic acid ($HOOC(CH_2)_4COOH$) was used for the organic-acid-enhanced limestone scrubber tests. Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) was the oxidation inhibition additive in all tests.

For each process, the pilot plant was first run without sodium thiosulfate to establish baseline performance. The scrubber slurry was then spiked with sodium thiosulfate to raise the thiosulfate concentration. Sodium thiosulfate was also added to the hold tank once per hour to replenish the losses and maintain constant thiosulfate concentration. The scrubber internals were inspected regularly to assess the extent of gypsum scaling. Slurry sulfate saturation level was obtained by liquid analyses and the Shawnee correlation: [7]

$$\% \text{ Sulfate saturation} = [Ca][SO_4] \left(\frac{26300}{3[Ca] + 3[Mg] + [SO_4]} + 4700\right) \quad (1)$$

where [Ca], [SO_4], and [Mg] are total calcium, sulfate, and magnesium concentrations in moles/liter, respectively. The sulfate saturation, which is a good index of oxidation level and scaling potential, is defined as the quantity of dissolved calcium sulfate divided by its solubility concentration and expressed as a percentage. Oxidation level was measured by sulfite/sulfate analyses of filter cake samples. Ultraviolet spectrophotometry (DuPont 400 SO_2 analyzer) was used to monitor the gas-phase SO_2 concentrations and SO_2 removal efficiencies. Solids dewatering properties were characterized by hold tank slurry settling rates and filter cake insoluble solids concentrations.

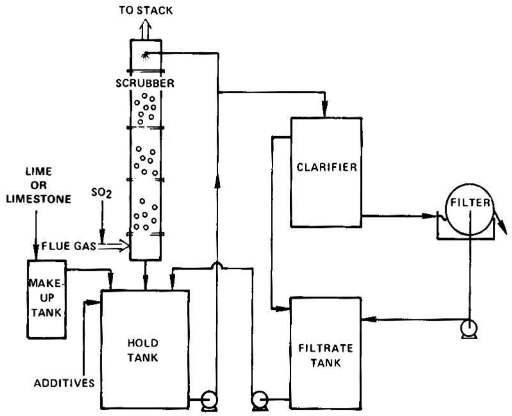

Figure 1. Flow diagram for thiosulfate tests in EPA/AEERL's 0.1 MW lime/limestone pilot plant system.

TABLE 1. OPERATING CONDITIONS FOR EVALUATION OF SODIUM THIOSULFATE ADDITIVE AT THE AEERL PILOT PLANT

Mobile bed absorber = Three beds with 10-cm static bed height each
Packing = 3.8-cm diameter nitrile foam spheres
L/G = 4.7-8 l/m³ (35 to 60 gal./1000 acf) for lime and 9.3 l/m³ (70 gal./1000 acf) for limestone
Flue gas SO_2 = 2500-3000 ppm
Flue gas oxygen = 7-8 vol. %
Hold tank solids = 5-10 wt.%
Hold tank pH = 6.5-7.5 for lime
5.5 for limestone
Hold tank residence time = 2-5 minutes for lime
10 minutes for limestone

The following analytical procedures were used for the analysis of sulfur species in the scrubbing liquor [6, 7]:

(1) Thiosulfate ($S_2O_3^{2-}$) by ion chromatography
(2) Total oxidizable sulfur (TOS) by oxidation with excess iodine and back titration with arsenous acid
(3) Sulfate (SO_4^{2-}) by ion chromatography
(4) Total sulfur by bromine oxidation and ion chromatography

Thiosulfate was also analyzed directly by formaldehyde fixation of sulfite/bisulfite followed by iodine oxidation and back titration of excess iodine with arsenous acid. Iodometric results agree reasonably well with ion chromatography results. The concentration of SO_3^{2-} plus HSO_3^- was estimated by the difference between results obtained from procedures (1) and (2). In addition to using procedure (4), total sulfur was also measured by H_2O_2/HCl oxidation and ion chromatography. However, bromine oxidation usually gave 10 to 20% more total sulfur than H_2O_2/HCl oxidation.

RESULTS AND DISCUSSION

As experienced in the TVA Shawnee tests [6], heavy doses of sodium thiosulfate were required initially to establish a sustainable sodium thiosulfate concentration. For example, in order to obtain a sustainable sodium thiosulfate concentration of 300 ppm, dosages sufficient to attain 2000 ppm sodium thiosulfate were used to spike the hold tank slurry at the beginning of the run. Usually, more than 80% of the spiked sodium thiosulfate disappeared within the first 24 hours, leaving only 200 to 300 ppm thiosulfate ions.

Results of pilot plant tests with and without sodium thiosulfate addition are summarized in Tables 2 to 7 for the five lime/limestone flue gas desulfurization processes tested. Table 2 shows that sodium thiosulfate addition effectively reduced oxidation, gypsum scaling, and sulfate saturation for all five FGD processes. The oxidation reduction is reflected by the significant drops of calcium and sulfate ion concentrations and by the observation that gypsum scaling disappeared after sodium thiosulfate addition (Tables 3 to 7). The unsaturated mode of operation (sulfate

TABLE 2. EFFECTS OF SODIUM THIOSULFATE ADDITION ON THE PERFORMANCE OF LIME/LIMESTONE SLURRY FGD SYSTEMS

Process Effect	Gypsum Scaling Abatement	Oxidation Reduction	Sulfate Saturation Reduction	SO_2 Removal Enhancement	Improved Solids Dewatering Properties
Limestone slurry	Yes	Yes	Yes		Yes
Lime slurry	Yes	Yes	Yes		
Magnesium-enhanced lime	Yes	Yes	Yes	slight	
Magnseium-enhanced limestone	Yes	Yes	Yes	Yes	
Adipic-acid-enhanced limestone	Yes	Yes	Yes	Yes	Yes

TABLE 3. SUMMARY OF LIMESTONE THIOSULFATE TEST RESULTS

Run No.	LS-0	LS-1	LS-2	LS-3	LS-4	LS-5
S_2O_3 level, ppm	0	100	500	1020	2250	1000
Gypsum scaling	Yes	No	No	No	No	No
Oxidation, %	20.6	—	6.1	5.1	1.2	1.3
Sulfate saturation, %	139.0	53.0	18.3	15.7	10.7	<2.3
Hold tank slurry settling rate, c/min	0.7	0.7	0.8	0.9	2.6	3.6
Filter cake solids, %	56	55	55	54	65	75
SO_2 removal, %	78	78	80	79	80	79
Limestone utilization, %	85	86	92	97	96	85
Ca, ppm	1000	520	270	250	250	1410
SO_4, ppm	2800	1450	790	660	370	<50
TOS[a] as SO_3, ppm	1100	—	2700	3100	3650	1320
TS[b] as SO_4, ppm	4100	—	5640	7300	9730	2980
Other sulfur as SO_4, ppm	0	—	750	1200	1120	160
Na, ppm	90	—	550	850	1350	760
Mg, ppm	300	360	420	380	450	890
Cl, ppm	<100	—	<100	<100	<100	3000
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.13	0.25	0.03
SO_2 oxidized, gmole/hr	4.7	—	1.4	1.2	0.28	0.30
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	2.6	5.5	10.7	1.3
Test period, hrs	82	28	92	82	87	96

[a] TOS = total oxidizable sulfur
[b] TS = total sulfur

TABLE 4. SUMMARY OF LIME THIOSULFATE TEST RESULTS

Run No.	L-0	L-1	L-2	L-3	L-4
S_2O_3 level, ppm	0	100	300	500	2000
Gypsum scaling	Yes	No	No	No	No
Oxidation, %	20.0	—	10.8	8.8	4.7
Sulfate saturation, %	144.0	96.8	82.8	57.3	22.4
Hold tank slurry settling rate, cm/min	0.4	0.3	0.3	0.4	0.4
Filter cake solids, %	52	52	53	52	53
SO_2 removal, %	66	66	66	66	67
Lime utilization, %	99	—	97	99	98
Ca, ppm	992	724	620	510	207
SO_4, ppm	3080	2540	2480	1970	1460
TOS as SO_3, ppm	1080	—	—	—	960
TS as SO_4, ppm	4380	—	6420	6670	9920
Other sulfur as SO_4, ppm	0	—	—	—	3880
Na, ppm	120	520	720	1020	1860
Mg, ppm	350	420	460	510	510
Cl, ppm	160	—	250	200	210
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.13	0.32
SO_2 oxidized, gmole/hr	5.9	—	3.13	2.6	1.4
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	2.07	4.4	10.7
Test period, hrs	78	38	82	86	82

saturation less than 100 percent) was sustained for all runs in the presence of thiosulfate ions.

Correlations between thiosulfate ion concentration and sulfate saturation/calcium ion concentration of the limestone slurry process were developed from the TVA/Shawnee spray tower test results. Comparisons of current data with the Shawnee correlations are shown in Figures 2 and 3. These show that the effects of thiosulfate on sulfate sat-

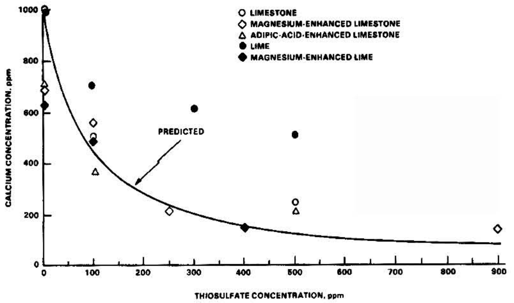

Figure 2. Predicted and measured calcium concentration as a function of thiosulfate concentration.

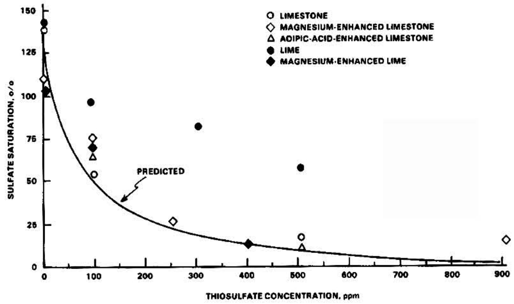

Figure 3. Predicted and measured sulfate saturation as a function of thiosulfate concentration.

uration and calcium ion concentration observed at the RTP pilot plant agree with the Shawnee results for all limestone tests. For the lime processes, the effects of thiosulfate concentration were less than predicted. However, for both cases, only 100 to 200 ppm thiosulfate ions were needed to significantly reduce the sulfite oxidation and avoid gypsum scaling.

Three possible inhibition mechanisms have been proposed by Miller *et al.* [6] to explain the oxidation reduction effects of thiosulfate. The first mechanism postulates that the overall oxidation can be reduced by the formation of an unoxidizable compound between sulfite and thiosulfate or by selective oxidation of thiosulfate rather than sulfite. Current data do not support these mechanisms because the thiosulfate required would be equal to the amount of sulfite normally oxidized in its absence. The results in Tables 3 through 7 indicate that the thiosulfate consumption rate is at least an order of magnitude less than the sulfite oxidation rate. Table 4 and 5 show that even with lime processes, for which thiosulfate addition is less effective, 0.06 gmole/hr of thiosulfate reduces sulfite oxidation by more than 2.5 gmole/hr, thus totally invalidating the selective oxidation mechanism.

It has been recognized that the sulfite is usually oxidized via a series of free radical chain reactions [8] which are initiated/catalyzed by several metal ions even at trace levels. Therefore, the second possible oxidation inhibition mechanism is that metal-thiosulfate complexes, which interrupt the chain reactions and reduce sulfite oxidation, are formed in the lime/limestone slurries. Selected values for several metals considered to be oxidation catalysts are given in Table 8 [9]. The metal-thiosulfate equilibrium constant, K, was used to calculate the residual concentration of metal ion in solution, assuming a metal ion concentration of 50 ppm and thiosulfate ion concentration of 250 ppm prior to complexing. The calculations show that the concentrations of transition metals, such as Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, are not significantly affected by the presence of thiosulfate ion. On the other hand, substantial concentration reductions are possible if Fe^{3+} is present. Heavy metal ions such as Cu^{+} and Cu^{2+} can even be eliminated by the addition of thiosulfate. Thus, oxidation inhibition by complexing the catalysts with thiosulfate is possible, especially when the oxidation reaction is catalyzed by metals ions such as Fe^{3+}, Cu^{+}, and Cu^{2+}.

Metal-thiosulfate complexing mechanisms cannot fully explain the oxidation inhibition observed in the pilot plant tests. First, the metal ion concentrations in RTP pilot plant scrubbing liquor are normally less than 50 ppm. Therefore, less than 200 ppm sodium thiosulfate is needed to form the metal-thiosulfate complex. However, current test results and TVA/Shawnee data indicated that the system had to be initially spiked with sodium thiosulfate sufficient for 2000 ppm. Second, previous pilot dual alkali data [4] showed that the thiosulfate level required for effective oxidation reduction is proportional to sulfite concentration. Therefore, in addition to metal-thiosulfate complexing, another (the third) mechanism involving sulfite ions is postulated.

The third possible mechanism is based on the assumption that, with free radical chain reactions, the oxidation of sulfite can also be slowed by reaction of thiosulfate with a chain-sustaining radical (e.g., $\cdot SO_3^-$) to form a nonreactive stable compound. The concentration, or generation rate, of the free radicals is very likely a function of sulfite concentration; thus, the effective oxidation reduction concentration of thiosulfate as indicated by dual alkali testing. Current data also show that there are always "unknown sulfur species" in the scrubbing slurry with thiosulfate addition. Chemical analyses of the Shawnee spray tower samples found significant amounts of polythionates (up to pentathionate) which are the typical products of thiosulfate-radical reactions [10]. If the oxidation is inhibited by free-radical scavenging of thiosulfate, current testing indicated that significant amounts of sodium thiosulfate are needed for initial quenching of chain reactions and establishing a sustainable thiosulfate level.

The sodium thiosulfate makeup rates shown in Tables 3 to 7 are the average $Na_2S_2O_3 \cdot 5H_2O$ feed rates after the initial spikes for each run. The makeup rate includes sodium thiosulfate required to replenish the loss with scrubbing liquor contained in filter cake and the thiosulfate consumed (degraded) by reaction with metal ions or free radicals. For purposes of scale-up and material balance, the sodium thiosulfate consumption rate was normalized against SO_2 absorption rate. The pilot test data shown in Tables 3 to 7 indicate that the normal thiosulfate consumption rate for oxidation/scaling inhibition should be in the range of 1 to 3 mmole $Na_2S_2O_3$ added/mole SO_2 absorbed for both the lime and limestone slurry FGD systems.

Results specific to each process tested are discussed in the following sections.

Limestone Slurry Process

Four runs were made with sodium thiosulfate concentrations ranging from 100 to 2250 ppm [Table 3]. In addition to decreases in oxidation and sulfate saturation, the most significant effect observed with thiosulfate additive was improved solids qualities (Tables 2 and 3). When the thiosulfate ion concentration was increased to 2250 ppm (run LS-4), the hold tank slurry settling rate also increased to 2.6 cm/min (vs. 0.7 cm/min for the base case, run LS-0) and filter cake insoluble solids reached 65% (vs. 56% for the base case). The slurry settling rate was taken as average descending rate of the meniscus in a 100-ml graduated cylinder over the first 2 minutes as shown in Figure 4. Although a Coulter Counter analysis did not show a

TABLE 5. SUMMARY OF MAGNESIUM-ENHANCED LIME TEST RESULTS

Run No.	LM-0	LM-1	LM-2	LM-3
S_2O_3 level, ppm	0	100	400	3000
Gypsum scaling	Light	No	No	No
Oxidation, %	17.0	—	10.0	5.2
Sulfate saturation, %	102	70.3	18.4	0.76
Hold tank slurry settling rate, cm/min	0.3	0.3	0.3	0.3
Filter cake solids, %	43	43	43	42
SO_2 removal, %	95	95	97	98
Lime utilization, %	97	—	98	99
Ca, ppm	630	490	260	40
SO_4, ppm	8550	7120	2780	690
TOS as SO_3, ppm	1040	—	1680	—
TS as SO_4, ppm	9800	—	8760	13200
Other sulfur as SO_4, ppm	0	—	3280	—
Na, ppm	30	—	480	1840
Mg, ppm	2020	2010	2030	2010
Cl, ppm	30	—	40	40
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.38
SO_2 oxidized, gmole/hr	6.2	—	3.7	1.9
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/ mole SO_2 absorbed	0	—	1.6	10.4
Test period, hrs	68	32	76	85

TABLE 6. SUMMARY OF MAGNESIUM-ENHANCED LIMESTONE TEST RESULTS

Run No.	LSM-0	LSM-1	LSM-2	LSM-3	LSM-4
S_2O_3 level, ppm	0	100	250	900	7000
Gypsum scaling	light	No	No	No	No
Oxidation, %	19.2	—	8.3	4.1	—
Sulfate saturation, %	110.3	75.3	26.9	17.9	7.0
Hold tank slurry settling rate, cm/min	0.7	0.7	0.8	0.7	1.0
Filter cake solids, %	54	54	54	54	56
SO_2 removal, %	83	83	85	88	—
Lime utilization, %	92	92	93	94	93
Ca, ppm	701	562	221	170	140
SO_4, ppm	5960	4620	3660	3020	1500
TOS as SO_3, ppm	1625	—	2810	4010	4670
TS as SO_4, ppm	7810	—	7820	—	19400
Other sulfur as SO_4, ppm	0	—	360	—	296
Na, ppm	90	—	364	812	3500
Mg, ppm	1250	1250	1270	1240	1250
Cl, ppm	90	—	90	80	80
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.04	0.12	—
SO_2 oxidized, gmole/hr	4.5	—	2.0	1.0	—
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	1.7	4.5	—
Test period, hrs	68	36	76	83	81

significant difference in the hold tank slurry particle size distributions between runs LS-0 and LS-4 (Figure 5), scanning electron micrographs (Figures 6 and 7) indicate that the platelet-like solid particles obtained with a 2250 ppm thiosulfate concentration are generally larger and have fewer defects than those obtained without sodium thiosulfate addition.

Significant solids quality improvement was also noted in TVA/Shawnee spray tower testing with sodium thiosulfate addition. However, the effects observed at the RTP pilot plant differ from the TVA/Shawnee findings in three respects: (1) no changes in solids qualities were obtained until the thiosulfate concentration reached 2000 ppm at RTP, whereas the TVA/Shawnee tests showed a significant increase in filter cake solids at thiosulfate ion concentrations as low as 500 ppm; (2) the oxidation was usually below 5% when solids quality changed at RTP, as contrasted with improvements in solids quality at TVA/Shawnee with oxidation as high as 15%; and (3) at RTP, increases in filter cake insoluble solids were always accompanied by higher settling rate, but only filter cake solids increases were reported by TVA/Shawnee testing.

Interesting results were derived from a run (LS-5) made with calcium chloride added to the hold tank to raise the chloride ion concentration to 3000 ppm while maintaining a 1000 ppm thiosulfate concentration (Table 3). An oxidation of 1.3% was obtained with sulfate saturation less than 2.3%. The hold tank slurry settling rate was 3.6 cm/min, and filter cake insoluble solids reached 75%. A Coulter Counter analysis indicated that the mean particle size was considerably larger than those from runs without calcium chloride addition (Figure 5). Scanning electron micrographs (Figure 8) also reveal significant changes in crystal morphology. Thick, bulky crystals (instead of thin platelets) were obtained after the calcium chloride addition. The results suggest a synergistic effect of $CaCl_2$ on thiosulfate in terms of both oxidation reduction and solids quality improvement.

TABLE 7. SUMMARY OF ADIPIC-ACID-ENHANCED LIMESTONE TEST RESULTS

Run No.	LA-0	LA-1	LA-2	LA-3	LA-4
S_2O_3 level, ppm	0	100	500	2200	2000
Gypsum scaling	Light	No	No	No	No
Oxidation, %	17	—	5.3	2.9	0.9
Sulfate saturation, %	185.8	64.1	10.6	4.3	4.0
Hold tank slurry settling rate, cm/min	—	1.2	1.2	1.8	4.0
Filter cake solids, %	48	49	52	59	69
SO_2 removal, %	88	89	93	95	96
Lime utilization, %	95	—	90	91	93
Ca, ppm	710	372	220	180	530
SO_4, ppm	9270	4820	1250	610	220
TOS as SO_3, ppm	3580	—	2890	4450	3660
TS as SO_4, ppm	—	—	6220	—	8920
Other sulfur as SO_4, ppm	—	—	640	—	540
Na, ppm	6650	—	4220	5060	5230
Mg, ppm	830	962	1230	1270	1320
Cl, ppm	5610	—	6040	5810	7490
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.29	—
SO_2 oxidized, gmole/hr	6.7	—	2.02	1.192	0.38
Adipic acid makeup, g/hr	25	—	25	25	25
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	1.6	7.6	—
Test period, hrs	258	38	248	72	78

Lime Slurry Process

Pilot plant tests were conducted in 1978 to evaluate sodium thiosulfate additive as an oxidation inhibitor in lime FGD systems [5]. No significant differences in overall oxidation were obtained between runs with and without thiosulfate. It was concluded that sodium thiosulfate was not an effective oxidation inhibitor in the lime scrubber.

Four pilot tests were conducted during the current test series to further investigate the oxidation inhibition effect of sodium thiosulfate in the lime scrubber (Table 4). One run (L-0) was made without sodium thiosulfate to provide a basis for comparing the effect of the additive on oxidation. The system was operated saturated with respect to sulfate (116% sulfate saturation in the hold tank). Filter cake analyses show that 20% oxidation was obtained, which is very close to the 23% attained during the 1978 tests [5]. Substantial decreases of calcium and sulfate ion concentrations in scrubbing liquor were obtained following the addition of sodium thiosulfate (runs L-1, L-2, and L-3). The system was operated unsaturated with respect to sulfate with thiosulfate addition, although no improvement of solids dewatering properties was obtained at 2000 ppm thiosulfate. Solid analyses also showed that oxidation was significantly reduced. Therefore, based on the results of current testing, it is apparent that sodium thiosulfate is an effective oxidation inhibitor in lime scrubbers.

TABLE 8. EQUILIBRIUM CONSTANTS OF METAL-THIOSULFATE COMPLEXES

Metal ion	i[a]	K[b]	Metal ion complexed, %[c]
Mn^{2+}	1	89	15.6
Fe^{2+}	1	148	23.1
Fe^{3+}	1	447	45.0
Co^{2+}	1	112	18.6
Ni^{2+}	1	115	18.9
Cu^{+}	3	10^{13}	>99
Cu^{2+}	2	10^{12}	>99

[a] i = number of thiosulfate ions assumed complexed with the metal ion

[b] K = metal-thiosulfate complex equilibrium constant = [complex]/([metal ion][thiosulfate]^i)

[c] 50 ppm metal ion and 250 ppm thiosulfate ion concentrations prior to complexing

To explain the discrepancy between the 1978 data [5] and current results, operating conditions and test procedures were compared. The main differences are the flue gas compositions and the scrubbing liquor chloride ion concentrations. The scrubber inlet flue gas contained no HCl, and the scrubbing liquor chloride ion concentration

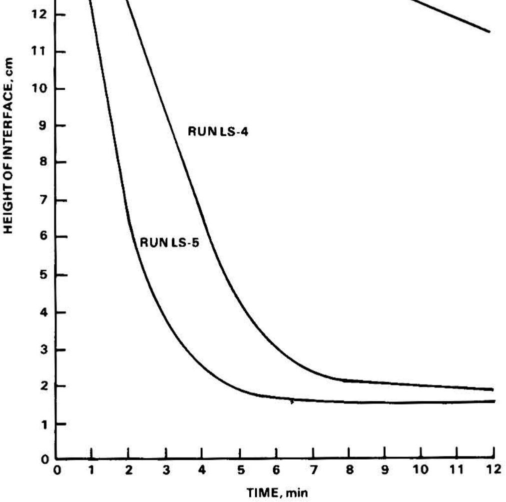

Figure 4. Settling curves for runs LS-0, LS-4, and LS-5.

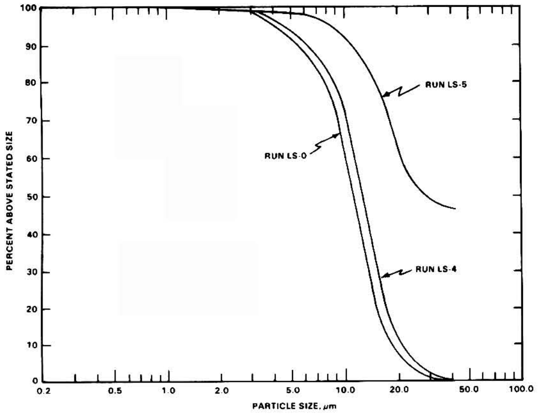

Figure 5. Results of coulter counter particle size analysis.

was below 300 ppm for current tests. However, during the 1978 tests, chloride was fed as HCl gas into the scrubber inlet duct, and the scrubbing liquor chloride ion concentration reached as high as 14,700 ppm. The data showed a strong correlation between the oxidation and the chloride ion concentration, regardless of whether thiosulfate was present or not. It is very likely that the effect of chloride on oxidation was greater than the effects of thiosulfate addition under the operating conditions of 1978 tests. In view of the fact that no high chloride runs were made during the current testing, it is concluded that sodium thiosulfate is an effective oxidation inhibitor in lime scrubbers when the scrubbing liquor chloride ion concentration is below 300 ppm. When the HCl in flue gas causes high chloride ion concentrations, thiosulfate could be less effective.

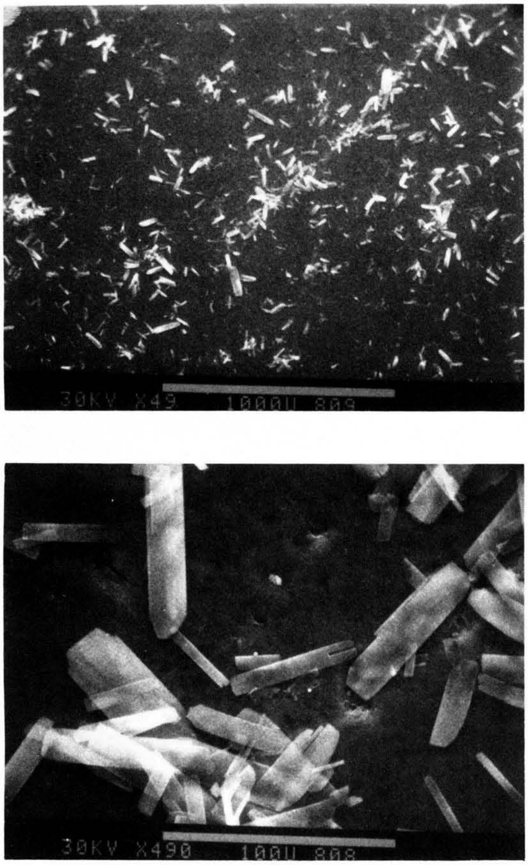

Figure 6. Scanning electron micrographs of solid products from limestone thiosulfate base case test (run LS-0, no thiosulfate addition). (a) Base case; 50x. (b) Base case; 500x.

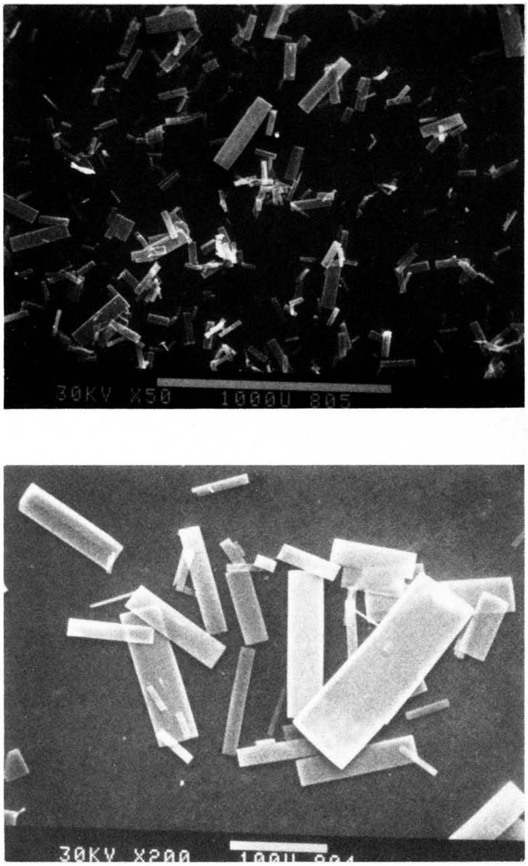

Figure 7. Scanning electron micrographs of solid products from limestone thiosulfate test with 2250 ppm thiosulfate (run LS-4). (a) 2250 ppm thiosulfate; 50x. (b) 2250 ppm thiosulfate; 200x.

Magnesium-Enhanced Lime/Limestone Slurry Processes

The SO_2 scrubbing capacity of lime/limestone slurry can be enhanced by increasing total magnesium. Magnesium acts to promote high concentrations of the ion pairs, $MgSO_4^\circ$ and $MgSO_3^\circ$, with the magnesium sulfite ion pair reacting with dissolved SO_2 to enhance SO_2 removal. Cronkright and Leddy [*11*] suggested that the ion pair equilibrium relationship can be expressed as:

$$\frac{[MgSO_3^\circ]}{[MgSO_4^\circ]} = \frac{\gamma_{CaSO_3}}{\gamma_{CaSO_4}} \times C = R \qquad (2)$$

where γ is the saturation level and C is a constant. If the calcium sulfate saturation, γ_{CaSO_4}, is substantially reduced by sodium thiosulfate addition and the sulfite saturation remained relatively constant, Equation (2) indicates that the value of R should increase substantially. Furthermore, Equation (2) also indicates that, when the total magnesium is constant, the $MgSO_3^\circ$ concentration, and thus SO_2 scrubbing capacity, should increase with R. Therefore, ad-

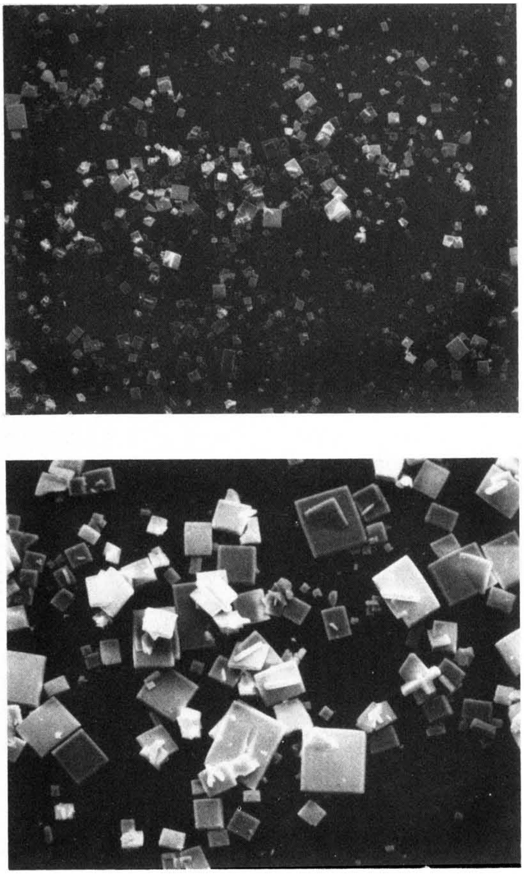

Figure 8. Scanning electron micrographs of solid products from limestone thiosulfate tests with 3000 ppm chloride and 1000 ppm thiosulfate (run LS-5). (a) 3000 ppm chloride, 1000 ppm thiosulfate; 50x. (b) 3000 ppm chloride, 1000 ppm thiosulfate; 200x.

dition of sodium thiosulfate to magnesium-enhanced lime/limestone scrubbers could result in greater SO_2 removal.

It is difficult to estimate the ion pair concentrations; however, they can be related to other measurable quantities. At constant pH and total magnesium, the ratio of magnesium ion pairs should be proportional to the ratio of total sulfite to sulfate:

$$\frac{[MgSO_3°]}{[MgSO_4°]} = C' \frac{[SO_3]_T}{[SO_4]} \tag{3}$$

where C′ is a proportionality constant. Combining Equations (2) and (3) and using data without sodium thiosulfate addition as the base case (labeled by subscript B), the following relationship is obtained:

$$\frac{([SO_3)_T/[SO_4])}{([SO_3]_T/[SO_4])_B} = \frac{(\gamma_{CaSO_4})_B}{(\gamma_{CaSO_4})} \tag{4}$$

Figure 9 shows the comparisons between pilot plant data and Equation (4). The deviation could be caused by factors such as sulfite and sulfate activity coefficients and the variation in sulfite saturation levels not included in Equation (4).

The increase of SO_2 removal efficiency with sodium thiosulfate addition was also verified by pilot plant testing. Table 6 shows that, for the magnesium-enhanced limestone scrubbing, SO_2 removal efficiency increased from 83% to 85% by adding 250 ppm thiosulfate. A further increase of SO_2 removal to 88% was obtained at 900 ppm thiosulfate. Slight increases in SO_2 removal were also obtained with the magnesium-enhanced lime scrubber as shown in Table 5.

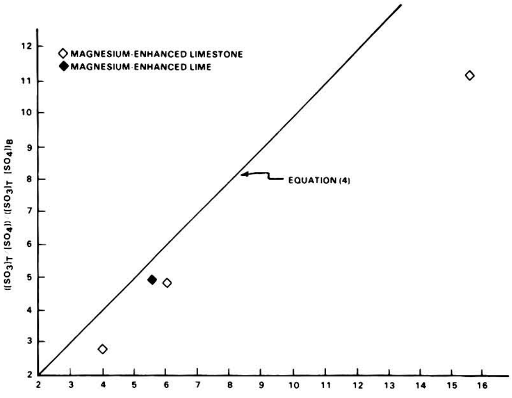

Figure 9. Comparison of pilot plant data with prediction curve of Equation (4).

Adipic-Acid-Enhanced Limestone Slurry Process

In addition to oxidation inhibition, the purpose of this testing series was to evaluate thiosulfate effects on adipic acid consumption. Previous long-term material balance tests showed substantial losses of adipic acid in excess of that expected from scrubber solution removed with filter cake [*12*]. Laboratory experiments indicated that organic acid degradation is one of the major mechanisms of excessive adipic acid losses. It was suspected that adipic acid was decarboxylyzed into shorter chain organic acids, ethane, methane, and carbon dioxide by free radicals generated during oxidation of the SO_2 species [*13*]. Since sodium thiosulfate can inhibit oxidation and possibly deactivate those free radicals, it is likely that the adipic acid consumption can also be reduced by the presence of thiosulfate ions.

The adipic acid feed rate was maintained at 25 g/hr for the base case (run LA-0) and for run LA-2 with 500 ppm thiosulfate (Table 7). As the scrubber approached steady state, significant reduction in oxidation was obtained with sodium thiosulfate addition. However, the adipic acid concentration remained constant; i.e., there are no apparent effects of sodium thiosulfate on the adipic acid consumption rate. The data indicate that the mechanism of oxidation inhibition by thiosulfate may be different from that of adipic acid degradation. More data are required to identify the mechanism of each reaction.

An unexpected result obtained during this series of tests was the increase in SO_2 removal efficiency with thiosulfate addition. The SO_2 removal was 93% at 500 ppm $S_2O_3^{2-}$ (run LA-2), or 5% higher than the 88% in the base case (run LA-0). Although part of the increase is due to higher magnesium ion concentrations, the data suggest that there is no negative effect of sodium thiosulfate on the mass transfer enhancement by adipic acid.

Improvement in solids dewatering properties was observed when the thiosulfate ion concentration was raised to 2200 ppm (run LA-3). The hold tank slurry settling rate increased from 1.2 to 1.8 cm/min, and filter cake insoluble solids also increased from 52 to 59%. The synergistic effects of calcium chloride and thiosulfate were confirmed by run LA-4. After the chloride ion concentration was raised to 7500 ppm, oxidation decreased to 0.9%, hold tank slurry settling rate reached 4.0 cm/min, and the filter cake insoluble solids increased to 69%.

CONCLUSIONS

The following conclusions are drawn from the pilot testing data:

1. Sodium thiosulfate is an effective additive for inhibiting sulfite oxidation. Both sulfate saturation and gypsum scaling were significantly reduced by $Na_2S_2O_3 \cdot 5H_2O$ addition in all five lime/limestone slurry FGD processes tested.
2. Deactivation of free radicals is the most likely oxidation inhibition mechanism of sodium thiosulfate. The concentrations of thiosulfate ion required to maintain unsaturated FGD operation and thus avoid gypsum scaling are 100 to 200 ppm. However, part of the thiosulfate added degrades or transforms into other sulfur species such as polythionates and accumulates in the scrubbing slurry.
3. In order to attain a sustainable thiosulfate concentration, the scrubber had to be spiked with doses of $Na_2S_2O_3 \cdot 5H_2O$ about 10 times higher than that required by a material balance. Pilot plant data indicate that, after the initial spiking, the normal consumption rate to achieve the oxidation inhibition effect should be in the range of 1 to 3 mmole $Na_2S_2O_3$/mole SO_2 absorbed for both the lime and limestone slurry FGD systems.
4. Sodium thiosulfate is an effective oxidation inhibitor in lime slurry scrubbers when the scrubbing liquor chloride ion concentration is below 300 ppm. When the HCl in flue gas caused high chloride ion concentration, thiosulfate addition could be less effective.
5. Improvement of solids dewatering properties was observed with the addition of sodium thiosulfate to both conventional and adipic-acid-enhanced limestone processes. Pilot plant data indicate that after the thiosulfate ion concentration reached 2000 ppm, both slurry settling rate and filter cake solids concentration increased. The effectiveness of thiosulfate on oxidation inhibition was enhanced by calcium chloride addition. However, thiosulfate accumulation had little effect on solids properties in the lime and magnesium-enhanced lime/limestone scrubbers.
6. The SO_2 removal efficiency of magnesium-enhanced lime/limestone scrubbers can be increased by thiosulfate addition through the decrease of sulfate saturation and increase of magnesium sulfite ion pair concentration.
7. No adverse effects of sodium thiosulfate addition on adipic-acid-enhanced limestone scrubbers were found. The SO_2 removal efficiency increased with the accumulation of thiosulfate in the pilot plant. Although oxidation was substantially reduced, no significant differences in adipic acid consumption rate were obtained between runs with and without thiosulfate.

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Treatment and Disposal of Wastes From Dry SO_2 Control Processes

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Sulfur dioxide (SO_2) control processes which produce dry waste products have attracted increased interest in recent years based on economic and environmental considerations. This paper compares the chemical composition and physical properties of fly ash and dry waste products from existing SO_2 control processes with the properties of dry waste from emerging technologies such as furnace sorbent injection and fluidized bed combustion. Based on this information, design features are reviewed for material handling systems and for dry waste landfill sites. Environmental impacts from dry waste handling and disposal are discussed. The potential for commercial utilization of dry wastes from emerging SO_2 control technologies is also addressed.

INTRODUCTION

Sulfur dioxide (SO_2) control processes which produce dry wastes include dry flue gas desulfurization (FGD), fluidized-bed combustion (FBC), and furnace sorbent injection (FSI). Dry waste products are considered to be a major advantage for these processes compared to conventional wet FGD due to the elimination of waste dewatering equipment. A comparison of the chemical composition and physical properties of waste products from dry SO_2 control processes is discussed in this paper. Comparisons are also made with the composition and properties of coal fly ash, since this material has a long history of dry landfill disposal.

Utilities and industries have amassed extensive experience over the past 10 years with the dry landfill disposal of fly ash, bottom ash, and fixated wet FGD waste from coal-fired power plants. The use of wet ponding for ash or FGD waste disposal has come under increased regulation (or prohibition) at the state and local level, which has stimulated increased interest in dry landfill disposal. Dry landfill experience with ash and fixated wet FGD waste will be useful in determining the design of waste handling systems and landfills for new SO_2 control technologies which produce dry waste products.

Dry FGD systems (spray dryers) have been selected by many utilities and industries in the last five years as an economically attractive method of SO_2 control at power plants firing low-sulfur coal. The waste product, which generally contains a high percentage of fly ash, is similar to fly ash in its physical properties. Dry landfill disposal has been universally selected as the disposal method for spray dryer FGD waste from utility installations. Emerging technologies, such as fluidized-bed combustion (FBC) and furnace sorbent injection (FSI), offer revolutionary changes in SO_2 control. Although the physical properties and chemical composition of their waste products have not yet been well documented, dry landfill disposal is also expected to be selected for these wastes.

COMPARATIVE CHEMICAL COMPOSITION OF DRY WASTES

The chemistry of wet scrubber FGD systems has been thoroughly described elsewhere. Briefly, wet scrubber systems operate through the reaction of SO_2 with an alkali slurry, usually formed by the slaking of lime (CaO) or by wet grinding of limestone ($CaCO_3$). The SO_2 is first absorbed by the slurry droplets. Subsequent reactions with dissolved limestone ($CaCO_3$) or slaked lime ($Ca(OH)_2$) results in the precipitation of a waste product which is primarily hemihydrated calcium sulfite ($CaSO_3 \cdot 1/2H_2O$). Two forms of calcium sulfate are also present to varying degrees. Under conditions of limited oxidation, hemihydrated calcium sulfate ($CaSO_4 \cdot 1/2H_2O$) can form a solid solution with the sulfite, in amounts up to 15% of the total moles of calcium. Under conditions of high sulfite oxidation, the sulfate will precipitate separately as dihydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$). The relative amounts of sulfite and sulfate formed depend on several factors, including boiler excess air, type of reactant, slurry pH, coal sulfur content, SO_2 collection efficiency, and the use of chemical additives or forced oxidation. Sulfate concentrations are generally kept below 20% of the total moles of calcium to prevent scaling in the absorbers, unless the system is designed for forced oxidation and subsequent dewatering or wet ponding of the waste. The most common process for producing a dry waste product from wet scrubber sludge is the waste fixation process, in which fly ash and additive lime are mixed with the waste sludge in a pug mill. This promotes the formation of pozzolanic compounds which result in a final product with properties similar to a low-strength concrete.

Dry FGD systems (spray dryers) operate in a similar manner. The SO_2 must first be absorbed by the atomized lime slurry droplets. Within the droplets, the absorbed SO_2 reacts with the slaked lime to form hydrated calcium sulfite and sulfate. As the reaction products precipitate, the water evaporates and the reaction is restricted to the remaining interstitial water. By the time the particle leaves the absorber, evaporation and the chemical reaction have removed all but a small residual water content (generally less than 5%). The dry waste product is then collected with the fly ash in a particulate control device, usually a baghouse. A percentage of the collected product, which typically contains 60% to 80% fly ash, is generally slurried and recirculated to the absorber to increase lime utilization and to take advantage of the inherent alkalinity of some fly ashes. The sulfite/sulfate ratio in the dry waste product is not substantially different from that for wet FGD systems where forced oxidation is not employed. By wetting the dry waste, pozzolanic reactions similar to those in fixated waste are produced, resulting in a product which sets up. The use of additive lime is usually not required due to excess lime reactant and the high lime content of the fly ash from low-sulfur western coals often associated with dry scrubbing.

FSI involves the injection of a pulverized lime or limestone sorbent directly into the upper furnace of a pulverized coal-fired boiler. The SO_2 reacts with the sorbent at the elevated furnace temperature to form anhydrous calcium sulfate. Little calcium sulfite is formed in the oxidation environment of the furnace. The sulfate waste is removed along with the fly ash in an electrostatic precipitator or baghouse collector. To date, FSI systems have not included waste recirculation to increase lime utilization. The waste product therefore contains significant amounts of free lime.

In the FBC process, limestone sorbent is injected into the fluidized-bed combustor for SO_2 control. The limestone is calcined to lime at the bed temperature (typically 1500 F to 1600 F (1089 K to 1144 K) for optimum SO_2 control), and the SO_2 reacts with the lime to form an anhydrous calcium sulfate waste. As with the FSI process, little sulfite is formed in the oxidizing environment of the combustor. The sulfate waste is collected along with the fly ash in a primary cyclone and a secondary baghouse or electrostatic precipitator. Some of the waste may be recycled to the combustor bed to increase sorbent utilization and promote more complete combustion.

Three types of dry waste are produced in the FBC system: spent bed material, cyclone catch, and fly ash. The wastes may be mixed for disposal or may be disposed of separately. Spent bed material, primarily partially spent sorbent with a lesser amount of coal ash, is removed from the combustor at the bed temperature and must be cooled before being conveyed to a silo. Rotating drum or screw conveyor coolers have been used for this purpose. The heat extracted may be used to produce low-pressure steam, to heat combustion air, or to dry the incoming sorbent. Combustion products leaving the furnace pass through a cyclone collector to remove and recycle unburned coal particles. Some of the cycle catch also goes to waste.

Fly ash, collected in the particulate collector (typically a baghouse) and economizer hoppers, has a higher coal ash content. It also contains partially spent sorbent, partially calcined sorbent, and unburned carbon. The relative amounts of fly ash and spent bed material produced depend on the design of the combustion bed and on the sorbent particle size distribution.

Table 1 lists typical chemical compositions for dry waste products from SO_2 control processes. The compositions listed are for the waste as produced; no account is taken for subsequent pozzolanic reactions. The remaining waste constituents not listed in Table 1, aside from a small percentage of sorbent inerts, are associated with the fly ash and can vary widely depending on the type of coal fired. Trace element analyses of various dry wastes are largely dependent on the fly ash constituents.

An examination of Table 1 reveals several significant differences between the waste products. Fixated wet FGD waste is distinguished by a relatively high water content. Pozzolanic reactions will occur in this waste if given sufficient time. The other wastes require water addition for pozzolanic reactions to occur. The lime content of the fixated waste is the lowest of the four wastes tabulated, and includes additive lime which is blended with the waste as part of the fixation process. The lime is hydrated by the water in the FGD waste to form calcium hydroxide ($Ca(OH)_2$).

Spray dryer waste typically has a much lower water content and a higher lime content than fixated waste. The unreacted lime is also in the form of calcium hydroxide. The analysis in Table 1 represents waste from a dry FGD system where recirculation is used to increase lime utilization. Typical analyses for FSI and FBC wastes shown in Table 1 are based on the limited data available. The values shown for FBC waste represent the combined fly ash and spent bed material. The major difference between these wastes and the fixated and spray dryer wastes is that the FSI and FBC sorbent products are in the form of anhydrous calcium sulfate rather than hydrated calcium sulfite and sulfate. The water content of these wastes is lower than that of spray dryer waste while the lime content is higher, especially for the FSI process which does not use sorbent recirculation in its present form. Unlike fixated and spray dryer wastes, the unreacted sorbent is present as calcium oxide (CaO).

POZZOLANIC REACTIONS IN DRY WASTE PRODUCTS

The fixation of sludge from wet FGD systems converts a wet waste product to a material which can be landfilled. The raw sludge, typically 50% solids, is first blended with fly ash and small quantities (2% to 5% by weight of the dry solids) of lime, producing a product with reduced water content. Fly ash typically represents from 30% to 70% of the total waste on a percent solids basis. Pozzolanic reactions, similar to those which occur in portland cement, take place in the fixated FGD waste. The most important reaction is:

$$3Al_2O_3 \cdot 2SiO_2 + 12CaO + 21H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3(3CaO \cdot Al_2O_3 \cdot 6H_2O)$$

This reaction will also occur in unblended wetted fly ash if the ash has a high lime content or if lime is added to the ash. Additional pozzolanic reactions occur between the calcium sulfite and sulfate and the ash in the waste. These include:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + 20H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + CaSO_3 \cdot 1/2H_2O + 1/2H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 7H_2O$$

Due to the high water content of fixated wet FGD waste, the pozzolans will react without further processing. The reactions typically take one month or more to reach completion.

Wastes from spray dryer FGD systems exhibit the same reactions outlined above. However, the material will not set up unless water is added, due to the low water content of the waste. Water is typically added at the plant site or at the disposal site just prior to placement in the landfill. Experience gained with spray dryer waste over the past several years has not revealed any unusual difficulties compared to the disposal of fly ash or fixated FGD waste. Little experience is available with the disposal of FSI or FBC wastes. The high lime content of these wastes should promote pozzolanic reactions without lime addition. However, water addition is required as with spray dryer waste.

The fact that FSI and FBC wastes contain anhydrous calcium sulfate and calcium oxide affects the reactions occurring in these wastes. Pozzolanic reactions can take a month or more to go to completion. Water added to FSI or

TABLE 1. TYPICAL CHEMICAL COMPOSITION OF DRY WASTE PRODUCTS [6]

Chemical Constituents	Fixated FGD Waste	Spray Dryer FGD Waste	Furnace Sorbent Injection Waste	Fluidized-Bed Combustion Waste
$CaSO_3 \cdot 1/2H_2O$	18%	14%	—	—
$CaSO_4 \cdot nH_2O$	8%	8%	—	—
$CaSO_4$ (anhydrous)	—	—	28%	32%
CaO[1]	8%	19%	38%	23%
$CaCO_3$, $Ca(OH)_2$	4%	3%	—	—
H_2O	30%	2%	1%	1%
SiO_2, other ash constituents and reactant inerts[2]	32%	54%	33%	43%

[1] Includes CaO in fly ash

[2] Primarily fly ash constituents

FBC waste would rapidly be used to hydrate the calcium sulfate and free lime. These reactions are exothermic and have produced high temperatures and steaming in the waste. Steaming and heaving of FSI wastes in the landfill have been reported. Sufficient water must be provided to support long-term pozzolanic reactions in the face of short-term hydration water requirements, without excessive deterioration of physical properties of the waste, such as compressive strength and angle of repose. The use of retarding agents such as calcium lignin sulfonate may be required for reactive wastes to slow the cementitious reactions.

ENVIRONMENTAL IMPACTS FROM DRY WASTE PRODUCTS

The U.S. EPA has ruled that fly ash, fixated FGD waste, and spray dryer FGD waste from existing power plants are not hazardous wastes as defined under the Resource Conservation and Recovery Act (RCRA) regulations. In a recent study performed for the EPA, it was concluded that FBC waste should be similarly classified as nonhazardous. However, these wastes are regulated as solid waste under RCRA, and the potential for leaching of undesirable substances from landfill disposal sites for these wastes may require the collection and treatment of leachate.

The potential for leaching from dry landfill waste disposal sites is a function of the permeability and the chemical composition of the waste material and underlying soils. The presence of leachable elements in the waste largely depends on the type of fly ash with which the FGD waste is codisposed. The chemical composition of the leachate is, therefore, more a function of the fuel fired than the SO_2 control process selected.

Spray dryer FGD systems have been most widely utilized on units firing low-sulfur western coal. Fixated waste from wet FGD systems may be associated with any type of coal, although medium- to high-sulfur midwestern coals and Texas lignites are most prevalent. FSI, though still in the development phase, is likely to have its greatest application as a retrofit technology to reduce SO_2 emissions from older units firing medium- to high-sulfur midwestern coal. FBC is distinguished by great fuel flexibility; although the use of low-sulfur coal is unlikely for economic reasons, a wide variety of other fuels can be burned, such as petroleum coke or coal mining wastes.

Table 2 lists the average trace element contents of ash from coals of various rank. In general, the low-sulfur subbituminous and lignite fuels used with the spray dryer FGD systems tend to have higher concentrations of barium, boron, copper, and strontium, while midwestern medium- to high-sulfur bituminous coals associated with wet FGD or FSI systems contain larger amounts of beryllium, cobalt, nickel, scandium, and vanadium.

Representative physical properties for dry waste products are listed in Table 3. The waste materials should have a permeability of less than 10^{-5} cm/sec to be suitable for dry landfill disposal. All of the dry wastes are expected to meet this criterion, although wetting of the wastes (other than fixated waste) is necessary to promote pozzolanic reactions that reduce permeability to these levels. Permeability generally decreases with time after disposal as the waste material cures.

Atmospheric fugitive emissions are generally not a problem with fixated FGD waste due to the high water content. It is routinely stacked out in curing piles without any form of dust suppression. Fly ash, spray dryer waste, FSI waste, and FBC waste must be wetted prior to open handling or landfill disposal, or significant fugitive dust problems could occur. These wastes can be transported to the disposal site by pneumatic conveyors or closed trucks and can be wetted just prior to placement in the landfill. The waste can also be wetted at the plant site for transport to the landfill in open trucks. Water at 18% to 25% by weight has been added to fly ash with good results. Reactive low-sulfur coal fly ash will set up in the trucks if too much water is added. The maximum added water may be as low as 8% to 12% if the fly ash lime content exceeds 15%. In some cases, subsequent spray wetting of the landfill surface with water or a surfactant may be necessary to suppress wind- or vehicle-induced fugitive dust emissions.

FSI and FBC wastes may present additional environmental concerns due to their high calcium oxide content. Added water at 15% to 30% by weight may be required. Laboratory tests with FBC wastes have produced leachate pH values of 10 to 12. Neutralization of collected leachate and rainfall runoff may be necessary at the disposal site. High sulfate and calcium concentrations and high total dissolved solids have also been observed in the leachate. Another problem unique to these wastes is their thermal activity, due to the heat of hydration of the calcium oxide and calcium sulfate present. If the wetted waste is stacked out in a curing pile, then steaming of the waste may result.

LANDFILL SITE DESIGN

Landfill sites for dry waste disposal should be sized to contain the waste generated over the life of the plant at the projected capacity factors while firing coal with the maximum anticipated ash and sulfur contents. Since this leads to a disposal site which is quite large, cellular development of the site is desirable. The waste is distributed in horizontal layers by conventional earthmoving equipment in limited areas of the disposal site, which are filled, closed, and seeded before a new area is opened. Cellular development reduces the required capacity of runoff and leachate collection systems, lowers fugitive dust emissions, and distributes the cost of disposal site development over the life of the plant.

Prior to disposal site design, the subsurface soil strength should be evaluated and a bearing capacity and settlement analysis should be performed to determine how high the waste may be piled and at what rate the pile height may be increased. Side-slope design should include frequent benching to prevent slope failure.

TABLE 2. AVERAGE TRACE-ELEMENT CONTENTS OF THE ASH FROM U.S. COALS OF VARIOUS RANK (PPM) [*12*]

Element	Anthracite	Low Volatile Bituminous	Medium Volatile Bituminous	High Volatile Bituminous	Lignite and Subbituminous
Silver	<1	<1	<1	<1	<1
Boron	90	123	218	770	1010
Barium	866	740	896	1253	5027
Beryllium	9	16	13	17	6
Cobalt	81	172	105	64	45
Chromium	304	221	169	193	54
Copper	405	379	313	293	655
Gallium	42	41	—	40	23
Germanium	<20	<20	—	—	—
Lanthanum	142	110	83	111	62
Manganese	270	280	1432	120	688
Nickel	220	141	263	154	129
Lead	81	89	96	183	60
Standium	61	50	56	32	18
Tin	962	92	75	171	156
Strontium	177	818	668	1987	4660
Vanadium	248	278	390	249	125
Yttrium	106	152	151	102	51
Ytterbium	8	10	9	10	4
Zinc	—	231	195	310	—
Zirconium	688	458	326	411	245

The data in this table was determined by using atomic absorption analysis on coals which were ashed in air at 1100 F (866 K). The number of coal samples which were tested varied with the rank of the coal. A total of 57 coal samples were tested. In addition to the variations in trace-element content with rank indicated, considerable variation in samples within any particular rank can also be expected.

Although the disposal of fixated FGD waste generally does not require a low-permeability lining to prevent groundwater contamination, regulating agencies may require linings on a case-by-case basis. Landfill sites designed by Sargent & Lundy have included evaluation of the need for a liner beneath all types of dry disposal piles, and suitable impermeable barriers have been provided at the request of state regulators. Typically, a 12-inch (30 cm) thick bentonite clay layer with 10^{-7} cm/sec permeability was recommended. If required by the state, a drainage blanket is provided above the clay lining. Typically composed of bottom ash, the drainage blanket prevents saturated conditions in the pile that can cause loss of stability, prevents capillary rise of groundwater into the pile, and facilitates leachate collection. Bottom ash not used in the drainage blanket is usually disposed of separately, since it is a salable product. A cross-section of a dry landfill disposal site with leachate collection is presented in Figure 1.

Preliminary laboratory testing has indicated that conventional synthetic liners and bentonite clay liners are compatible with leachate from FBC waste. All of the liners showed some loss of strength with time of exposure, with Hypalon™ (chlorosulfonated polyethylene) exhibiting the least decrease in strength.

A perforated metal pipe collection system delivers leachate from the drainage blanket to one or more collection ponds where settling occurs. For FBC and FSI wastes, chemical neutralization of alkaline leachate may be necessary. The leachate ponds should be provided with a synthetic liner to isolate the groundwater from any undesirable substances. The liner should be thick enough to withstand stresses produced by local settling. The clarified leachate is then pumped back to the plant for treatment and reuse. If the leaching rate is small and the disposal site is remote, it may be more economical to haul the clarified leachate back to the plant by truck.

A separate sedimentation pond and system of drainage ditches should be provided to handle disposal pile runoff. The runoff is typically retained until settling of suspended solids brings the runoff within the applicable water discharge standards. It is then directed to the natural drainage course.

Closure of one or more landfill cells begins with shaping the pile to prevent rainfall accumulation. The pile is then covered with 2 feet (60 cm) of soil, typically 6 inches (15 cm) of clay, 12 inches (30 cm) of random material, and 6 inches (15 cm) of topsoil. The cover layer is then seeded. Paved downcomers should be provided from the top of the pile and the side benches to prevent side erosion of the slopes and to convey the runoff to the natural drainage course.

WASTE HANDLING

Transfer of dry waste products from particulate collection hoppers to a common collection point (silo) can be by vacuum or pressure pneumatic systems or drag chain conveyors. Options for the conveying of dry waste products to the final disposal site include belt conveyors, pneumatic conveyors, and trucking. Wet sluicing of the waste is also possible, but not used for high-calcium wastes because of scaling of the sluice piping. Trucking is the most flexible method and results in the highest availability, since trucks can be readily replaced. Private contractors can be used to haul all of the waste or to supplement a utility-owned fleet of trucks. However, trucking is labor-intensive, resulting in operating costs which may rise significantly over the life of the plant. Belt conveyors require fixed loading and discharge points and have higher capital and operating costs but a lower rate of depreciation.

A primary factor in selecting whether waste should be trucked or conveyed to the landfill site is the proximity of the site to the power plant. The use of belt or pneumatic conveyors is generally not practical unless the disposal site is adjacent to the plant. In particular, pneumatic con-

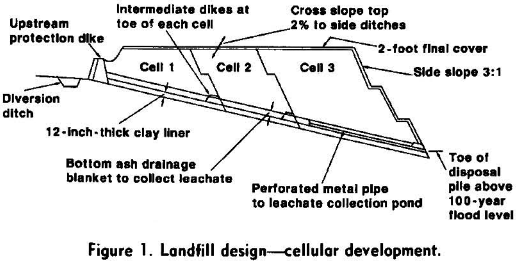

Figure 1. Landfill design—cellular development.

TABLE 3. PHYSICAL PROPERTIES OF DRY WASTE PRODUCTS [22, 23]

Waste Products	Permeability (cm/sec)	Compressibility[1] (psi)	Density[2] (lb/ft^3)
Fixated FGD waste	$5 \times 10^{-5} - 10^{-7}$	180-340	95-105
Spray Dryer FGD waste	$10^{-6} - 10^{-7}$	50-1,350	60-90
Fly ash			
Bituminous	$10^{-4} - 10^{-7}$	260-3,230	70-120
Subbituminous	$1 \times 10^{-5} - 3 \times 10^{-6}$	1,300-6,500	75-105
Lignite	$9 \times 10^{-6} - 1 \times 10^{-7}$	1,300-141,000	100-120

Notes:
1. 1 lb/ft^3 = 16.02 kg/m^3
2. 1 psi = 6895. N/m^3

veying is not practical for distances much over 1,000 feet (300 meters) due to the high power consumption of the conveying air blowers. In any case, trucking of waste from the conveyor discharge to various locations in the landfill will probably be required (particularly if cellular site development is used), so that trucking over the entire route may be preferable.

Conveyors should be sized to permit handling, during a single shift per day, of all of the waste generated in a full day at 100% load while firing coal with the maximum ash and sulfur contents. Belt conveyors are typically used for fixated wet FGD waste, which is not easily fluidized due to its high moisture content. However, belt conveyors should be enclosed to reduce fugitive dust and waste freezing problems.

Pneumatic conveyors are used for fly ash and spray dryer waste, and can be expected to be equally suitable for FSI and FBC wastes. Long pneumatic conveyors require short-term silos and booster blowers at intermediate points to provide sufficient conveying air pressure. Redundant blowers are required to provide adequate system availability.

If the disposal site is remote from the plant site, then trucking is the only viable alternative. If public highways are to be used to haul the waste, then trucks in the 25-ton (22,700 kg) range or smaller generally must be used to comply with vehicle width and weight regulations. If a private haul road is to be constructed, then trucks in the 50-ton (45,400 kg) or larger capacity range may be employed to minimize the number of trips. If the disposal site is near the power plant, then an asphalt-paved private haul road is desirable to minimize public visibility and to limit offsite fugitive emission problems. Crushed-rock haul roads are adequate at the disposal site. If the number of truck trips per day is excessive, the haul roads may require the construction of overpasses at major highway crossings. Either open trucks or closed trucks may be used to haul the waste. Open trucks are readily used for fixated waste, but should be covered with a tarpaulin to prevent windborne loss of material. Fly ash, spray dryer waste, FSI waste, and FBC waste must be wetted in a pug mill-type mixer prior to transportation in open trucks to suppress fugitive emissions. For these wastes, closed trucks with provision for self-contained pneumatic unloading may be the best choice.

Fixated waste is generally dumped on the ground at the plant site following fixation to form a curing pile, since fugitive emissions are not a problem from this type of waste product. Front-end loaders are then used to load the material into trucks. Fly ash, spray dryer waste, FSI waste, and FBC waste should be stored in silos provided with fugitive dust collection devices. Sufficient storage capacity should be provided for any of the waste products to permit landfill disposal during a single shift per day, as nighttime operations are generally impractical. It may be desirable to aircure FBC and FSI wastes due to the heat and steam generated on wetting, although fugitive emissions must meet environmental regulations.

WASTE UTILIZATION

Fly ash and bottom ash are the waste products with the most extensive history of utilization (Table 4). Fly ash has been used fairly widely as a fill material and as an additive to concrete. Although limited tests have shown that FGD wastes can also be commercially utilized, this has not been done on a significant scale. Less than 1% of wet FGD wastes are presently being utilized. The forced oxidation of wet FGD waste has been used to produce marketable gypsum for use in wallboard and cement, particularly in Japan. However, FGD production of marketable gypsum has been limited in the United States due to the availability of natural gypsum and the presence of fly ash and chlorides in the FGD gypsum. Fly ash results in discoloration of the wallboard product, while high chloride content can corrode nails used for wallboard installation and can result in debonding of the paper from the surface of the wallboard.

Limited-scale demonstrations have shown that fixated wet FGD waste can be used as a fill material, as a filler in concrete, as a base material for roads and parking lots, and to create artificial reefs. Laboratory investigations have shown that spray dryer FGD waste has better pozzolanic properties due to its higher lime content, and can also be used for these purposes. Spray dryer waste can also be mixed with water and compressed into pellets to produce a gravel-like material. However, FGD wastes have not been able to displace currently used materials in these applications, and the market for fixated or spray dryer wastes is limited compared to the amount of waste generated.

Due to their high free-lime content, FSI and FBC wastes may have uses in addition to those already noted for other wastes. One study investigating the use of cemented FBC waste for road construction indicated that this material exhibited exceptionally high compressive strength. Agricultural uses, such as the neutralization of acidic soil as well as neutralization of municipal and industrial wastes, may be practical. However, due to the larger particle sizes in the waste (especially for the FBC system), grinding of the waste may be necessary before utilization.

TABLE 4. UTILIZATION OF COAL ASH [21]
(PERCENT)

Use	Fly Ash	Bottom Ash
Aggregate	0.7	1.3
Blasting grit	NA	24.5
Cement additive	18.6	9.7
Concrete admixture	35.6	2.5
Concrete block	3.6	0.9
Dam construction	1.8	0.0
Fill material	4.5	13.8
Grouting	6.2	NA
Hazardous waste fixation	0.7	NA
Ice control	0.5	11.4
Road construction	2.6	11.8
Roofing granules	NA	13.6
Miscellaneous	25.1	10.4

CONCLUSION

SO_2 control processes which produce dry waste products are increasingly being applied to both utility and industrial boilers. The wastes generated by these processes, which typically contain large quantities of coal ash, can be treated and disposed of using techniques similar to current practice for coal fly ash. An important difference between fly ash and the dry SO_2 control waste products is the increased lime content of the wastes and the resulting hydration reactions (for FSI and FBC) which occur when water is added. These same properties, however, should increase the marketability of wastes from dry SO_2 control processes.

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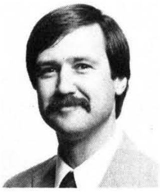

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A Rapid Procedure for Selecting Attenuators for IITRI Dynamic Dilution Olfactometers

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Dynamic dilution olfactometers provide a range of odor dilutions for presentation to panelists. Reliable odor thresholds of source emissions can be evaluated consistently only if the unknown odor thresholds fall in the middle of the dilution range of the olfactometer being used for a given test.

This paper describes a fast and reliable procedure for ensuring that individual panelist thresholds will fall in the middle of the dilution range through selection of appropriate attenuators. The recommended approach makes use of the best capabilities of the ASTM and IITRI methods. It has been tested successfully with acetic acid vapors.

INTRODUCTION

The establishment and enforcement of odor control regulations require fast and reliable procedures for the determination of both ambient and source odor levels. The assessment of community odor problems often implies measurements at very low concentrations of mixtures of odorants, rather than single chemicals. Physico-chemical methods for measuring such low concentrations require cumbersome procedures. The instrumentation needed for such work is simply not practical for routine measurements in the field or laboratory. Fortunately, the human nose is so sensitive that it can respond to thousands of different odorous stimuli and detect both low and high concentration of odorants simultaneously. However, all human noses do not have the same sensitivity for odor detection [*1*].

Literature abounds with conflicting claims with respect to odor thresholds even for pure substances [2, 3]. The different values of odor thresholds are due, at least in part, to the variety of equipment and procedures adopted for the odor measurements.

Leonardos [4] reports that the static odor test room procedure tends to give threshold values similar to those obtained by the dynamic dilution techniques. He also found that the ASTM syringe method produced considerably different threshold values than those established by the odor test room or the odorhood techniques.

Dravnieks and Prokop [5] showed that thresholds obtained by the dynamic dilution forced choice triangle method did not agree well with the corresponding ASTM odor values. A comparison of the Hemeon Odor Meter [6], another dynamic dilution method, with the ASTM static dilution method [7] shows similar trends. The differences between the two threshold values increase at lower concentrations. Dravnieks et al. [8] have also developed a relationship between ambient odor measurements made with a dynamic dilution forced choice triangle olfactometer and a scentometer [9], a device commonly used for odor control regulation.

A study conducted by The Research Corporation of New England on typical process emissions from rendering, pulp and paper, food processing, oil refining, steel mill, resin and enameling plants [*10*] has shown that the reproducibility of the odor measurement systems varied with odor type and level. Dynamic dilution systems produced lower variations (52 to 78% based on a 95% confidence limit) than the static method (83 to 144%). According to this study, the forced choice dynamic dilution technique of presenting odor samples was the best method for minimizing panel guessing ("false positive" responses) and panel leader influence. In practice, the high flow sample streams of 10 to 75 cubic feet per minute in the Hemeon Odor Meter created confusion among panelists. They were not sure whether they were sensing odor or reacting to odorous gas stream pressure in their noses [*11*]. High odor flow rates also increased the chance of contaminating the background odor levels. The low flow of the sample streams in the forced choice dynamic dilution method tended to increase the effect of background air at low odor levels thus requiring a high degree of cleanliness.

In spite of their limitations, the scentometer [9] and ASTM syringe method [7] are still being used by many environmental agencies. However, they are now considered to be inadequate for rigorous regulatory purposes.

The popular ASTM static method [7] is not an effective means of presenting an odor to a panelist. Under poor supervision, panelists may not rigorously follow the rules related to expulsion of the sample into the nose for odor sensing. Since the method is a static one, only 100 mL of the odorant are available. This amount of sample is usually not adequate for the panelists to reinforce their original judgements. Preparation of syringes for presentation to panelists may not necessarily provide reproducible dilution levels. The ASTM syringe method also requires significant time to make up all the dilutions needed for an eight to ten member panel as well as to clean the syringes and the transfer needles to maintain them free from any contamination.

According to Research Corporation of New England studies [12], the performance of the ASTM method deteriorates with increasing odor levels, and is generally poor for sulfur compounds such as hydrogen sulfide and dimethyl disulfide, due to odorant adsorption onto glass surfaces of the syringes. Consequently, there has been a general trend towards the dynamic olfactometer approach.

Dynamic dilution methods are simpler, faster and probably more accurate. They provide a continuous flow of odor sample. However, the choice of odor flow rate is difficult. Odor flow rates corresponding to normal inhalation rates seem to be desirable from a perceptual point of view, but high flows could confuse panelists if they are not sure whether they sense the odor or are reacting to odorous gas stream pressure in their noses [11]. High odor flow rates also increase the chance of contaminating the background. In addition, they consume the sample very rapidly.

The Illinois Institute of Technology Research Institute (IITRI) olfactometer [13], which presents odor samples by the forced choice dynamic dilution technique, is a method for minimizing some of the problems associated with the ASTM syringe procedure. Continuous flow of odorant permits panelists to recheck their original judgement prior to signalling. The low sample flows associated with the IITRI olfactometer reduce panel fatigue and require only small amounts of sample. However, low sample flows can create confusion among panelists as to whether they are sensing the given odor or the background, especially at low odor levels.

In spite of its apparent advantages over static methods, recent studies with the IITRI olfactometer on a variety of industrial stacks show that with any source odor of unknown strength it is difficult to measure odor thresholds with a high degree of precision unless some pre-testing is carried out. A threshold value can be measured with confidence only if the unknown odor threshold value lies approximately in the middle of the dilution range available for a given test. For example, by design, the IITRI olfactometer provides a range of six dilution levels according to the scheme:

Port Number:	D_1	D_2	D_3	D_4	D_5	D_6
Dilution Level:	1600	540	180	60	20	7
	maximum dilution					minimum dilution

In conducting an odor test, several situations can arise with an unknown odor sample. If the overall panel detectability variation is greater than D_1/D_6 some panelists would not detect any odor at either the minimum or the maximum dilution levels. For odors that are too weak to be detected at the minimum dilution level of 7, most panelists would miss detection at all dilution levels. Usually, this is not a problem with typical source emissions. On the other hand, if an odor is too strong at the maximum dilution level, essentially all panelists would detect the odor at all dilution levels. This would make the test useless. Some additional problems may also arise. Strong odors could contaminate the olfactometer to such an extent as to require several hours to restore the odorfree conditions within the instrument as well as the odor room. Also, the strong odors may damage the olfactory sensitivity of the panelists.

Although there is no simple mechanism for changing the D_1/D_6 ratio of the IITRI instrument, its range can be extended by means of attenuators. Table 1 provides different attenuation factors for various ranges of source odor dilution levels. It has been designed to ensure that individual panelist thresholds will fall in the middle of the D_1-D_6 dilution range. However, choosing the appropriate attenuator is an arbitrary exercise. No published data are available on how a correct attenuator should be selected for proper odor detection tests.

TABLE 1. ATTENUATORS FOR VARIOUS RANGES OF SOURCE ODOR DILUTION LEVELS

Source Odor Dilution Level	Attenuation Factor
180-60	1
540-180	3
1080-360	6
2160-720	12
3240-1080	18
10,800-2160	36

The need for the development of a standard procedure for selection of an appropriate dilution range without trial and error arises from limitations on the total amount of sample available for testing and also from the degradation of the sample with time. To minimize these difficulties, a procedure for determining threshold values of unknown source odors has been developed.

EXPERIMENTAL DETAILS

The objective of this investigation was to develop a reliable procedure for evaluating odor thresholds for a variety of odorous source emissions. Because of the difficulties associated with multicomponent odorous samples, the reliability of the proposed attenuator selection procedure was established through laboratory source simulation studies focussing on the determination of the detection threshold of the readily recognized odor of acetic acid.

Odor Sample Preparation

Figure 1 provides a schematic representation of the equipment used to simulate odor samples for a wide spectrum of studies. Compressed air from the 40 psig laboratory air line, controlled by a pressure regulator, was passed through a filter where oil and dirt were removed. The volumetric flow rate of the air was measured by means of a calibrated rotameter and controlled with a needle valve.

Liquid odorants were injected into the clean air line by means of a motor driven 30 mL syringe device equipped with a variable speed control and revolution counter. The variable speed controller permitted regulation of the odorant feed rate into the system. The odorant injection system was calibrated by discharging the syringe contents into a rubber stoppered bottle (to prevent escape of the odorant vapors) and weighing the contents of the bottle.

For any specific test, the odorant was introduced into the clean air after the desired flow was established. The system was allowed to operate for about 15 minutes to ensure a steady state odorant flow. This was checked from time to

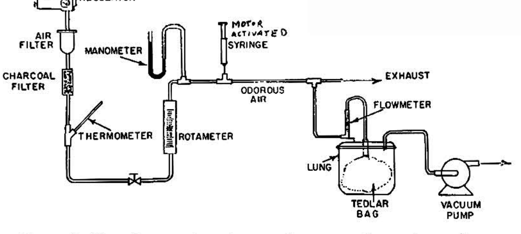

Figure 1. Flow diagram for odor sample preparation and sampling.

time by sniffing a portion of the odorous air stream. The system was then ready for sampling. A portion of the odorous air was diverted to the sampling system with the remainder being vented to the fume hood.

After termination of sampling, the odorant feed was turned off and the air was allowed to pass through the system at a reduced rate for several hours to deodorize the unit.

An odor sample from the odorous air preparation system was drawn through a regulated flow meter into a plastic bag, which was contained inside a "lung" consisting of a 20-litre stainless steel pressure vessel. Sample acquisition was accomplished by evacuating the "lung" by means of a vacuum pump. When the bag was filled with an eight to ten litre sample in about ten minutes, the valve at the flow meter inlet was closed and the pump was disconnected. The lid was then removed, the inflated bag detached from the bottom of the bulk-head fitting passing through the air-tight lid, and the diaphragm valve closed.

The olfactometer used in this study was a standard IITRI model [*13*]. Each port supplied approximately 500 mL/min of diluted air. Attenuators were used with the IITRI olfactometer to provide a variety of dilution ranges for strong odorant samples. This was accomplished by deodorizing a portion, (for example, 5/6 for an attenuating factor of 6), of the odorant sample by passing it through a deodorizing unit, which contained activated carbon and permanganate coated alumina (Purafil). The odor free gas was mixed with the remaining 1/6 of the odorant sample which by-passed the deodorizer. The total flow always remained the same but attenuation reduced the odorant concentration by a factor of 6. The adsorption capacity of Purafil was checked frequently by passing through a known concentration of the odorant which was removed with 99% efficiency based on total hydrocarbon (THC) determinations.

The IITRI Dynamic Triangle Olfactometer is normally supplied with only one attenuator which provides a dilution ratio of 27×. Therefore, several attenuators capable of establishing ratios of 2×, 3×, 6×, 12×, 18× and 36× were fabricated to provide a wider range of dilutions of odor samples. Attenuators were made from stainless steel capillaries of different lengths and diameters which were purchased from:

1. Supelco Company, Supelco Park, Bellafonte, PA 16823.
2. Anallabs, Inc., 80 Republic Drive, North Haven, CT 06473.

These capillaries were calibrated after each odor test. Typical capillary sizes and corresponding attenuations are listed in Table 2.

Odor Test Room

The odor test room was 1.2 m long × 1.2 m wide × 2.4 m high. It was constructed as a totally enclosed double walled chamber, equipped with a door, a glass window, an interior light, a portable electronic air cleaner and an exhaust fan for ventilating odors. The test room housed the olfactometer and a wooden stool for seating the panelists during odor perception tests. The inside walls and ceiling of the room were constructed of washable arborite. Washable vinyl tiles with neutral color schemes were used as the floor lining. A remote control signal box was mounted on one exterior wall where the panel leader could record individual panelist responses during odor measurement.

TABLE 2. ATTENUATOR DETAILS

Capillary Size		
Internal Diameter mm	Length cm	Attenuation Factor (approximate)
1.27	30.48	2
1.02	30.48	6
0.76	30.48	7
6.76	63.50	12.7
0.51	30.50	17.5
0.51	43.18	36
0.51	66.04	52

The air cleaner was capable of delivering odor free background air into the test room at low and high flows of 2.8 m³/min and 4.2 m³/min respectively. It consisted of a two stage electrostatic precipitator for particulate removal down to 0.03 microns, a replaceable activated charcoal filter for odor elimination, and an outside lint screen for trapping larger dust particles.

An exhaust fan was used when required to evacuate the test room air completely. An odor free background could be restored inside this chamber in about two hours.

MEASUREMENT TECHNIQUES

ED_{50} Determination by Dynamic Olfactometer

Odorous gas samples collected in Tedlar bags from the source simulation unit were transported as quickly as possible to the odor test room. All samples were analyzed for total hydrocarbon content prior to the odor threshold determinations. A modified Varian Aerograph series 1200-2 chromatograph, was used for the determination of total hydrocarbon content (THC). This analyzer, equipped with a flame ionization detector, incorporated a six port gas sampling valve with a two mL sample loop and a recorder. Before each analysis, the analyzer was calibrated with standard 97 ppm and 980 ppm butane gas. The analyzer response was a linear function of butane concentration.

Single panelists interacted with the olfactometer in the enclosed odor test room while sitting on a stool. Each panelist began from the left side of the unit where the largest dilution (weakest odor) was available. The odor testing program involved decisions at six different odor levels. Any number of sniffs was permitted before deciding which port was odorous. Because this procedure is based on a ternary forced choice principle, the panelists were required to guess in case they were not sure that they could decide correctly. A decision was signaled by pressing the button (switch) corresponding to the port suspected of discharging the odorous stream.

The panel members numbering eight to ten were selected from different age groups representing both sexes. Most had previous experiences with the odor evaluation procedures.

ASTM Procedure for Source Odor Prescreening

The standard ASTM method which follows the text of D-1391-57 (Reapproved 1967) [7] was used for the determination of the approximate number of dilutions required to ensure that the unknown odor threshold values would fall in the middle of the IITRI olfactometer dilution range.

An odor sample was collected in a 100 mL syringe, which was thoroughly flushed with odorous gas from the sample bag. The sample syringe, with cap on to prevent loss of odor, was taken to the odor free room where clean air was available for making dilutions. Measured quantities of the odorous sample were injected into the dilution syringes partially filled with clean air either directly from the sample syringe or through a transfer syringe. The dilution syringes were filled with the clean air to their 100 mL capacity. Other dilutions, differing by a factor of 2, were prepared in the same manner.

Each diluted odorous sample was presented to two panelists along with an air blank. According to the standard procedure the panelists were instructed to inject the contents of each syringe into one nostril by depressing the syringe plunger and then to indicate which of the syringes contained the odorous sample at each dilution level. The highest dilution (lowest odor concentration) at which a panelist made a correct judgement and continued to be correct at the next two higher concentration levels consecutively was taken as his threshold. The geometric mean of the individual thresholds gave the two member panel threshold to be used for selecting appropriate attenuators for the IITRI instrument.

All syringes and needles were thoroughly scrubbed with unperfumed detergent and chromic acid solution. They were washed with hot tap water, then rinsed with distilled water. After boiling in distilled water for half an hour they were dried in a clean oven at about 110°C. Before use, cleaned syringes and needles were allowed to cool and condition in room atmosphere.

RESULTS AND DISCUSSION

Since problems can arise as a result of arbitrary selection of attenuators, it becomes necessary to develop a consistent procedure by which the choice of dilution range can be made.

The following steps provide a standardized methodology for selection of an appropriate attenuation factor for odor threshold determinations of unknown source emissions:

Step 1: Draw a 100 mL odor sample into a syringe from the odor container.

Step 2: Determine the threshold value (dilution level) of the sample by the ASTM syringe method using the geometric mean of two panelists. This step provides a quick estimation of dilution level (threshold value in odor units).

Step 3: Select the attenuator corresponding to the measured dilution level using Table 1. Because the ASTM procedure generally underestimates the required dilutions, experience shows that when an overlapping range is encountered the higher dilution level should be used for the attenuator selection.

Step 4: Install the correct attenuator in the olfactometer according to the IITRI Instruction Manual [*13*].

Step 5: Complete the odor measurement test with nine panelists and calculate ED_{50} of the odor according to the IITRI Instruction Manual [*13*].

The recommended procedure was tested with acetic acid odor whose initial concentrations varied from 47 to 13,000 ppm. The results are presented in Table 3. The ED_{50} values determined by this procedure exhibit only minor differences. The observed variations in the measured threshold values are quite normal and are often expected in odor measurement work. However, Tests 3 and 7 show how improper selection of attenuators can affect the magnitude of an ED_{50} value. According to the instructions provided in Step 3 of the newly developed procedure, attenuation factors of 12 and above 36 should have been used during Tests 3 and 7 respectively.

A comparison of threshold values determined by this procedure and the odor room method [*14*] shown in Table 4 suggests that there is consistency between the values obtained by the two methods.

CONCLUSIONS

By design the IITRI Dynamic Olfactometer is limited to six dilution levels for any particular test. If the ultimate odor threshold value does not fall in the middle of the dilution range, the instrument will produce an ED_{50} value of low confidence. Consequently, several different attenuators are needed to provide appropriate dilution ranges for odors of varying strengths. In practice, attenuators ranging from 2 to 36 dilutions are generally sufficient.

A fast, reliable and practical procedure for odor threshold determinations of unknown samples has been developed. This procedure utilizes the static ASTM syringe method to guide the choice of dilution range for the dynamic evaluation. The odor threshold value of acetic acid determined with this procedure for the range 47 to 13,000 ppm shows excellent reproducibility, as well as consistency with the literature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Air Resources

TABLE 3. ED_{50} DETERMINATION OF ACETIC ACID ODOR USING PROCEDURE DEVELOPED FOR THE IITRI DYNAMIC OLFACTOMETER

Test	Initial Acetic Acid Concentration (ppm)	ED_{50} by ASTM (odor units)	Attenuation Factor Used	ED_{50} by IITRI Olfactometer	
				(odor units)	(ppm)
1	47	59	1	241	0.19
2	215	222	3	1076	0.19
3	1627	1110	6	2234	0.73
4	1836	1529	18	8110	0.23
5	2110	2638	18	5278	0.40
6	6992	3089	36	30,027	0.23
7	12,924	16,155	36	22,981	0.56

TABLE 4. COMPARISON OF ODOR THRESHOLD VALUES FOR ACETIC ACID

Odorant	Odor Threshold ppm	Measurement Technique	Investigator
Acetic Acid	0.19-0.40 (50% detection)	Dynamic (IITRI)	This work
Acetic Acid	1.0 (100% recognition)	Odor Room (four panelists)	Leonardos et al. [*14*]

Branch of the Ontario Ministry of the Environment and Imperial Oil Limited.

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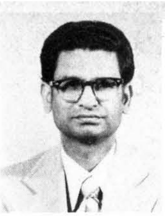

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A Study on the Systematic Control of CO_2 Emissions From Fossil-Fuel Power Plants in the U.S.

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The increase in atmospheric CO_2, which results primarily from combustion of fossil fuels for energy, could cause dramatic global climatic and environmental changes—the so-called "greenhouse effect." This study explores the technical feasibilities and the cost of controlling CO_2 emissions from the stacks by removing, recovering, and disposing of CO_2 from fossil-fuel power plants in the U.S. It is estimated that up to a 10% reduction in the annual incremental atmospheric CO_2 content would be achieved by the study control system. The total power required for such a control system ranges from 11 to 16% of the power-generating capacity in various regions of the U.S. Overall, the study system could essentially increase the capital investment of a power plant by 70 to 150%, and increase production cost of electricity by 56 to 100%, depending on the location of the plant.

INTRODUCTION

The increase in atmospheric carbon dioxide (CO_2) has primarily resulted from the consumption of fossil fuels for energy in various anthropogenic activities. The atmospheric CO_2 is transparent to visible light but absorbs infrared radiation returning from the earth. Thus, the build-up of the atmospheric CO_2 may alter the radioactive balance of the earth and thus raise the global temperature. This so-called "greenhouse effect" could dramatically cause global climatic and environmental changes [*1*] in precipitation, storm patterns, and increases in sea level.

Many of the early studies of the CO_2 issue have been directed toward gaining a better insight into the relationship among CO_2 emissions and its increase in the atmosphere (i.e., carbon cycle), and regional and global climate changes and the associated consequences [*2*, *3*]. The growth rate of carbon emissions, which averaged 4.5%/yr from 1950 to 1973, is now down to less than 2.5%/yr. With no CO_2 emission control, the global CO_2 emission resulting from fossil fuel burning was about 5.3 gigatons (10^9 tons) of carbon in 1981 [*4*]. The airborne fraction (i.e., retention ratio) of such emitted CO_2 is about 50% [*4*], while the remaining CO_2 is assumed to be absorbed by the oceans and by the land biota. The global average temperature increase resulting from doubling the pre-industrial atmospheric CO_2 concentration of 295 ppm, which will most likely occur before the end of next century, is estimated to be 2°-3°C [*4*].

Since there is a chance that naturally occurring or anthropogenic factors will not fully counter the effects of increasing atmospheric CO_2 concentration, to mitigate the increase of future atmospheric CO_2 and the consequent global climatic and environmental changes, measures of CO_2 emission control may become necessary. Several potential CO_2-control sites such as residential, commercial, and automobiles are available for reducing CO_2 emissions. Since fossil-fuel power plants are the major highly concentrated sources of CO_2, one logical response to choose sites of CO_2 emission control is the power plants' stacks. Thus, the objective of this study is to explore the technical feasibilities and the cost of controlling the CO_2 emissions from stacks by performing a systematic study of removing, recovering, and disposing CO_2 from fossil-fuel power plants. Data about locations and power capacities of fossil-fuel power plants in the U.S. are used in the study. The fossil carbon emitted from power plants accounts for about 30% of the overall fossil carbon emissions in the U.S., which in turn contributes about 30% of global emissions in 1980.

CO_2 REMOVAL AND RECOVERY FROM FLUE GASES

A schematic diagram for the removal and recovery of CO_2 from power-plant flue gases using a solvent absorption/stripping process is shown in Figure 1. CO_2 is removed in the absorber by reacting chemically with lean solvent solution flowing countercurrent to the flue gas. CO_2 is then stripped from the rich solvent solution flowing down through the regenerator countercurrent to stripping steam generated in the solution reboiler. The thermal energy in the form of steam is needed to reboil and remove CO_2 from the solvent. In addition, electrical energy is needed for blowers and pumps to drive the gas through the absorber and the liquid through the absorption and regeneration towers. Table 1 compares the energy need for the monoethanolamine (MEA) solvent to that for the Dow Alkanolamine-based solvent, so-called Gas/Spec FS-1 [*5*]

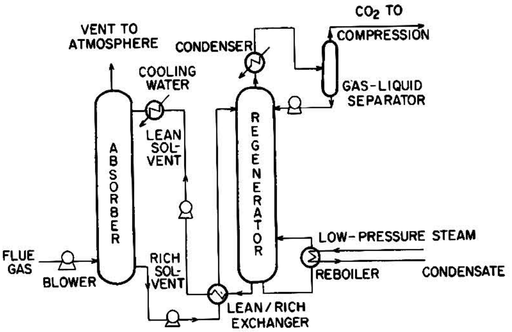

Figure 1. Flow sheet for CO_2 removal and recovery from power plant flue gas using dow gas/spec FS-1.

for 90% CO_2 recovery from the flue gases. Because of its relatively low energy requirement, MEA solvent was used by Albanese and Steinberg [6] to study CO_2 removal from stack gases. Table 1 shows, however, that the Dow Gas/Spec FS-1 is more energy efficient than MEA for the removal and recovery of CO_2. Hence, the Dow-solvent process is employed in the present study.

The recovered CO_2 is then liquefied for transmission to the ultimate disposal site. The liquefaction of recovered CO_2 is accomplished in the four-stage compression system equipped with coolers, water knockout drums, and a dryer. The gas is compressed to 2,000 psia in the fourth stage, passed through a cooler, and liquefied in a condenser at about 80°F. The energy required for liquefying CO_2 amounts to 0.047 kwh(e)/lb CO_2 recovered, comparing to an equivalent of 0.043 kwh(e)/lb CO_2 recovered being required for removing and recovering 90% of CO_2 from flue gases, as shown in Table 2 for a 1000 ton/day CO_2 recovery plant.

INTEGRATION OF POWER PLANT AND CO_2 RECOVERY SYSTEM

Figure 2 shows the integration of the CO_2 recovery process with the power plant operation by using the low back-pressure steam from the power-generating turbine to provide the necessary heat for solvent regeneration. The extraction of latent heat from the low-pressure steam which otherwise would be lost in the condenser, and the conversion of this heat to usable energy for solvent regeneration markedly reduces the energy required for the CO_2 recovery from power plants. Assuming a conventional power plant efficiency of 38% and the efficiencies of boiler and reboiler of 90% and 85%, respectively, along with the energy required for the Dow solvent process for recovering 90% of CO_2 (Table 1), integrating the CO_2 recovery system with the power plant in this manner lowers about 5-8% of power plant efficiencies (Table 3). Table 3 also shows that if part of the thermal energy from the fuel fed to the power plant is consumed as either equivalent steam or electric energy to strip and recover the CO_2, the resultant power-plant efficiencies are reduced more drastically, by 36-63%. Thus, the integration of the low pressure steam from the turbines with the CO_2 recovery process is used in the present study.

TABLE 1. COMPARISON OF ENERGY REQUIREMENTS FOR MONOETHANOLAMINE (MEA) AND DOW FS-1 SOLVENT SYSTEMS FOR CO_2 REMOVAL AND RECOVERY[a], [b], [c]

	MEA	Dow FS-1
Heat duty required, million Btu/ton of CO_2[d]	5.4	4.8
Electric energy, kWh(e)/ton of CO_2	20	13

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[a] Basis: 1000 tons per day of CO_2 from flue gas. 1 ton/day = 1.050×10^{-2} kg/s.
[b] Solvent concentration: 20%.
[c] 90% CO_2 removal from flue gas, CO_2 concentration: 8-15%.
[d] 1 Btu/ton = 1.163 J/kg.

TABLE 2. ENERGY REQUIREMENT FOR A 1000 TONS PER DAY CO_2 RECOVERY PLANT WHICH IS 100 MILES FROM COLLECTION CENTER[a]

Process	Equivalent Thermal Energy KWH(t)/lb CO_2	Equivalent Electrical Energy KWH(e)/lb CO_2
Removal and recovery[b]	0.721	0.043
Liquefaction[c]	0.124	0.047
Disposal		
6-in. pipe[d]	0.002	0.001
36-in. pipe[e]	0.003	0.001
Total	0.850	0.092

---

[a] CO_2 removal efficiency is 90%. The 1000 tons per day CO_2 recovery plant corresponds to 51-MW(e) coal-fired, 65-MW(e) oil-fired, and 90-MW(e) gas-fired power plants, respectively. 1 ton/day = 1.050×10^{-2} kg/s.
[b] includes the equivalent thermal and electric energy required as for absorption/stripping.
[c] CO_2 compression and liquefaction to 2000 psia in four stages. 1 psi = 6.8948×10^3 Pa.
[d] the pumping power required for transporting 1000 ton/day CO_2 through a 6-in. line, with a pumping efficiency of 60%.
[e] based on a pumping rate of 15×10^6 lb/hr and pumping efficiency of 60%. 1 lb/hr = 1.260×10^{-4} kg/s.

CO_2 DISPOSAL

Three methods of ultimate disposal are considered: (1) injection in the deep ocean, (2) storage in spent oil and gas wells, and (3) storage in excavated salt caverns.

Ocean Disposal

In the two-box model, the ocean is represented by two reservoirs separated by a thermocline [7] The upper reservoir consists of a surface layer about 75 meters deep, while the second or deeper layer extends from 75 meters to the ocean floor. Because of wind stress, mixing occurs rapidly in the surface layer. In the deeper layer, mixing depends on the rate of advection and turbulence which cross vertical density gradients. Exchange between the boxes is very slow. The upper layer is close to equilibrium with the atmosphere and thus the concentration of CO_2 in this layer depends on the concentration of CO_2 in the atmosphere. Since there is no direct exchange between the atmosphere

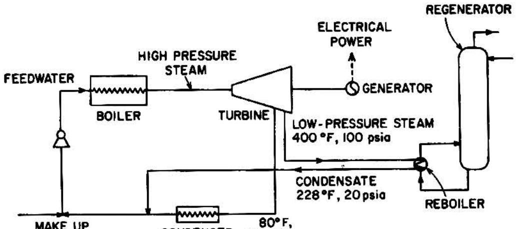

Figure 2. Integral schematic flow diagram of power plant and reboiler for the removal and recovery of CO_2.

TABLE 3. POWER PLANT EFFICIENCY COMPARISON FOR POWER PLANTS INTEGRATED WITH THE CO_2 RECOVERY SYSTEM

	Efficiency[a], [b], [c], (%)	
Fuel type	Integrated plant using low-pressure steam from P.P. in reboiler	Non-integrated plant using thermal energy from fuel directly
Coal	0.349	0.137
Oil	0.355	0.189
Gas	0.363	0.244

[a] Assuming a conventional power plant efficiency of 38%.

[b] Assuming the efficiencies of boiler and reboiler are 90% and 85%, respectively.

[c] Assuming the CO_2 removal efficiency is 90%.

and the second deeper ocean layer, the deep ocean in a promising vast reservoir for CO_2 disposal. Two choices could be made for selecting the distance off-shore and the depth to which the liquid CO_2 would be pumped.

Although the density of liquid carbon dioxide is less than that of sea water at depths less than about 3000 meters, it is much more compressible and has a much higher thermal coefficient of expansion [*8*]. The density of CO_2 increases quite rapidly with depth and is greater than that of seawater of similar temperature (37°F) at about 3000 meters. Hence, if the liquid CO_2 is piped to a somewhat greater depth, it could be expected to form a liquid CO_2 pool and sink to the ocean floor. Ocean depths of 3000 meters which correspond to a pressure of about 4400 psia are accessible at about 200 miles from the northeastern shoreline of the United States.

Another mechanism for disposal below the ocean thermocline is to dissolve the CO_2 using a 2000-psi liquid CO_2 at a depth of 500 meters. Since the ocean's surface layer usually extends to a depth of only about 75 meters, a 500-meter injection depth should be permissible for CO_2 disposal. The additional 425 meters would allow for dissolution of the injected CO_2. Ocean depths of 500 meters are accessible at about 100 miles from the shoreline of the northeastern United States, which is approximately the width of the continental shelf. On the western coast of the United States, the continental shelf is narrower and the ocean depth at 100 miles from the shoreline is greater than 500 meters.

In this study, a 100-mile main pipeline and 500-m ocean depth were selected as adequate for disposal (Figure 3). If it is found necessary to pump the CO_2 200 miles off-shore and down to 3000-m depths, Table 4 shows that the additional pipeline cost and compression energy requirement are not significantly greater. The increased capital investment and production cost of electricity are less than 2%. The additional energy required to compress CO_2 to 4500 psia from 2000 psia at the collection centers for a 3000-m depth ocean disposal is about 0.004 kWh(e)/lb CO_2. Some experimental work may be necessary to study the CO_2 concentration distribution for various depths of CO_2 ocean disposal to determine appropriate depth. Such experiments would shed light on the dissolution behavior of CO_2 at the disposal point and indicate how the interaction of CO_2 chemical and biological processes regulate the distribution of CO_2 in the ocean.

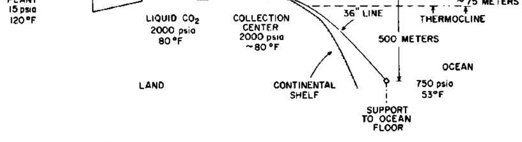

Figure 3. Schematic diagram for ocean disposal system.

Oil and Gas Wells Disposal

The availability of 12,000 spent oil and gas wells throughout the U.S. suggests a possible approach to the disposal of CO_2 on land [9]. The pressure of depleted oil and gas wells is usually in the range of 100 to 500 psia, [*10*] so that CO_2 at 2000 psia can be readily injected into the abandoned wells. However, the liquid CO_2 will not remain at its initial temperature of 80°F, and will slowly increase to the temperature of the surrounding well. The final supercritical temperature and pressure of the CO_2 will depend on the well depth. An increase of about 10°F is usual for every 1000 ft of depth. For an average 10,000-ft well, the CO_2 will be heated to 180°F, resulting in a final pressure of 3000 psia or more. A bottom well pressure of 4000 psia is not unusual at these depths. In fact, pressures in excess of 10,000 psia are frequently encountered at greater depths. Thus, after capping, the containment of the CO_2 under supercritical conditions in a depleted well is feasible. As an approximation, in order to determine the annual depleted volume being made available for CO_2 disposal, this study assumed a value equal to the annual production of oil and gas. Actually, a larger volume is available during the first year of disposal because of their inventory of depleted oil and gas wells accumulated over the past 100 years of production. Locations of oil and gas wells in the U.S. and their annual production are available in reference [*11*].

Salt Caverns Disposal

Salt caverns constitute additional potential CO_2 disposal sites. The mining of multimillion-barrel salt caverns for the strategic petroleum reserve (SPR) is routine in the United States [*12*]. A solution-mining technique has been used to produce large excavated salt caverns. Locations of underground gas reservoirs and salt deposits in the U.S. are available in reference [*13*]. In addition to the Gulf Coast area, other large salt caverns have been used to store gas in Ohio, Michigan, Pennsylvania, West Virginia, and New York. These could be used for CO_2 storage. In the West, the potential sites of salt domes include the Paradox Basin of Utah, the Piercement salt masses in Colorado, the Supai Basin of Arizona, and salt masses in North Dakota. Salt domes for gas storage can contain gas pressures of 3000 psia or higher. The salt is plastic and self-sealing of any cracks. The cost of excavating a salt dome varies with the availability of water for solution mining and the accessibility of salt solution disposal areas. Estimates range from \$1.00 to \$3.50 per barrel of volume excavated [*12, 13*]. The western sites are probably unsuitable for solution mining because of water shortages. Therefore, only depleted oil and gas wells are used. In the Great Lakes region, solution mining could be feasible because of the availability of fresh water, if disposal of the brine is allowed. Excavated salt domes in these regions, therefore, present an optional method of disposal.

REGIONAL CO_2 DISPOSAL DESIGN

In order to study the feasibility of the disposal system for the recovered liquid CO_2 from the stack gases in different areas of the U.S., along with their energy requirements, capital investments, and power generation cost, the design of the disposal system is laid out on a regional basis ac-

Table 4. Power Required for Removal, Recovery and Disposal of CO_2 Based on a 100-MW(e) 38% Efficient Coal-Fired Power Plant[a]

	Power Requirement, MW(e)	
	200-mi.-3000-m-depth	100-mi.-500-m-depths
1. Equivalent electrical power for CO_2 recovery system (provided from thermal loss in back-pressure turbines)	7.9	7.9
2. Power for pumping in absorption/stripping CO_2 recovery system	1.1	1.1
3. Power for CO_2 liquefaction	8.3	7.7
4. Net pumping power for 6-inch and 36-inch pipeline to ocean disposal site	0.9	0.3
Total energy consumption	18.2	17.0
Net power plant capacity	81.8	83.0

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[a] CO_2 generation = 181.8×10^{13} lb CO_2/day. 1 lb/day = 5.250×10^{-6} kg/s.

cording to the Department of Energy-Federal Regions for Utility Operations, as shown in Figure 4 [*14*]. Data on the number of fossil-fuel power plants and the power capacity in each of the regions for 1980 are presented in Figure 5.

Generally, the design concept for the disposal system is to pump the liquid CO_2 recovered from each of the fossil-fuel power plants via a six inch pipeline to a collection center, from there a 36 inch pipeline transports the liquid CO_2 to the ultimate disposal site, e.g., ocean depth, oil and gas wells or excavated salt domes. The pipeline sizes were chosen to optimize cost and for size uniformity. Concerning the transporting of liquid CO_2, it should be noted that liquid CO_2-coal slurry pipelines are being proposed to convey finely-ground coal from mine site to the coal-burning load center [*15*].

The location of power plants in each region is obtained from the National Emission Data System (NEDS) 1977 and computerized at Brookhaven National Laboratory [*16*, *17*] for plants of 40-MW(e) and larger. Figure 6 shows the distribution of the locations of fossil-fuel power plants and the distances of a six inch diameter pipeline along with 36 inch diameter pipelines at indicated collection centers for the Southeastern Region 4. All the other regions have been designed in a similar manner and can be found in the detailed DOE report [*18*].

Ocean disposal in general is used for coastal regions, while depleted oil and gas wells, and salt cavern disposal are more appropriate for the inland regions, particularly Regions 5, 7 and 8. The resultant regional CO_2 disposal systems are summarized in Table 5. The average length of a six inch pipeline from power plant to collection center in each region was estimated by averaging the distance between each power plant and the associated collection center. The number of 36 inch diameter pipelines at each collection center was estimated from the rate of CO_2 collected at each center divided by the optimum capacity of a 36 inch diameter pipeline. An optimum capacity of 15×10^6 lbs CO_2/hr which corresponds to a liquid CO_2 velocity of 11 ft/sec was used in the study. The rate at which CO_2 is collected at the collection center is assumed to be proportional to the capacity and number of power plants piping the CO_2 recovered to the center.

Figure 4. Department of energy-federal regions for utility operations.

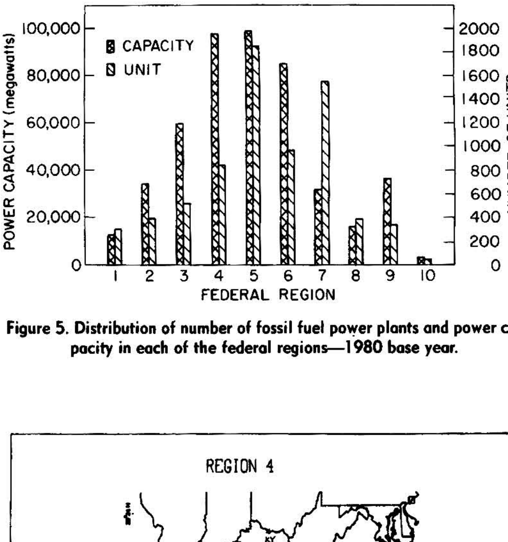

Figure 5. Distribution of number of fossil fuel power plants and power capacity in each of the federal regions—1980 base year.

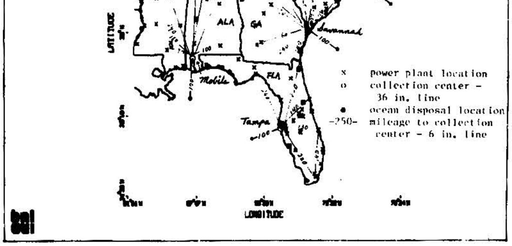

Figure 6. CO_2 disposal system for federal region 4—location and distribution of power plants and distance of 6" pipeline from power plant to collection centers for ocean disposal.

It should be noted in Table 5 that two alternative disposal systems are given for Regions 3 and 5. In Region 3, one is given for ocean disposal and the other for ocean and salt caverns. In Region 5, the systems are for ocean and salt caverns.

ENERGY REQUIREMENTS

In Table 6, the number of units and the power capacity are given in terms of coal-, oil-, and gas-fired power plants in each region. By employing the appropriate carbon dioxide coefficients (i.e., CO_2 release per unit of fuel consumed) Table 7, the rate of CO_2 generated for various fuels in each of the regions is calculated. The power required for recovering 90% of the CO_2 generated which includes energy required for CO_2 compression and liquefaction for each region can then be estimated. The pumping power required to transport CO_2 from each power plant to the collection centers can also be calculated since the total length of a six inch diameter pipeline has been estimated.

The main feature noted in Table 6 is that the total power required for the entire disposal system represents from 11% to 16% of the power generating capacity in each of the regions. Furthermore, the power required for the removal and recovery of CO_2 is much greater than the pumping power required for the disposal of CO_2. At most (Region 4), the pumping power represents less than 5% of the removal-recovery (including liquefaction) power.

One can see from Table 6 that for coal-burning dominant regions (e.g., Regions 3-5), the CO_2 control system re-

TABLE 5. CO_2 DISPOSAL SYSTEM DESIGNS BASED ON THE FEDERAL REGIONS

Federal Region	Disposal site[a]	Average length of 6-in. pipe from power plants to collection centers (miles)	Location of coastal collection centers and the number of 36-in. pipe-lines for ocean disposal at each center	Location of collection centers and the number of 36-in. pipelines for oil, gas and salt cavern disposal	Pipeline unit — installed capital cost (\$/kW(e) generated)
1	Ocean	86	Boston, MA, 1 New London, CT, 1	-0-	105
2	Ocean	88	New York, NY, 3 Atlantic City, NJ, 1	-0-	54.6
3	Ocean	130	New York, NY Atlantic City, NJ Baltimore, MD, 5 Norfolk, VA, 1	-0-	60.4
3	Ocean and salt cavern	67	New York, NY Atlantic City, NJ Baltimore, MD, 1 Norfolk, VA, 1	Pittsburgh, PA, 2 Charleston, WV, 2	33.3
4	Ocean	220	Wilmington, NC, 3 Savannah, GA, 3 Tampa, FL, 2 Mobile, AL, 3	-0-	96.6
5	Ocean	740	Baltimore, MD, 11 Mobile, AL, 1	-0-	64.8
5	Salt cavern	220	-0-	Columbus, OH, 5 Chicago, IL, 5 Lansing, MI, 2	181
6	Ocean and oil and gas wells	130	New Orleans, LA, 1 Lake Charles, LA, 1 Houston, TX, 4	Oklahoma City, OK, 1 Carlsbad, NM, 1 — Midland, TX	70.3
7	Oil and gas wells	220	-0-	Springfield, MO, 2 — Shreveport, LA Wichita, KS, 2 — Dallas, TX	500
8	Oil and gas wells	150	-0-	Gillette, WY, 1 Raton, CO, 2 — Lubbock, TX	194
9	Ocean	130	San Francisco, CA, 1 Los Angeles, CA, 2 San Diego, CA, 1	-0-	62.7
10	Ocean	150	Astoria, OR, 1	-0-	146.1

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[a] Ocean disposal sites are 100 miles distant from the coast as shown in Figure 6. 1 mile = 1.6093 km.

TABLE 6. POWER REQUIREMENTS FOR CO_2 CONTROL SYSTEM AND POWER CAPACITY FOR EACH OF THE FEDERAL REGIONS, BASE YEAR — 1980

Federal Region Fuel Type	Electrical capacity (MW(e))	Number of power plants	Rate of CO_2 generated (10^3 lb/hr)	Power required for CO_2 removal and recovery(a) (MW(e))
Region 1				
Coal	489.2	5	890	
Oil	12098.3	290	17280	
Gas	8.9	9	9	
Subtotal	12596.4	304	18180	1678
Region 2				
Coal	4185.2	38	7610	
Oil	29731.9	342	42470	
Gas	191.0	10	200	
Subtotal	34108.1	390	50280	4638
Region 3				
Coal	42239.6	146	76800	
Oil	17196.0	356	24570	
Gas	236.6	13	240	
Subtotal	59672.2	515	101600	9324
Region 4				
Coal	65095.5	265	118400	
Oil	26822.5	456	38320	
Gas	5638.5	121	5810	
Subtotal	97556.5	842	162500	14910
Region 5				
Coal	77640.9	557	141200	
Oil	19117.3	1032	27310	
Gas	2006.6	263	2070	
Subtotal	98764.8	1852	170600	15640
Region 6				
Coal	19673.7	42	35770	
Oil	5071.3	189	7240	
Gas	60040.4	737	61900	
Subtotal	84785.4	968	104900	9611
Region 7				
Coal	21566.6	170	39210	
Oil	4553.0	934	6500	
Gas	5936.1	447	6120	
Subtotal	32055.7	1551	51830	4752
Region 8				
Coal	14063.1	87	25570	
Oil	1619.2	240	2310	
Gas	347.2	57	350	
Subtotal	16056.5	384	28230	2612
Region 9				
Coal	6202.9	15	11280	
Oil	28903.2	305	41290	
Gas	1364.7	18	1410	
Subtotal	36470.8	338	53980	4974
Region 10				
Coal	1860.0	3	3380	
Oil	1014.6	46	1450	
Gas	171.0	6	180	
Subtotal	3045.6	55	5010	460
Total	475,112.4	7196	747100	68600

(a) Power requirement for CO_2 removal and recovery includes the energy (thermal and electrical) required for separating 90% of CO_2 from flue gas and that required for liquefaction of recovered CO_2. The total power required is given in MW(e) equivalents.

Table 6 continued

Federal Region Fuel Type	Pumping Power Required to Dispose of CO_2 (MW(e))	Net Electrical Capacity (MW(e))	% Reduction in Electrical Capacity due to CO_2 Control
Region 1			
Coal			
Oil			
Gas			
Subtotal	4	10910	13.4
Region 2			
Coal			
Oil			
Gas			
Subtotal	41	29430	13.7
Region 3			
Coal			
Oil			
Gas			
Subtotal	271 140	50080 50210	16.1(c) 15.9(d)
Region 4			
Coal			
Oil			
Gas			
Subtotal	687	81960	16.0
Region 5			
Coal			
Oil			
Gas			
Subtotal	633 171	82490 82960	16.5(c) 16.0(e)
Region 6			
Coal			
Oil			
Gas			
Subtotal	114	75060	11.5
Region 7			
Coal			
Oil			
Gas			
Subtotal	9	27300	14.8
Region 8			
Coal			
Oil			
Gas			
Subtotal	14	13430	16.4
Region 9			
Coal			
Oil			
Gas			
Subtotal	97	31400	13.9
Region 10			
Coal			
Oil			
Gas			
Subtotal	4	2582	15.2
Total	1874 1281	404600 405200	14.8(c) 14.7(d, e)

(b) Net power capacity = total power capacity less the power requirement for CO_2 removal and recovery-pumping power for CO_2 disposal.

(c) Ocean disposal, or

(d) Ocean and salt cavern disposal, or

(e) Salt cavern disposal.

TABLE 7. CO$_2$ GENERATION FOR VARIOUS FOSSIL FUELS

Fuel Type	Heating Value (Btu/lb)[a]	CO$_2$ generated lb CO$_2$/lb fuel	CO$_2$ generated lb CO$_2$/1000 Btu	Energy generated kWh(e)/lb CO$_2$ generated[b]
Bituminous Coal	12,700	2.59	0.204	0.55
Fuel Oil & Gasoline (petrol dist.)	19,600	3.14	0.160	0.70
Natural Gas	24,000	2.75	0.115	0.97

[a] 1 Btu/lb = 2.326 KJ/kg.
[b] Assuming a power plant efficiency of 38%. 1 kWh/lb = 7.937 MJ/kg.

duces the power-generating capacity by about 16% as opposed to 11% for gas-consuming dominant regions. The average national power consumption for the total CO$_2$ control system designed in this study is about 15% of total national electrical power generating capacity.

Because the pumping power required is small, the total net power difference between utilizing ocean versus salt cavern disposal for Region 5 is about 1%, despite the three-fold difference in related 6 inch diameter pipeline lengths.

Capital Requirements and Power Generation Costs

Costs of CO$_2$ Recovery Plants: The capital costs and operating expenses of the CO$_2$ recovery plants depend on the concentration of CO$_2$ in the flue gas [5]. The conventional coal-fired power plant emission contains about 13% CO$_2$, while that from the natural gas-fired power plants contains about 8% CO$_2$. The capital cost for a plant designed to recover 1000 tons of CO$_2$ per day, at 8% CO$_2$ input concentration, without compression and liquefaction, is estimated to be about 14 million U.S. 1980 dollars, and decreases as CO$_2$ concentration increases [5]. The capital cost is directly proportional to plant size in the range of 100 to 1000 tons CO$_2$ per day, which is equivalent to a coal-fired power plant capacity range of 5.1 to 51-MW(e). For higher capacities, the six-tenths factor rule for capital cost estimation was applied. The operating cost, which does not vary much with plant size, is about $15 (1980 U.S. dollars) per ton of CO$_2$ at 8% carbon dioxide and higher, and decreases as the plant size becomes larger than 1000 tons CO$_2$ per day. The capital investment for the CO$_2$ compression and liquefaction is about $10 million (1980 U.S. dollars) for a 1000 tons per day CO$_2$ recovery plant [19].

Cost of pipeline: Once the disposal system for each region is designed, the total cost of the pipelines which includes six inch and 36 inch diameter pipelines can be estimated. The pipeline cost was estimated from data given in reference 20 and indexed to the 1980 base year used in this study. Table 5 indicates that, for ocean disposal, pipeline capital investment per unit of net electrical production runs from a low of $55/kW in Region 2 to a high of $146/kW in Region 10. In Region 3, by disposing of the CO$_2$ from Western Pennsylvania and West Virginia into the salt caverns with Pittsburgh and Charleston as collection centers, respectively, the pipeline capital investment per unit of electrical production can be reduced to almost half the ocean disposal system alone. For oil and gas wells and salt dome disposal, the pipeline investment runs between $181/kW for Region 5 and $500/kW for Region 7/. In general, for inland regions, owing to the shorter pipeline distance, the pipeline costs for oil and gas wells and/or salt caverns disposal are less than those of ocean disposal.

Capital Investments and Power Generation Costs: Estimates of the required capital investment and the electricity production costs for power plants with CO$_2$ control system in each Federal Region are summarized in Tables 8 and 9, respectively [21-25]. It is noted that the CO$_2$ control system represents an appreciable fraction of the initial capital investment in power plants, ranging from about 70% in the oil and gas-burning dominant regions to as high as 150% in the coal-burning dominant regions. A large portion, in the range of 0.5 to 0.95, of increasing capital investment and electricity production costs is attributed to the CO$_2$ removal and recovery process, and the remaining increase resulted from the disposal piping system. In such inland Regions as Regions 5, 7, and 8, the capital costs for the removal, recovery, and storage of CO$_2$ can exceed the initial costs of the power plant itself because of the greater dependence on coal. On average, the retrofit of flue gas CO$_2$ control systems would double the initial capital costs of the fossil-fuel power plants in the U.S.

Power generation costs for inland regions that normally use more coal could double by applying a CO$_2$ control system. However, in the coastal regions, the power-generating cost with CO$_2$ control is about 60% higher than that of without CO$_2$ control. It is estimated that the average increase in the power generation cost in the U.S. by applying a CO$_2$ control system could amount to about 75% of conventional power plants.

By assuming a 100% plant operating factor instead of the more realistic 50% to 65% in the calculations, some cost components such as annual energy and CO$_2$ control operating costs were estimated conservatively high. However, by doing so, the results provide a basis for assessing the economic penalties of the CO$_2$ control system. In addition, since the base cost of power plants is an exogenous factor in the study, the economical calculation framework is not affected by this cost change. The economic penalty of incorporating a CO$_2$ control system into a power plant generally decreases with increasing base cost of the power plant.

A possible way to reduce these costs is not to install the CO$_2$ control system for those power plants having a capacity smaller than 5 MW, especially for oil and gas-fired plants, since the capital and operation costs increase rapidly as the CO$_2$ recovery plant capacity decreases below a certain size, probably on the order of 100 tons CO$_2$ per day which is about the rate of emissions of a 5-MW(e) coal-fired plant. To compensate for these smaller CO$_2$ emitters, we can slightly increase the recovery efficiency of some of the larger-size power plants, say, 100 MW and higher with practically no increase in cost, because in large power plants the cost of the CO$_2$ control system is less sensitive to small increases of recovery efficiency. Furthermore, pipeline costs from these smaller plants are eliminated since there is no need to transport CO$_2$. The pipeline cost can also be cut by sharing six inch lines for those nearby small power plants instead of separately pipelining CO$_2$ from each power plant to collection centers.

Costs of CO$_2$ removal and recovery can be further reduced in some regions; for example, the recovered CO$_2$ in Regions 6 to 8 can be used to enhance oil recovery in depleted oil wells in states such as Texas and Oklahoma. The CO$_2$ can then be sold as a by-product for the production of oil.

TABLE 8. CAPITAL INVESTMENT FOR POWER PLANTS AND CO_2 CONTROL SYSTEM FOR EACH OF THE FEDERAL REGIONS (IN BILLIONS (10^9) OF 1980 U.S. DOLLARS)

Region	Power plant[a]	CO_2 removal recovery[b]	CO_2 comp. Liq.[c]	Piping[d]	Salt cavern excavating[e]
1	7.2	2.7	2.0	1.1	0
2	19.4	7.6	5.4	1.6	0
3	34.0	15.4	11.0	3.0 1.7	0 [f] 2.3[g]
4	55.6	24.5	17.5	7.9	0
5	56.3	25.8	18.4	53.4 15.0	0 [f] 3.8[h]
6	48.3	15.9	11.3	5.2	0
7	18.3	7.9	5.6	13.7	0
8	9.2	4.3	3.0	2.6	0
9	20.8	8.1	5.8	2.0	0
10	1.7	8.0	0.5	0.4	0
Total	271	113	81	91 51	0 [f] 6.1[g,h]

Region	Total CO_2 control system cost	Total cost for plant and control system	Unit cost for control system \$/kW(e) net generated	CO_2 control system, % of power plant investment	CO_2 control system, % of total investment
1	5.8	13.0	532	80.6	44.6
2	14.6	34.0	496	75.3	42.9
3	29.4 30.4	63.4 64.4	587 605	86.5 89.4	46.4[f] 47.1[g]
4	49.9	105.5	609	89.7	47.3
5	97.6 63.0	153.9 112.0	1183 759	173.4 111.9	63.4[f] 56.2[h]
6	32.4	80.7	432	67.1	40.1
7	27.1	45.5	993	148.1	59.7
8	9.9	19.1	737	107.6	51.8
9	15.9	36.7	506	76.4	43.3
10	1.7	3.4	658	100.0	50.0
Total	284 251	555 514	673 633	104.8 92.6	51.2[f] 48.8[g,h]

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[a] at \$570/kW(e) which was estimated from reference 21.
[b] calculated from reference 5.
[c] calculated from reference 19.
[d] includes 6-in and 36-in line costs and were estimated from reference 20.
[e] at \$1.00/barrel based on reference 21.
[f] ocean disposal, or
[g] ocean and salt cavern disposal, or
[h] salt cavern disposal

IMPACT OF REMOVAL OF CO_2 FROM POWER-PLANT STACKS ON ATMOSPHERIC CARBON BALANCE

The median-case data of Woodwell et al [24] on the carbon balance in the atmosphere, as shown in Table 10, were used to calculate the impact of the present CO_2 control system on the build-up of the atmospheric CO_2. The calculations were done on the basis that the U.S. contributes about 30% of the global overall fossil-carbon, and its utilities are responsible for about 30% of the total U.S. emissions. In addition, it was assumed that 30% of the global fossil-carbon is from fossil-fuel power plants. Table 11 shows that up to 10% and 30% of the reduction in the annual incremental atmospheric content could be achieved if the fossil-fuel power plants in the U.S. and the world, respectively, adopt the present CO_2 control system.

CONCLUSIONS

The ten Department of Energy-Federal Regions for power generation provided the framework to perform the preliminary systematic study of the removal, recovery, and disposal of CO_2 from fossil-fuel power plants in the U.S. The primary factor affecting the practicability of a CO_2 control system is the energy required by the control system. The total power required for the present CO_2 control system ranges from 11% to 16% of the power generating capacity in various regions. Thus, the present system of CO_2 emission control is technically feasible. However, the cost of CO_2 control is significant when evaluated in light of its benefit. Overall, the CO_2 control system could essentially increase the capital investment of power plants by 70% to 150%, and increase the production cost of electricity by 56% to 100%, depending on the location of the plant.

The CO_2 issue is a global problem, and a worldwide effort would be required to control the level of atmospheric CO_2 effectively. Its global nature means that even should some nations curb their CO_2 emissions to the atmosphere, the problem over a long term still remains. However, from the larger viewpoint, the problem becomes one of making a balance between nations that contribute negligible amounts of CO_2 emissions with those that contribute

TABLE 9. ELECTRICITY PRODUCTION COSTS OF POWER PLANTS WITH CO_2 CONTROL SYSTEMS FOR VARIOUS FEDERAL REGIONS (MILLS/KWH(E) IN 1980 U.S. DOLLARS)

Region	Power plants(a)	CO_2 removal recovery(b)	Compression Liquefaction(c)	Piping(c)	Salt cavern excavating(c)
1	32	11.3	7.2	2.5	0.0
2	32	11.3	7.2	1.3	0.0
3	32	13.8	7.9	1.3 0.8	0.0 (d) 1.0 (e)
4	32	13.5	7.8	2.3	0.0
5	32	14.1	8.0	15.5 4.3	0.0 (d) 1.0 (f)
6	32	9.4	6.7	1.7	0.0
7	32	12.9	7.6	11.9	0.0
8	32	14.4	8.0	4.6	0.0
9	32	11.7	7.3	1.9	0.0
10	32	13.2	7.7	3.5	0.0
Av. Total	32	12.6	7.5	4.7 3.5	0.0 (d) 0.02(e,f)

Region	Total CO_2 Control System Operation Cost	Total Production Cost for Electricity	CO_2 Control System, % of Power Plant Production Cost	CO_2 Control System, % of Total Production Cost
1	21.0	53.0	65.6	39.6
2	19.8	51.8	61.9	38.2
3	23.0 23.5	55.0 55.5	71.9 73.4	41.8(d) 42.3(e)
4	23.6	55.6	73.7	42.3
5	37.6 27.4	69.6 59.4	117.5 85.6	54.0(d) 46.1(f)
6	17.8	49.8	55.6	35.7
7	32.4	64.4	101.2	50.3
8	27.0	59.0	84.4	45.8
9	20.9	52.9	65.3	39.5
10	24.4	56.4	76.3	43.3
Av. Total	24.7 23.8	56.7 55.8	77.3 74.3	43.0(d) 42.3(e,f)

(a) based on the same fuel cost for all regions and estimated from reference 21.

(b) estimated from reference 5.

(c) capital charge is 15% of capital investment in CO_2 compression, liquefaction and piping, based on 24 hrs/day, 350 annual operating days.

(d) ocean disposal, or

(e) ocean and salt cavern disposal, or

(f) salt cavern disposal

TABLE 10. 1980 WORLD CARBON BALANCE IN GIGATON/YR FOR MEDIAN CASE

World Increments of Atm CO_2	=	Fossil Fuel Release	−	Ocean Uptake	+	Terrestial Carbon Release	Total Release	Imbalance	Airborne Fraction Incr/Release
2.5	=	5.2	−	2.0	+	3.3	8.5	4.0	30%

TABLE 11. U.S. AND WORLD POWER PLANT CONTRIBUTION TO INCREMENT OF ATMOSPHERIC CO_2 (GIGATONS/YR)—1980 MEDIAN CASE

World Increment of Atm CO_2	Released by U.S. Power Plants	Fraction of Increment Due to U.S. Power Plants	Released by World Power Plants	Fraction of Increment Due to World Power Plants
2.5	0.5	10%	1.6	32%

significant quantities to the atmosphere. As a result, an effort to reduce CO_2 emissions by the major contributing nations could be of considerable value. It is estimated that a 10% reduction in the annual incremental atmospheric CO_2 content would be achieved with this system, if implemented for the U.S. alone, and up to 32% for the entire world. The application of this systematic study to the other major contributors in the world such as China, Russia, and Europe may be a worthwhile exercise. A cost/benefit analysis balancing the cost of this control system with the delay in increasing the CO_2 concentration in the atmosphere would also be worthwhile.

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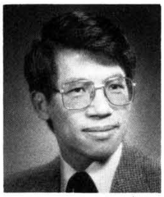

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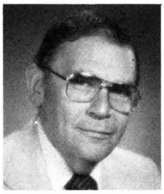

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Coal Cleaning: Progress and Potential

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Results from a detailed analysis of sulfur dioxide (SO_2) reductions achievable through "deep" physical coal cleaning (PCC) at 20 coal-fired power plants in the Ohio-Indiana-Illinois region are presented here. These plants all have capacities larger than 500 MWe, are currently without any flue-gas-desulfurization (FGD) systems, and burn coal of greater than 1% sulfur content (in 1980). Their aggregate emissions of 2.4 million tons of SO_2 per year represent 55% of the SO_2 inventory for these states. The principal coal supplies for each power plant were identified and characterized as to coal seam and county of origin, so that published coal-washability data could be matched to each supplier. The SO_2 reductions that would result from deep cleaning (Level 4) and moderate cleaning (Level 3) of each coal were calculated using a PCC computer model. For deep cleaning, percentage reductions in sulfur content ranged from zero to 52%, with a mean value of 29%, and costs ranged from a low of \$364/ton SO_2 removed to over \$2000/ton SO_2 removed. Because coal suppliers to these power plants employ some voluntary coal cleaning, the anticipated emissions reduction from current levels if deep cleaning were used should be near 20%. These emissions reductions were projected using conventional coal-cleaning-circuit designs. The basic elements of typical commercial PCC designs are briefly described, and current research and development activities in physical, chemical, and biological desulfurization of coal are reviewed. Possible governmental actions to either encourage or mandate coal cleaning are identified and evaluated.

INTRODUCTION

Although efforts to reduce sulfur dioxide (SO_2) emissions from stationary sources have long focused on new coal-fired power plants and industrial boilers, recent legislative initiatives have emphasized greater control of existing sources. Proposals calling for SO_2 reductions of 8 to 12 million tons per year from the 1980 level of 15.9 million tons in the Acid Rain Mitigation (ARM) region (the states east of the Mississippi River plus Iowa, Missouri, Arkansas, and Louisiana) would mandate the retrofitting of flue-gas-desulfurization (FGD) systems, physical coal cleaning (PCC), fuel switching, or combinations of these techniques.

The performance of PCC systems is difficult to evaluate on a regional or even statewide basis, because it is highly dependent on specific coal properties. Argonne National Laboratory (ANL), under contract to the U.S. Environmental Protection Agency (EPA), Region V, recently addressed this issue in a study designed to determine what SO_2 reductions could be obtained in the Ohio-Indiana-Illinois region by extensive application of PCC to specific fuels being burned by 20 major power plants [*1*]. These plants all have capacities of 500 MWe or greater, are currently without any FGD systems, and burn coal with a sulfur content exceeding 1% [2]. Because the issue addressed in the study is potentially sensitive, each plant was randomly assigned an identifying letter to be used in presenting the results.

COAL-CLEANING TECHNOLOGY

Physical coal-cleaning processes remove clay, shale, and pyrite from run-of-mine (ROM) coals. Cleaning is achieved by grinding the coal to liberate impurities that are not chemically bound and then taking advantage of specific-gravity differences between the organic matter that forms the coal (called macerals) and the denser mineral impurities. Sometimes differences in surface-wetting properties between macerals and impurities are used for separation. General cleaning strategies for plants depend on the desired level of coal cleaning. These levels are assigned as shown in Table 1.

PCC Commercial Technology

PCC plants may involve up to four major subsystems: 1) comminution (size reduction), 2) screening, 3) concentration, and 4) dewatering. These subsystems have to be tailored to the specific coal and desired level of cleaning.

Comminution: One of the main goals of the crushing operation is to achieve a specified top-size without creating excessive difficult-to-clean fines. The optimum size to which coal is crushed depends on its washability and end-use.

Rotary breakers are most often used for preparation of deep-mined material with a significant amount of roof and floor material. Stones, shales, logs, and other debris too large to pass through the perforations in the drum are con-

TABLE 1. LEVELS OF PHYSICAL COAL CLEANING

Level		Weight Yield (%)	Btu Recovery (%)	Reduction	
				Ash	Sulfur
0	No preparation (ROM)	100	100	None	None
1	Top size control	98-100	100	Fair	None
2	Coarse beneficiation	75-85	90-95	Good	Fair
3	Moderate beneficiation	60-80	80-90	Good	Fair
4	Deep beneficiation	60-80	80-90	Excellent	Good

veniently discarded. Breakers are the lowest in fines production.

Roll crushers squeeze the coal between tooth-covered rollers. They are also low in fines production and are capable of reducing ROM coal to 1½ in. or less.

Hammer mills throw coal against breaker blocks and grate bars until the product is reduced to the size of the grate opening. These machines produce a large quantity of fines in comparison with the above techniques.

Screening: Either wet or dry methods may be used to classify coal into different size ranges before introduction to coal-cleaning circuits. Screens remove rocks and foreign material prior to crushing, and later in the circuit other screens are used to separate coal into coarse and fine fractions for marketing or further preparation.

Concentration: Concentration is the operation in which the coal and impurities are actually separated. General methods can be classified as water-only, heavy-media, and dry separation. Some specialized fine-coal recovery methods include froth flotation and oil agglomeration.

Jigs are the oldest and simplest of all coal-washing devices, and they remain the most widely used devices in this country. Their principal service is on coarse-sized coal. In jigging, a series of pulses (at the rate of one pulse per second) moves up through the coal-filled bath to provide a rough classification of the coal and mineral impurities by density. The denser impurities are drawn off the bottom and discarded, while the top fraction is withdrawn as product coal. These devices produce a large "middling" product, which is either recycled or sent to other concentrating systems.

The concentrating table is widely used for fine-coal cleaning. Tables are large, tilted rhomboid-shaped decks with ridges (riffles) that span the table diagonally. Reciprocating motion of the table causes feed material to fan out onto the deck into strata of different density. Tabling concentrates the heaviest and finest of the particles at the bottom of the deck, while the lightest and coarsest particles congregate at the top of the deck. This system is particularly applicable for washing soft and friable coals that degrade easily.

Hydrocyclones are separating devices for medium- to fine-sized coal. These devices make use of high centrifugal forces to effect the separation of denser impurities from the coal. Heavy-media cyclones add 325-mesh magnetite to the wash circuit to increase the wash water's apparent density (to a specific gravity, or S.G., of 1.3-1.8), which provides for a finer "cut" on the pyritic impurities. Currently, this represents the most advanced form of physical coal cleaning available. The circuit is made more complicated by the need to recover magnetite so as to minimize processing costs. The dense-media recovery unit is generally a drum-type magnetic separator that provides for the effective recovery of all but the smallest of magnetite particles.

Froth flotation has come into wide use for the recovery of the heating value of coal fines produced by the comminution step. In contrast to the other concentrating processes, flotation does not use specific gravity as the basis of the separation. The wetting properties of the macerals and the impurities are characteristically different, the ash being hydrophilic (water-attracting) while the macerals are hydrophobic (water-repelling). Blowing fine bubbles of air through the aqueous phase (usually enhanced by surfactants) floats the coal up to the surface for recovery. Although flotation is effective in ash removal, one serious deficiency is its difficulty in selectively rejecting pyrites. The wetting properties of pyrites are similar to those of coal macerals, and it is generally necessary to reclean the froth, with slight modifications of the surface tension, so as to remove the pyrites.

Dewatering: After the coal has been washed, excess moisture must be reduced to minimize the penalties incurred in decreased heating value of the fuel, increased transportation costs, and handling and shipping problems. The types of equipment used in this service are directly related to the coal grind. They include screens, centrifugal dryers, various types of vacuum dryers, filter presses, belt filters, thermal dryers, and water clarifiers.

PCC Systems Overview: General cleaning strategies for plants depend on which of the following levels of coal cleaning are desired:

- *Size Control*—Level 1 involves no cleaning but reduces ROM coal to user's size specifications, prepares it for shipment, and possibly reduces moisture content (an important consideration for low-rank western coals).
- *Coarse-to-Moderate Beneficiation*—Levels 2 and 3 use low-efficiency separation devices to process easy-to-clean coals (coarse coal only in Level 2). These levels should be employed to remove pyritic sulfur from coal that complies or almost complies with SO_2 emission standards.
- *Deep Beneficiation*—Level 4 makes use of high-efficiency separation methods to clean the +28 mesh size fractions, while the ultrafine coal (−28 mesh) is cleaned using hydrocyclones. Thus, at this level all coal is cleaned.

The coal-processing equipment used will vary with coal characteristics and, to a lesser extent, with site-specific constraints that require the development of the most suitable combination of unit operations for each coal-cleaning case. Consequently, very few PCC plants are identical, clearly indicating that no standard solution for upgrading coal exists. Table 2 gives performance data for four representative PCC plants [3].

Cost of Coal Preparation: The cost of coal preparation is a function of coal washability, percentage of material discarded as refuse, level of preparation, and plant size. Costs for coal preparation vary for each plant depending on such factors as location, terrain, coal properties, mining technique, number of cleaning circuits, preparation specifications, and coal-production rate. Total capital investment for a 1000-ton/h plant generally ranges from \$20 to \$80 million (January 1983 dollars).

Total annual costs (January 1983) for coal preparation range from \$3.50 to \$16.00 per ton of cleaned coal, depending primarily on raw-material characteristics and type of cleaning process [3].

Advanced Coal-Cleaning Technologies

Advanced coal-cleaning processes can be grouped into the following three categories according to the technique used for separating coal from its impurities:

- Advanced physical coal cleaning
- Biological desulfurization
- Chemical coal cleaning

Advanced Physical Coal Cleaning: Advanced PCC processes still rely on physical-property differences between coal and its impurities. These physical properties include specific gravity, surface characteristics, magnetic properties, and conductivity.

Advanced Flotation is an extension of commercially used flotation techniques. An improved two-stage flotation process, developed by the U.S. Department of Energy, consists of a standard first-stage flotation step (to remove mainly ash and coarse pyrite), followed by a second flotation step, in which fine pyrite is floated and coal is depressed. Another process, developed by Pennsylvania State University, uses multistage flotation; easily floated coal is recovered in the first stage, and more elaborate flotation is performed in subsequent stages. The Advanced Fuels Technology (AFT) process is based on the contact of coal particles with air during spraying of the feed coal-water slurry into a specially designed flotation tank. Microbubble and column flotation processes use fine air bubbles to attach to micron-size coal particles in specially designed flotation equipment.

True Heavy-Liquid Beneficiation is an extension of the conventional technology, which uses finely ground magnetite particles dispersed in water as the heavy medium. In the advanced technique, the separation medium consists of a homogeneous liquid that permits complete dispersion of coal particles and results in a better removal of ash and pyrite than can be achieved by the commercial technology.

The earliest true heavy-liquid process, developed by Otisca Industries, Ltd., uses trichlorofluoromethane as the medium in a static bath. This process, tested in a 125-ton/h demonstration-scale plant, was discontinued in 1981 in favor of the cyclone process. The latter process, being developed under DOE's sponsorship, uses Freon-113 as the heavy medium. A third proprietary process, developed by Dow Chemical, uses chlorinated solvents (such as perchloroethylene) as the heavy medium. Because the separation media used in these true heavy-liquid beneficiation processes are organic, the recovery and recycling of these media constitute an integral part of these processes.

Electrostatic Separation relies on the electrostatic property differences between coal and its impurities. The electrostatic process developed by Advanced Energy Dynamics (AED) cleans fine coal (e.g., 60 mesh × 20 microns) in a dry medium (i.e., air). The pulverized coal is given a mild charge as it is fed to a drum-type, rotating electrostatic separator of opposite polarity. Pyrite and ash, having good electrical conductivity, lose their charge and drop off the drums, while the clean coal sticks to the drums and is scraped off later with a separator blade.

Fine-Coal Heavy-Media Cycloning involves the cleaning of fine coal in heavy-media cyclones using a magnetite-water mixture as the separation medium. It is an extension of the commercial technology, because cleaning is performed on fine-size coal and at low specific gravities with alterations to the conventional designs of magnetite recovery systems.

TABLE 2. COAL-PREPARATION PLANT PERFORMANCE

Plant	Coal Seam	State	Level of Cleaning	Wt Recov. (%)	Ash (%)			Total Sulfur (%)			Pyritic Sulfur (%)			Heat Content (Btu/lb)			SO_2 Emission Parameter (lb $SO_2/10^6$ Btu)		
					ROM Coal	Clean Coal	Reduction	ROM Coal	Clean Coal	Reduction	ROM Coal	Clean Coal	Reduction	ROM Coal	Clean Coal	Enhancement (%)	ROM Coal	Clean Coal	Reduction (%)
1	Pittsburgh No. 8	Penn.	4	75	27.3	12.0	56	2.15	1.87	13	1.23	1.08	12	10,879	13,370	23	3.94	2.79	29
2	Lower Kittanning	W.Va.	4	61	30.1	9.2	70	2.52	1.30	48	1.80	0.54	70	10,474	13,981	25	4.81	1.86	61
3	Kentucky No. 11	Ky.	3	62	32.4	10.2	69	3.63	3.43	6	2.14	1.32	38	9,612	13,041	36	7.55	5.26	30
4	Illinois No. 6	Ill.	3	75	28.4	13.0	54	3.54	3.35	5	2.18	1.39	36	10,207	12,773	25	6.93	5.24	24

High-gradient magnetic separation (HGMS) was first developed in 1969 to upgrade kaolin clays. Successful demonstration of this technique led to research for beneficiating coal by removing its paramagnetic impurities (i.e., ash and pyritic and sulfate sulfur).

An HGMS unit consists of a solenoidal magnet surrounded by an iron casing. Within the cylindrical volume of the magnet are fine strands of strongly ferromagnetic packing material, such as ferritic stainless steel wool. A high field intensity is generated in this volume, where magnetic components of the feed are captured in the packing-material matrix, and the nonmagnetic components are collected at the discharge of the unit. When the matrix becomes saturated with magnetic materials, the feed is stopped and the magnet is de-energized. The matrix is then backwashed with water to remove and collect the magnetic particles; the unit is thus made ready for use in the subsequent cycle. To overcome the cyclical mode of operation, a continuous process using a moving-matrix HGMS unit, called the Carousel Separator, was developed.

Another magnetic-separation technique is currently being investigated at Argonne National Laboratory with support from the State of Illinois. In this approach, finely ground dry coal is passed continuously through the open bore of a powerful superconducting quadrupole magnet. Pyrite and other minerals are drawn to the bore wall, while the carbonaceous material is concentrated in the center. Low energy consumption, continuous processing with no moving parts, and production of a dry product are advantages of this technique.

Agglomeration is another technique that relies on the surface-property differences between coal and pyrite. When a small amount of a water-immiscible liquid is added to a strongly agitated coal-water mixture, the carbonaceous components of the coal become wetted with this liquid and collect as a cluster (i.e., agglomerate). The mixture can then be screened to separate the agglomerates from water and the unagglomerated particles (primarily ash and pyrite).

Oil agglomeration has been commercially used to recover fine coal from refuse ponds. Organic-liquid agglomeration processes are in the developmental stage and require recovery and recycling of the water-immiscible liquid. A liquid-CO_2 agglomeration technique is in a very early developmental stage.

Biological Coal Cleaning: Results of bench-scale biological tests have shown that pyritic or organic sulfur can be removed from coal. Pyritic sulfur has been removed from pulverized coal suspended in an air-bubbled liquid medium containing a bacterium. This bacterium possesses an enzyme that catalyzes the oxidation reaction of sulfur into sulfate at a low pH (e.g., pH of 2.0 to 2.5). Tests performed at Ohio State University and Lehigh University, using the "sulfolobus acidocaldarius" bacterium, produced over 90% pyrite removal in five to ten days.

Removal of over 40% of the organic sulfur has also been achieved (at slightly acidic conditions) by researchers from Atlantic Research Corp., Lehigh University, and the University of Georgia.

Chemical Coal Cleaning: Chemical coal-cleaning processes remove sulfur by way of chemical reactions and produce a product in the solid form. In general, high processing costs have been a major barrier to commercialization of these processes.

Alkali Leaching reacts and dissolves organic and pyritic sulfur and most of the mineral matter in coal with an alkali hydroxide or hydroxides at high temperatures (205 to 375°C). The Gravimelt process uses a molten mixture of sodium and potassium hydroxide to chemically extract organic and pyritic sulfur and mineral matter from coal at ambient pressure. In the Microwave process, microwave irradiation enhances reactions with sodium hydroxide at ambient pressure. The Hydrothermal process uses a solution of sodium and calcium hydroxides at high pressures (250 to 2500 psi) to remove pyritic and organic sulfur from coal. Subsequent washing by an acid solution dissolves the ash.

Oxydesulfurization/Oxidation processes use oxidizing agents to remove pyritic and organic sulfur from coal. Types of oxidizing agents used in these processes include oxygen, air, chlorine, nitrogen dioxide, and ferric sulfate. The Ames process is based on oxidizing sulfur with oxygen dissolved in a hot alkaline solution at high pressures (25 to 300 psi). The JPL Chlorinolysis process uses chlorine gas dissolved in water at ambient pressure and a temperature of 50°C.

EFFECTIVENESS OF COAL CLEANING

Analysis of Coal Sources

Public utilities are required to file monthly statements with the Federal Energy Regulatory Commission (FERC) describing the sources of their coal. As part of the public record, this one-page form (FERC-423) requests information about the state, county, and name of the producing mine, coal quantities purchased, and the heating value, ash content, and sulfur content of the coal. By examining the FERC-423 forms for 1980 and reconciling those data with industry references such as the Keystone Coal Industry Manual, [4] as well as with previous studies, [5] we determined the seams being mined so that we could accurately analyze the performance of coal-cleaning systems and infer the extent to which coal cleaning currently is employed.

Typical coal-purchase data showed several noteworthy trends that could affect the implementation of any mandatory PCC strategy. These trends are as follows:

- Mine-mouth power plants typically make modest purchases each month from mines other than the adjacent one.
- Most other plants typically have from one to three major suppliers, but the plants also may buy small amounts from several sources.
- Very few plants make a large number of coal purchases in small volumes (<10,000 tons).

In most cases, a single principal supplier can be clearly identified for each power plant. This study considered only the coal from this principal supplier for cleaning.

The coals shipped by the suppliers were assigned to general categories corresponding to different "levels" of cleaning (as described previously):

- *Size Control* (Level 1).
- *Coarse-to-Moderate Beneficiation* (Level 2 and Level 3).
- *Deep Beneficiation* (Level 4).

The fraction of SO_2 emissions from each power plant attributable to each class of cleaned coal is shown in Fig. 1, while the total emissions are shown in Fig. 2. Coals that have undergone full (Level 4) cleaning — the type of PCC examined by this study — are unusual but are currently in limited use by some of the power plants. Some plants with fairly high emission rates may in fact have low total emissions due to low capacity factors. These plants are prime candidates for PCC if additional SO_2 control is deemed necessary.

Modeling of PCC Performance

A computer model of physical coal cleaning, developed for ANL by the Center for Energy and Environmental Studies of Carnegie-Mellon University, was used to esti-

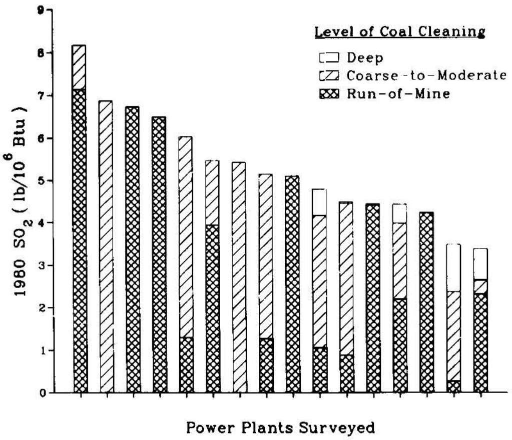

Figure 1. Power-plant SO_2 emission rates, 1980 (lb $SO_2/10^6$ Btu).

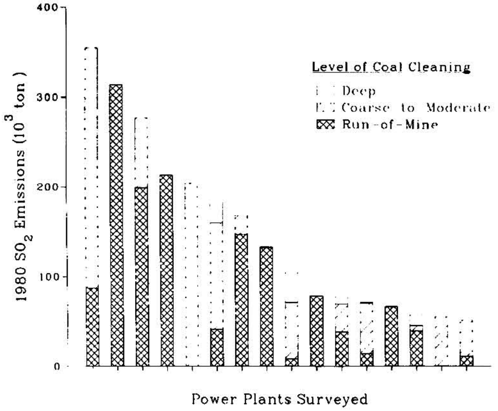

Figure 2. Power-plant SO_2 emissions, 1980 (10^3 tons SO_2/yr), as related to current use of washed coal.

mate PCC plant performance for specific coals. This model is described in Reference [6]. The weight recovery of the coal (that is, the ratio of mass output to mass input for moisture-free coal) is the controlling parameter in the current model.

Information on coal washability for each specific state, county, and coal seam was developed in the early phases of this study from a data base of such properties compiled in a previous ANL project [7] that integrated coal-washability data and coal-reserves data bases obtained from the U.S. Bureau of Mines. Two computer programs developed by Argonne matched the appropriate entries in each data set and then merged the data.

The PCC cost estimates were based on the following:

- Costs were adjusted to September 1984 dollars on the basis of the "CE Plant Cost Index" published in *Chemical Engineering.*
- ROM coal was assumed to have a base selling price at the mine mouth of \$28.15/ton for a 10,678-Btu/lb heating-value coal typical of the Illinois basin [8]. Cost adjustments were calculated at \$2.60/10^6 Btu · ton to account for the heating-value variation among the coals considered.
- Two different weight recoveries for the PCC Level 4 plant were selected for evaluation (87.5% and 80.0%) [9].
- Three coal grinds were treated in the PCC Level 4 plant — 3″ × ¼″, ¼″ × 28 mesh, and 28 mesh × 0. The two finer grinds were physically dewatered and then thermally dried.
- The PCC plant was assumed to be available for 3000 h/yr of operation.
- A single conservative shipment rate of \$4.64/ton was used for shipments from PCC plants that were not mine-mouth operations. This value was the mean value from a survey of shipment costs for 36 midwestern utilities' coal contracts [*10*].
- A constant cleaning cost of \$7.03/ton was used for the 80%-recovery PCC Level 4 plant of "grass-roots" construction with a 10,000-ton/d capacity [*11*].

Results

Emissions, estimated for each of the power plants in the study in terms of pounds of SO_2 per million Btu of coal, are presented both as emission rates (lb $SO_2/10^6$ Btu) and as annual emissions (tons/yr) in Table 3. Comparisons are made between actual 1980 emissions and the emissions that would have resulted (under 1980 operating conditions) if a plant had burned only the coal from its major supplier (as either ROM or cleaned PCC). Hence, for power plants at which the coal is already deep-cleaned, the application of this model showed that no additional reduction in SO_2 emissions would be anticipated. Differences between the sulfur emissions for the ROM values and the actual 1980 emissions values reflect a combination of several factors:

- Averaging of properties from all the coal purchases,
- Departures of the actual ROM coal from the mean value for the seam (used in this determination), and
- Existing application of some level of PCC to the coal.

The first of these factors could either increase or decrease the difference, while the third factor would almost always decrease the 1980 emission rate.

Initially, 24 power plants were to have been surveyed. Unfortunately, two plants with relatively high SO_2 emissions reported coal-purchase data in such a way that specific suppliers could not be identified. These plants had to be dropped from further consideration in the study. Two other plants were also dropped from consideration, one because its source of raw coal could not be adequately characterized and the other because it fired coal that was not amenable to cleaning (i.e., an unusually high-quality, low-sulfur West Virginia coal that showed no sulfur reduction after Level 4 PCC).

The percentage sulfur reductions achievable by cleaning the principal coals are presented in Table 3. The minimum reduction of sulfur was 0%, while a 50% reduction was predicted for one coal relative to ROM conditions. Reductions in SO_2 emissions relative to actual 1980 conditions ranged from 4 to 52%, with increases occurring for two plants. (Increases could occur because the 1980 emissions for most of the plants were lower than those for the principal coal alone, due to the existing use of coal cleaning and the purchase of small quantities of low-sulfur coal for blending.) Although the costs of cleaning are relatively low for a few plants, the incremental cost of additional sulfur removal rises rapidly (see Fig. 3). Even at very high cost, the total potential SO_2 reduction for the plants considered is less than one million tons per year. The costs for emission reductions for Level 4 PCC ranged from \$354 to \$2057/ton SO_2.

Annual SO_2 emissions with and without coal cleaning were also calculated and are shown in Fig. 4 for Ohio, Indiana, and Illinois. In spite of the plant-by-plant variation, no statistically significant variations (at a 95% confidence level) in percentage sulfur reduction or PCC costs existed among the three states included in this study. Actual power-plant SO_2 emissions in each state are lower

Plant	1980 Emissions (lb $SO_2/10^6$ Btu)	Emissions from Principal Coal, ROM (lb $SO_2/10^6$ Btu)	Emissions from PCC Level 4 Coal (lb $SO_2/10^6$ Btu)	% SO_2 Reduction ROM	% SO_2 Reduction 1980	PCC Cost (\$/ton SO_2)[a]
A	5.41	5.99	5.12	14.6	5.4	139
B	5.13	9.93	6.54	34.1	(27.5)[b]	364
C	4.22	4.94	3.01	39.2	28.7	631
E	4.40	4.31	3.27	24.1	25.7	1190
F	4.41	5.53	4.08	26.2	7.5	838
G	5.10	6.39	4.88	23.7	4.3	797
H	8.22	6.72	3.95	41.2	52.0	436
I	6.44	6.39	4.88	23.7	24.2	797
J	2.65	3.85	2.54	34.1	4.2	892
K	6.49	7.35	6.04	17.7	6.9	905
M	5.77	6.73	4.87	27.6	15.6	680
N	8.16	8.69	5.86	32.6	28.2	444
O	6.87	9.15	6.30	31.1	8.3	445
P	3.45	4.14	2.75	33.5	20.3	871
Q	5.47	5.50	4.91	10.6	10.2	2106
R	4.78	5.99	5.12	14.6	(7.1)[b]	1399
S	3.36	4.94	3.01	39.2	10.4	631
T	6.02	7.25	5.08	29.9	15.6	583
U	5.08	4.86	2.43	50.0	52.2	495
V	4.42	6.10	4.09	33.0	7.5	625

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[a] September 1984 dollars.

[b] Increase.

than those that would result if only the principal coal were burned with its ROM sulfur content. In Indiana, the total emissions are heavily influenced by two plants that already purchase cleaned coal. Consequently, the Indiana 1980 emissions closely resemble those for cleaning the major coal at 80% recovery (by weight). The plants surveyed in Illinois could only achieve a reduction of 50,000 tons annually if they burned only their principal coal after Level 4 PCC. The eight power plants in Ohio (a total of 12.4 GWe of capacity) emitted approximately 900,000 tons of SO_2 in 1980. Additional Level 4 PCC may be capable of reducing these emissions by 17% (150,000 tons/yr lower than 1980 levels).

Presenting these data in another way, Fig. 5 compares the aggregate costs for PCC Level 3 and Level 4 strategies. Typically, the incremental sulfur removed by PCC Level 4, as compared with Level 3, runs from 15 to 35%.

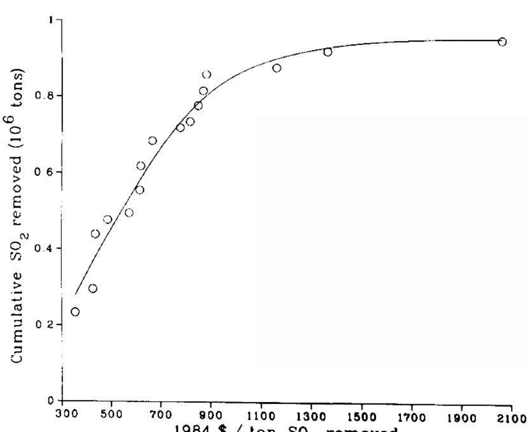

Figure 3. Cumulative SO_2 removal as a function of cost (based on firing only the principal coals at the study plants).

Matching or lowering these incremental-sulfur cleaning costs and improving the economics for the high-cost cases represent the best opportunities for the deployment of new coal-cleaning technologies.

REGULATORY AND INSTITUTIONAL CONSIDERATIONS

The existing use of coal cleaning is fairly widespread, but it is not directed primarily at sulfur reduction. The Electric Power Research Institute (EPRI), for example, not only has funded a coal-cleaning test facility, but has become an active proponent of the advantages of cleaned coal to utilities: lower shipping costs, improved boiler operation, and reduced sulfur emissions [*12*]. If cleaned coal is used to augment scrubbers, EPRI argues, FGD performance is improved and some of the operating costs (sludge disposal, limestone) are reduced. American Electric Power (AEP) has also been quoted as "enthusiastically endorsing coal cleaning" for the improvements in boiler performance and power-plant availability, not for the sulfur-reduction potential of cleaning [*13*]. The AEP said it would be "cheaper to buy high-quality cleaned coal to get peak availability from existing plants than to build new plants to replace what is lost to bad coal."

Experience in Ohio has indicated that it is quite difficult to put together an acceptable legislative and regulatory package for mandating PCC. Voluntary application of deep cleaning techniques (Level 4 PCC) is likely to be constrained by a number of factors, including the following:

- A less favorable tax status for PCC plants, as contrasted with FGD systems.
- Lack of an assured, stable market for the coal.
- Major capital-investment requirements.
- Economic disadvantages (scale factors) for small producers.
- Uncertainties about future environmental legislation and impacts of existing regulations under the Resource Conservation and Recovery Act (RCRA).
- A perceived lack of adequate data for investment decision-making.

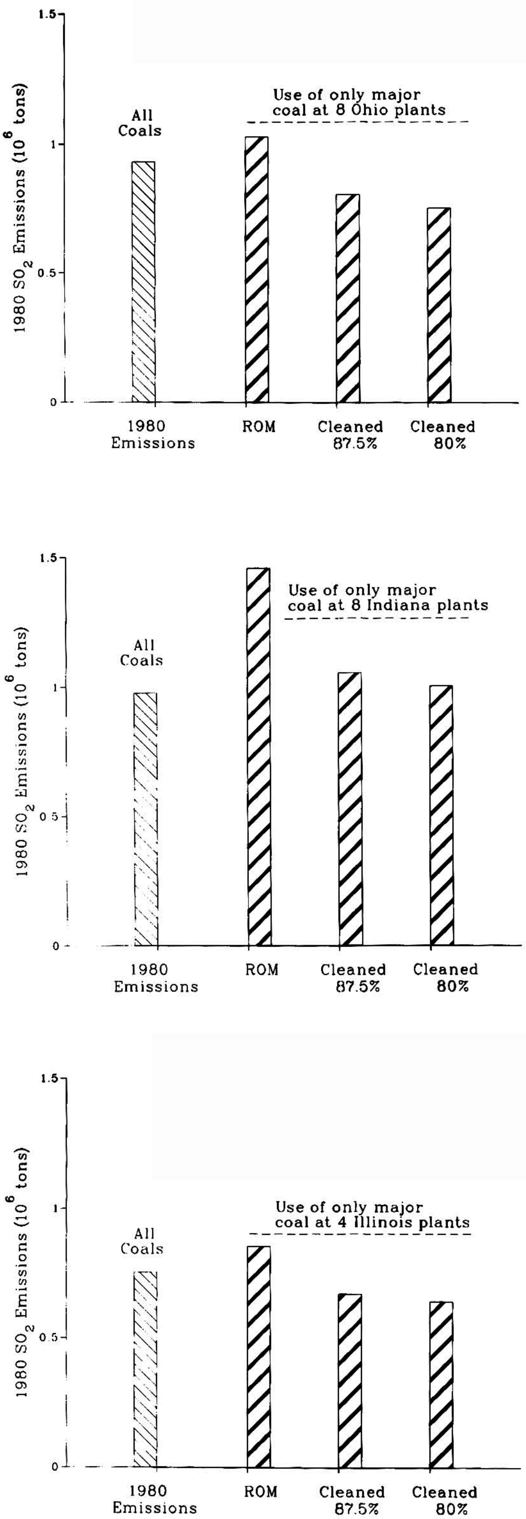

Figure 4. Annual SO_2 emissions for Indiana, Illinois, and Ohio and the projected effect on emissions if each power plant burned only its principal coal with no washing (ROM), or that coal with 87.5 wt. % or 80 wt. % recovery physical coal cleaning.

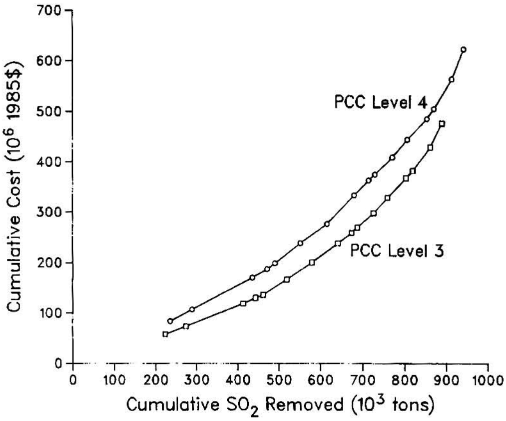

Figure 5. Annual aggregate costs for PCC Level 4 and Level 3 as a function of total sulfur removed.

Measures that could be undertaken to encourage the voluntary use of cleaned coal include loan and price guarantees, changes in the tax laws, and stabilization of regulations for a guaranteed period of time. None of these measures is likely to have much effect in the short term, and those requiring commitment of government funds would almost certainly be difficult to legislate.

Requirements for mandatory coal cleaning have been suggested at the federal level as part of acid-rain legislation. Although these requirements are still under consideration, the most likely governmental level for implementing a cleaning requirement is the state level. State Implementation Plans could be revised in the following ways:

- Require all sources to reduce a certain percentage of sulfur emissions by washing (e.g., washing to reduce the sulfur content of all coals in use by 25%). Such a requirement might be technically infeasible for some coals in a state or might be very inefficient in terms of energy losses. Therefore, limits would need to be set.
- Require the removal of X% of sulfur, if uncontrolled emissions are greater than Y lb $SO_2/10^6$ Btu and if energy losses are less than Z%. If washing the coal could not achieve an X% reduction, if the raw coal were already low in sulfur, or if significant losses in terms of energy content would occur, then the requirement would not be enforced.
- Set an emission cap for each power plant in the state. An emission cap would need to be carefully chosen to encourage the use of washed coal. This option combines mandatory and incentive approaches.
- Set regulations for each source. The results of this study suggest that a source-specific regulatory strategy would be the most effective choice for the states and utility plants reviewed. This alternative would place heavy demands on the staff of a regulatory agency. Moreover, in the absence of a local air-quality problem (such as nonattainment) or of a federal requirement for states to reduce SO_2 emissions, a selective regulatory action could face serious problems of acceptability. Equity issues could be raised about an initiative that would require one power plant to use washed coal, increasing the costs of its fuel, but would not require another power plant to do the same.

Regulations would have to be applied with care and flexibility to avoid driving certain coals (and coal producers) from the marketplace because of poor cleanability.

Furthermore, actions involving emission caps could stimulate the transportation of low-sulfur coals unless requirements for "local" coal use were also enacted.

CONCLUSIONS

This study has focused primarily on determining SO_2 emission reductions that could be obtained in the Midwest by applying extensive physical coal cleaning to coals now burned by 20 major power plants. At issue are strategies for achieving the level of SO_2 emission reductions (typically at least 50% reductions from 1980 levels) proposed in acid-rain legislation.

About one-third of the coal evaluated is now given some degree of cleaning by suppliers; very little coal receives the sort of "deep" cleaning modeled in this study. Deep cleaning of ROM coal could reduce emissions from individual plants by 0 to 52%, with an average value of about 29%. In comparison with 1980 emissions, a more realistic reduction is near 20%, because some cleaned or high-quality coals are currently in use.

Coal cleaning could be a cost-effective SO_2 control strategy for individual plants. However, its usefulness as a mandatory acid-rain-mitigation strategy is limited by the high degree of variation in washability among coals (even for different samples of coal from the same seam). By itself, deep physical coal cleaning could not reduce total SO_2 emissions by 50%, as proposed by some "acid-rain" legislation.

Voluntary application of deep-cleaning techniques could be encouraged by such measures as loan guarantees, changes in the tax laws, and stabilization of regulations for a guaranteed period of time. However, the most likely governmental level for encouraging coal cleaning is the state level. State Implementation Plans could be revised to do the following:

- Require all power plants to reduce SO_2 emissions by a certain percent.
- Set an emission cap for each power plant.
- Require a certain percentage removal of sulfur if uncontrolled emissions are greater than a threshold value.
- Regulate SO_2 levels for each source individually.

Regulations, unless flexible and applied with care, would drive certain coals (and coal producers) from the marketplace because of poor cleanability. Furthermore, actions involving emission caps could stimulate the transportation of low-sulfur coals unless requirements for "local" coal use were also enacted. While physical coal cleaning should be considered in formulating any SO_2 control strategy, problems arising from coal variability, limited efficacy compared with that of FGD, and multiplicity of coal suppliers make a universal cleaning requirement difficult to design and implement.

ACKNOWLEDGMENTS

This paper is based largely on work sponsored by the U.S. Environmental Protection Agency (EPA), Region V, Air Management Division. The authors gratefully acknowledge the valuable contributions of the EPA project officers, Rizalino Castanares and John Paskevicz. The opinions expressed in this article are those of the authors alone and should not be construed as representing the policies of Argonne National Laboratory or the U.S. Environmental Protection Agency. The authors also wish to acknowledge the valuable contributions of John Anderson (Argonne National Laboratory) and Doris Garvey (now with Los Alamos National Laboratory) to the performance of this work.

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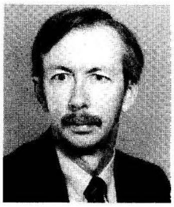

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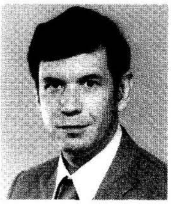

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Coal Desulfurization in a Fluidized Bed Reactor

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Fluidized bed reactor technology was investigated as a means of developing a new simple and low cost process for coal desulfurization. Preliminary experimental results obtained in a 2.54 cm batch fluidized bed reactor have shown that over 80% total sulfur reductions can be achieved by sequential chlorination and dechlorination/hydrodesulfurization of high sulfur pulverized coals. Proximate and ultimate analyses of desulfurized coals have revealed enhanced carbon and fixed carbon levels and substantially reduced volatile, oxygen and hydrogen contents. While there was a minor increase in the ash content and heating value, nitrogen and chlorine contents were essentially unchanged. Compared to an earlier slurry phase process, the fluidized bed reactors process has specific advantages such as shorter reaction times, fewer processing steps and reduced reactant requirements. A fluidized bed reactor process may thus have a potential of being developed into a simple and economic means of converting high sulfur coals to environmentally acceptable fuels.

INTRODUCTION

An evaluation of the available alternate fuels, as suitable substitutes to petroleum, shows that coal will be a major resource of energy in the U.S. in the coming years. While the U.S. possesses the largest known reserves of coal, a majority of these, particularly the Eastern and mid-Western coals, are of a high sulfur variety making them unacceptable to be employed as such in the power plants. Consequently, it has become imperative to develop coal cleaning technologies which will facilitate large scale utilization of coal without causing serious air pollution.

The emerging of pre-combustion coal cleaning in recent years, as a viable alternative to post-combustion flue gas cleanup has resulted in the development of a wide variety of processes for coal desulfurization. However, cost evaluations have shown that at the present time none of these processes may be commercially attractive. The dwindling petroleum prices have also contributed to this lack of interest in chemical coal cleaning. At the same time, it is also realized that a rebound in coal usage is inevitable, and in the meantime, there is a need to reevaluate the economics and technology of chemical coal cleaning so as to evolve more cost effective methods. The present investigation is one attempt in that direction.

The principal coal desulfurization processes have been critically evaluated in some recent publications [*1*-*3*]. A majority of these processes involved treating coal, most often in an aqueous medium, with oxidizing agents or alkalies [*4*-*8*] in order to convert the sulfur in coal to a form amenable for extraction. Chemical coal desulfurization

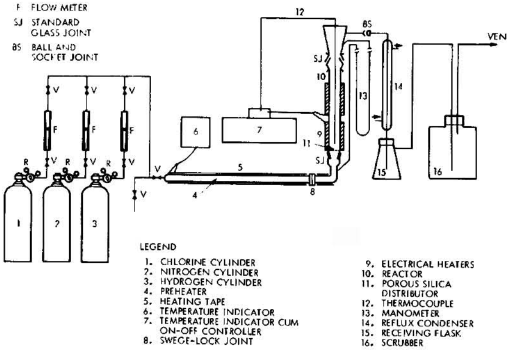

Figure 1. Batch fluidized bed reactor system for coal desulfurization.

This paper presents the results of one phase of research work carried out at the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, and the JPL Director's Discretionary Fund.

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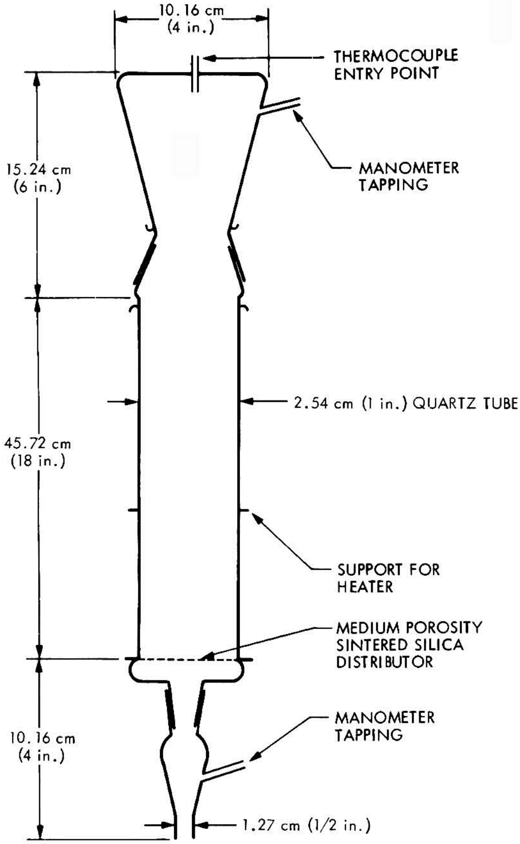

Figure 2. Fluidized bed reactor.

employing oxidants ranging from strong oxidants (HNO_3 and H_2O_2) to metal ions (Fe^{+3}, Ag^+) and gaseous species (air, O_2, SO_2, NO_2, Cl_2, etc.) has been extensively studied [*9-13*].

Though the oxidation potential of chlorine has been known for a long time, use of chlorine for coal desulfurization is fairly recent. Chlorine either in an aqueous state or in a gaseous form readily reacts with sulfur. However, earlier investigators reported poor sulfur removals from coal [*14, 15*]. A major advance in coal desulfurization by chlorine is reported by the Jet Propulsion Laboratory. The JPL "Low Temperature Chlorinolysis Process" consisting of chlorination of a coal-water slurry followed by dechlorination/hydrodesulfurization in the dry state was re-

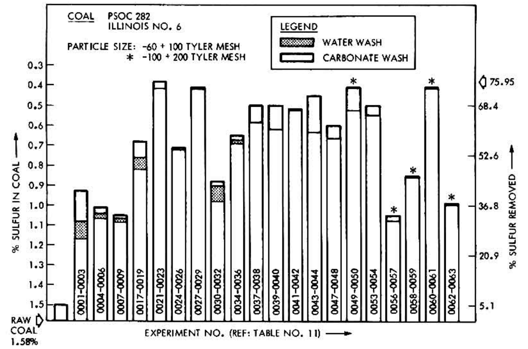

Figure 3. Experimental results of fluidized bed coal desulfurization, PSOC 282, Illinois No. 6.

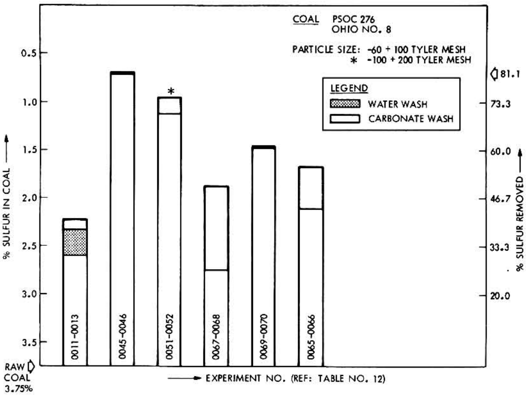

Figure 4. Experimental results of fluidized bed coal desulfurization, PSOC 276, Ohio No. 8.

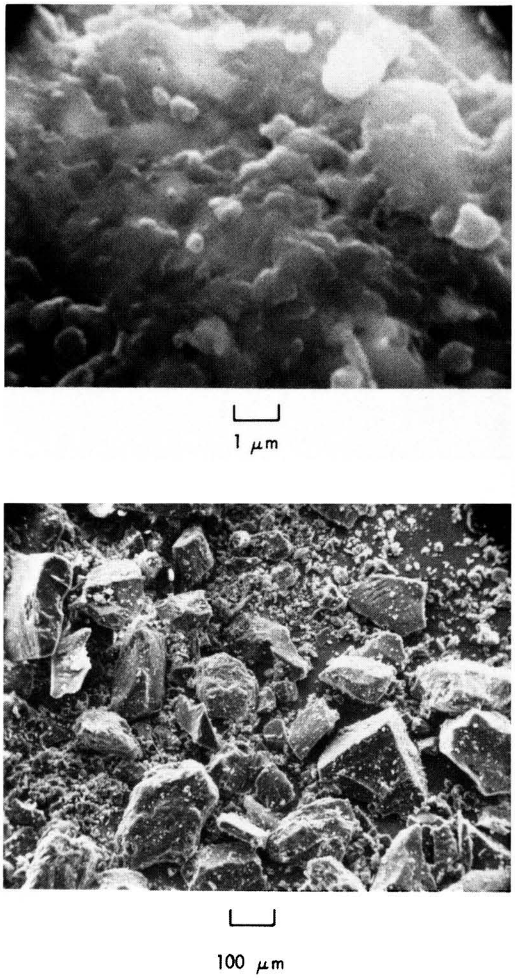

Figure 5. SEM photograph of PSOC 282 raw coal.

TABLE 1. EXPERIMENTAL CONDITION AND RESULTS
COAL: PSOC 282, Illinois No. 6 (−60 + 100 Tyler Mesh)

Total Sulfur: 1.581 (Wt%)[a]

Experiment No.	Chlorination	Intermediate Wash	Dechlorination with Nitrogen	Advanced Dechlorination with Hydrogen	Post-Treatment	% Total Sulfur in Product[a]	% Desulfurization
0001	15 min, ambient	—	30 min, 400°C[f]	—	—	1.170	26.1
0002	15 min, ambient	—	30 min, 400°C	—	water wash	1.082	31.6
0003	15 min, ambient	—	30 min, 400°C	—	carbonate wash[b]	0.925	41.5
0004	15 min, ambient	—	60 min, 400°C	—	—	1.06	32.7
0005	15 min, ambient	—	60 min, 400°C	—	water wash	1.04	34.2
0006	15 min, ambient	—	60 min, 400°C	—	carbonate wash	1.01	35.9
0007	15 min, ambient	—	30 min, 500°C	—	—	1.07	32.2
0008	15 min, ambient	—	30 min, 500°C	—	water wash	1.06	32.7
0009	15 min, ambient	—	30 min, 500°C	—	carbonate wash	1.05	32.8
0010	—	carbonate wash[b]	—	—	—	1.50	5.1
0017	15 min, 100°C[f]	—	—	30 min, 600°C[f]	—	0.82	48.4
0018	15 min, 100°C	—	—	30 min, 600°C	water wash	0.76	52.1
0019	15 min, 100°C	—	—	30 min, 600°C	carbonate wash	0.68	57.2
0020	15 min, 100°C	—	—	—	—	—	—
0021	15 min, 100°C	carbonate wash[b]	—	30 min, 600°C	—	0.41	74.1
0022	15 min, 100°C	carbonate wash[b]	—	30 min, 600°C	water wash	0.41	74.1
0023	15 min, 100°C	carbonate wash[b]	—	30 min, 600°C	carbonate wash	0.38	76.0
0024	15 min, 100°C	water wash	—	30 min, 600°C	—	0.72	54.6
0025	15 min, 100°C	water wash	—	30 min, 600°C	water wash	0.72	54.6
0026	15 min, 100°C	water wash	—	30 min, 600°C	carbonate wash	0.71	55.1
0027	15 min, 100°C	carbonate wash	—	30 min, 700°C	—	0.41	74.1
0028	15 min, 100°C	carbonate wash	—	30 min, 700°C	water wash	0.41	74.1
0029	15 min, 100°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.41	74.1
0030	—	—	—	30 min, 600°C	—	0.976	38.3
0031	—	—	—	30 min, 600°C	water wash	0.902	42.9
0032	—	—	—	30 min, 600°C	carbonate wash	0.883	44.1
0033	15 min, 100°C	—	—	—	carbonate wash	—	—
0034	15 min, 100°C	carbonate wash	—	30 min, 500°C	—	0.690	56.3
0035	15 min, 100°C	carbonate wash	—	30 min, 500°C	water wash	0.677	57.2
0036	15 min, 100°C	carbonate wash	—	30 min, 500°C	carbonate wash	0.652	58.7
0037	5 min, 100°C	carbonate wash	—	30 min, 700°C	—	0.581	63.2
0038	5 min, 100°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.498	68.5
0039[c]	15 min, 100°C	—	—	30 min, 700°C	—	0.614	61.1
0040[c]	15 min, 100°C	—	—	30 min, 700°C	carbonate wash	0.496	68.6
0041[d]	15 min, 100°C	carbonate wash	—	30 min, 700°C	—	0.517	67.3
0042[d]	15 min, 100°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.517	67.3
0043	15 min, 100°C	carbonate wash	—	10 min, 700°C	—	0.632	60.0
0044	15 min, 100°C	carbonate wash	—	10 min, 700°C	carbonate wash	0.449	71.6
0047	5 min, 100°C	carbonate wash	—	10 min, 700°C	—	0.662	58.1
0048	5 min, 100°C	carbonate wash	—	10 min, 700°C	carbonate wash	0.600	62.0
0049[e]	15 min, 100°C	carbonate wash	—	30 min, 700°C	—	0.521	67.0
0050[e]	15 min, 100°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.409	74.1
0053	15 min, 250°C	carbonate wash	—	30 min, 700°C	—	0.547	65.4
0054	15 min, 250°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.500	68.4
0055	15 min, 100°C	—	—	—	—	1.09	29.2
0056[e]	15 min, 100°C	—	30 min, 400°C	—	—	1.076	31.9
0057[e]	15 min, 100°C	—	30 min, 400°C	—	carbonate wash	1.052	33.5
0058[e]	15 min, 100°C	—	30 min, 400°C	30 min, 700°C	—	0.849	46.3
0059[e]	15 min, 100°C	—	30 min, 400°C	30 min, 700°C	carbonate wash	0.850	46.2
0060[e]	15 min, 100°C	carbonate wash	—	30 min, 700°C	—	0.412	73.9
0061[e]	15 min, 100°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.410	74.1
0062[e]	5 min, 100°C	—	—	10 min, 700°C	—	0.990	37.4
0063[e]	5 min, 100°C	—	—	10 min, 700°C	carbonate wash	0.985	37.7

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[a] LECO analysis.

[b] Soaked in 10% Na_2CO_3 solution for 30 min, followed by washing with distilled water until free of alkali, then dried.

[c] Coal initially washed with 10% Na_2CO_3 solution and dried.

[d] Chlorination with a 4:1 mixture of nitrogen and chlorine.

[e] - 100 + 200 Tyler Mesh.

[f] -T°K = t(°c) + 273.15.

Table 2. Experimental Condition and Results

COAL: PSOC 276, Ohio No. 8 (−60 + 100 Tyler Mesh) Total Sulfur: 3.75 (Wt%)[a]

Experiment No.	Chlorination	Intermediate Wash	Dechlorination with Nitrogen	Advanced Dechlorination with Hydrogen	Post-Treatment	% Total Sulfur in Product[a]	% Desulfurization
0011	15 min, 100°C[d]	—	30 min, 400°C[d]	30 min, 600°C[d]	—	2.60	30.6
0012	15 min, 100°C	—	30 min, 400°C	30 min, 600°C	water wash	2.33	37.9
0013	15 min, 100°C	—	30 min, 400°C	30 min, 600°C	carbonate wash[b]	2.23	40.5
0045	15 min, 100°C	carbonate wash[b]	—	30 min, 700°C	—	0.708	81.1
0046	15 min, 100°C	carbonate wash[b]	—	30 min, 700°C	carbonate wash	0.699	81.3
0051[c]	15 min, 100°C	carbonate wash	—	30 min, 700°C	—	1.113	70.3
0052[c]	15 min, 100°C	carbonate wash	—	30 min, 700°C	carbonate wash	0.943	74.9
0064	5 min, 100°C	—	—	—	—	2.81	27.4
0065	30 min, 100°C	—	30 min, 600°C	30 min, 700°C	—	2.11	43.7
0066	30 min, 100°C	—	30 min, 600°C	30 min, 700°C	carbonate wash	1.67	55.5
0067	5 min, 100°C	—	10 min, 600°C	10 min, 700°C	—	2.750	26.7
0068	5 min, 100°C	—	10 min, 600°C	10 min, 700°C	carbonate wash	1.870	50.1
0069	5 min, 100°C	carbonate wash	10 min, 600°C	10 min, 700°C	—	1.47	60.8
0070	5 min, 100°C	carbonate wash	10 min, 600°C	10 min, 700°C	carbonate wash	1.46	60.9

[a] LECO analysis.
[b] Soaked in 10% Na_2CO_3 solution for 30 min followed by washing with distilled water until free of alkali, then dried.
[c] −100 + 200 Tyler Mesh.
[d] −T(°K) = t(°C) + 273.15.

ported to be very effective in removing both the organic and inorganic sulfur fractions from coal [16-18].

The present program of work was undertaken to investigate the feasibility of bringing about coal desulfurization in the solid phase itself in a fluidized bed reactor employing gaseous chlorine. Preliminary experimental results obtained in a 2.54 cm diameter laboratory scale batch fluidized bed reactor demonstrating the feasibility of the concept are presented herein for two high volatile bituminous coals.

EXPERIMENTAL

Apparatus: A schematic diagram of the experimental set-up and details of the FBR are presented in Figures 1 and 2 respectively. The reactor made of 1-inch diameter quartz tube was enclosed in a close fitting 264 watt Thermcraft cylindrical heater. Temperature in the reactor was monitored and controlled by means of a K type iron-constantan thermocouple connected to a Wheelco ON-OFF Temperature Controller.

Flow rates of nitrogen, chlorine and hydrogen were monitored by calibrated rotameters. Pressure drop across the fluidized bed was monitored by a manometer and the

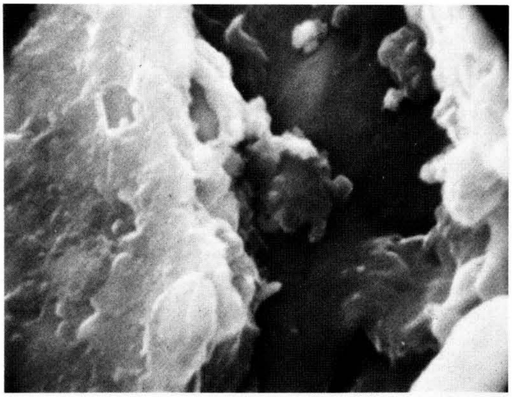

Figure 6. SEM photograph of PSOC 282 treated coal (Run No. 0032).

TABLE 3. TOTAL SULFUR AND FORMS OF SULFUR IN SELECTED PRODUCT COALS,[a] PSOC 282

Sample No.	Experiment[b] No.	Total Sulfur[c] wt%	Total Sulfur[c] % Removed	Pyritic Sulfur[c] wt%	Pyritic Sulfur[c] % Removed	Sulfate Sulfur[c] wt%	Sulfate Sulfur[c] % Removed	Organic Sulfur[c,d] wt%	Organic Sulfur[c,d] % Removed
—	Raw Coal	1.54	—	0.43	—	0.36	—	0.75	—
1	0017	0.84	45.4	0.04	90.8	<0.05	86.1	0.80	+6.7
2	0039[e]	0.63	59.1	0.04	90.7	<0.05	86.1	0.59	21.3
3	0041[f]	0.58	62.3	0.03	93.0	<0.05	86.1	0.55	26.7
5	0055[g]	1.09	29.2	0.22	48.8	0.29	19.5	0.58	22.7
6	0058	0.81	47.4	0.03	93.0	<0.05	86.1	0.78	+4.0
7	0060	0.51	66.9	0.02	95.4	<0.05	86.1	0.49	34.7

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[a] Analyses carried out at CSMRI.

[b] For experimental details refer to Table 1.

[c] As determined basis.

[d] By difference.

[e] Coal pretreated with 1 M Na_2CO_3 solution.

[f] Mixture of N_2/Cl_2 (4:1) during chlorination.

[g] Chlorination only.

TABLE 4. TOTAL SULFUR AND FORMS OF SULFUR IN SELECTED PRODUCT COALS,[a] PSOC 276

Sample No.	Experiment[b] No.	Total Sulfur[c] wt%	Total Sulfur[c] % Removed	Pyritic Sulfur[c] wt%	Pyritic Sulfur[c] % Removed	Sulfate Sulfur[c] wt%	Organic Sulfur[c,d] % Removed	wt%	% Removed
—	Raw Coal	3.87	—	2.63	—	0.06	—	1.17	—
4	0045	0.70	81.9	0.03	98.8	<0.05	—	0.67	42.7
8	0064[e]	2.81	27.4	0.72	72.6	1.02[g]	—	1.07	8.5
9	0067	2.29	40.8	0.13	95.0	<0.05	—	2.16[g]	—
10	0069[f]	1.73	55.3	0.04	98.5	<0.05	—	1.69[g]	—

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[a] Analyses carried out at CSMRI.

[b] For experimental details refer to Table 2.

[c] As determined basis.

[d] By difference.

[e] Chlorination only.

[f] 5 min chlorination and 10 min dechlorination and hydrodesulfurization.

[g] Anamolous results showing a substantial increase.

TABLE 5. COMPARISON OF TOTAL SULFUR ESTIMATION BY ESCHKA AND LECO METHODS

Sample No.	Experiment No.[a]	Eschka Analysis[b]	LECO Analysis[c]	Difference Eschka-LECO	% Deviation
		PSOC 282 COAL (Illinois No. 6)			
—	Raw Coal	1.54	1.58	−0.04	−2.5
1	0017	0.84	0.82	+0.02	+2.4
2	0039	0.63	0.61	+0.02	+3.3
3	0041	0.58	0.52	+0.06	+11.5
5	0055	1.09	—	—	—
6	0058	0.81	0.85	−0.04	−4.7
7	0060	0.51	0.41	+0.10	+24.4
		PSOC 276 COAL (Ohio No. 8)			
—	Raw Coal	3.87	3.75	+0.12	+3.2
4	0045	0.70	0.71	−0.01	−1.4
8	0064	2.81	—	—	—
9	0067	2.29	2.75	−0.46	−16.7
10	0069	1.73	1.47	+0.26	+17.6
		Percent Average Deviation: 8.8			

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[a] For experimental details refer to Tables 1 and 2.

[b] Analyses carried out at CSMRI.

[c] Analyses carried out at JPL.

pressure drop fluctuations were considered as indicative of fluidization. Exit gases from the reactor were scrubbed with 1 M Na_2CO_3 solution before they were vented off.

Procedures: PSOC 276 (Ohio No. 8) and PSOC 282 (Illinois No. 6) coals employed in the study were obtained by sieving the ground coals to provide 60/100 and 100/200 Tyler mesh particles. For each experiment 0.05 kg of dried coal (previously dried in an oven at 373°K for 6-8 hrs.) were charged to the reactor. The bed was initially fluidized with nitrogen. Subsequently, depending on the treatment, chlorine, nitrogen or hydrogen were substituted as the fluidizing medium. Chlorination treatments lasted from 5-15 minutes at about 373°K. Dechlorination of chlorinated coals was accomplished with nitrogen at 673°-873°K for 10-30 minutes, while hydrodesulfurization was carried out at 773-973°K for 10-30 minutes. The bed

TABLE 6. PROXIMATE AND ULTIMATE ANALYSES OF SELECTED PRODUCT COALS[a]

Coal	Sample No.	Experiment No.[b]	Moisture[c] %	Ash, %		Volatile Matter, %		Fixed Carbon, %		Heating Value, Btu/lb[g]		Carbon, %	
				AD[c]	Dry[d]	AD	Dry	AD	Dry	AD	Dry	AD	Dry
PSOC 282	O	Raw Coal[f]	3.1	—	6.70	—	33.80	—	59.50	—	13,092	—	74.8
PSOC 282	A	0055	3.61	5.88	6.10	34.50	35.80	56.00	58.10	10,752	11,150	62.40	62.70
PSOC 282	B	0060	2.13	6.78	6.93	5.77	5.90	85.30	87.20	13,372	13,666	84.00	85.80
PSOC 276	O	Raw Coal[f]	1.89	—	11.50	—	37.20	—	51.30	—	12,755	—	71.60
PSOC 276	C	0064	2.73	10.40	10.70	35.30	36.30	51.60	53.00	11,165	11,478	63.60	65.40
PSOC 276	D	0069	1.31	12.80	13.00	7.09	7.18	78.80	79.80	12,580	12,744	79.10	80.10

Sample No.	Hydrogen, %		Sulfur, %		Nitrogen, %		Chlorine, %		Oxygen, %[e]	
	AD	Dry	AD	Dry	AD	Dry	AD	Dry	AD	Dry
O	—	4.82	—	1.60	—	1.69	—	0.47	—	10.00
A	4.22	3.96	1.16	1.20	1.27	1.32	12.40	12.90	12.70	9.82
B	2.20	2.00	0.48	0.49	1.60	1.64	0.50	0.51	4.44	2.63
O	—	5.67	—	3.91	—	1.28	—	0.16	—	5.87
C	4.70	4.52	2.84	2.92	1.11	1.14	4.43	4.55	12.90	10.80
D	2.21	2.09	1.63	1.65	1.38	1.40	0.13	0.13	2.75	1.63

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[a] Analysis carried out at CSMRI.
[b] For experimental details refer to Tables 1 and 2.
[c] As determined basis.
[d] Dry basis.
[e] By difference.
[f] From Phase III Report (Ref. 18).
[g] 1Btu/lb = 23 26 J/kg

was cooled to the ambient temperature after the desulfurization treatment in a stream of nitrogen.

Some of the product coals were also subjected to a washing treatment both before and after hydrodesulfurization.

Some experiments were also conducted to study the effect of chlorine concentration by employing a mixture of nitrogen and chlorine (4:1) during chlorination and the effect of higher temperatures during chlorination.

Raw coals, and product coals were analyzed for total sulfur content by a modified Leco acid-base method immediately after an experiment. More complete analyses for sulfur distribution, and proximate and ultimate analyses were carried out at the Colorado School of Mines Research Institute (CSMRI). Coal samples for SEM and EDAX analyses were prepared by standard techniques. Details of analyses procedures are reported elsewhere [*19*].

RESULTS AND DISCUSSION

Fluidized bed desulfurization tests were conducted by sequential chlorination and dechlorination/hydrodesulfurization employing two high volatile bituminous coals (PSOC 276 and 282).

Details of treatments and extent of total sulfur removed as estimated by Leco analysis are presented in Tables 1 and 2. The results are also presented in a more convenient form as bar charts in Figures 3 and 4.

PSOC 282 Coal: A maximum level of 74% total sulfur removal was achieved (Experiments 0021 and 0027) based on 1.58% total sulfur in raw coal. However, based on the total sulfur content of unwashed mined coal (2.2%), the level of desulfurization is 81%.

Chlorination by itself did not remove sulfur to any significant extent. Dechlorination by nitrogen not only increased the desulfurization level but also reduced the chlorine remaining in the coal. While higher temperatures and longer times during dechlorination did not markedly enhance the level of desulfurization over that achieved at 673°K for 30 minutes, they were effective in reducing the chlorine level in product coals.

A dramatic increase in the level of desulfurization was achieved by substituting hydrogen during dechlorination. In fact, hydrodesulfurization was found to be more effective than successive dechlorination and hydrodesulfurization. Carbonate wash of the chlorinated coals prior to hydrodesulfurization was found to further enhance the desulfurization level (Experiment 0021).

The process could be made more economic by reducing the chlorine demand. This could be done by either reducing the chlorination time or by reducing the chlorine concentration. Both these approaches were tried. Even five minute chlorination followed by hydrodesulfurization results in 63% desulfurization (Experiment 0037) while a mixture of chlorine and nitrogen (1:4) during chlorination yielded 61% desulfurization (Experiment 0041). However, higher chlorination temperatures did not significantly enhance the level of desulfurization (Experiment 0053).

In general, depending on the level of desulfurization needed, the operating variables could be suitably adjusted. However, an extensive parametric study is needed.

In one experiment even a five minute chlorination and ten minute dechlorination/hydrodesulfurization was found to be capable of removing a fair proportion of sulfur from coal (Experiment 0048). Pretreatment of coal with alkali was also found to enhance sulfur removal in the subsequent treatments (Experiment 0040).

PSOC 276 Coal: Relatively fewer number of experiments were carried out with PSOC 276 Coal. Here again, the maximum level of desulfurization achieved was 81% (Experiment No. 0045). The results were similar to those obtained with 282 Coal.

CSMRI Analyses: Ten desulfurized coal samples from typical experiments were analyzed at CSMRI for total sulfur and sulfur forms distribution by ASTM approved methods. The results are presented in Tables 3 and 4. Total sulfur estimations by Leco and Eschka methods are found to be in good agreement as can be seen from the data presented in Table 5. From the sulfur distribution data presented in Tables 3 and 4, it can be seen that pyritic sulfur removals over 90% were achieved in the process. Some anomalies were observed with regard to organic sulfur estimation which resulted in its apparent increase.

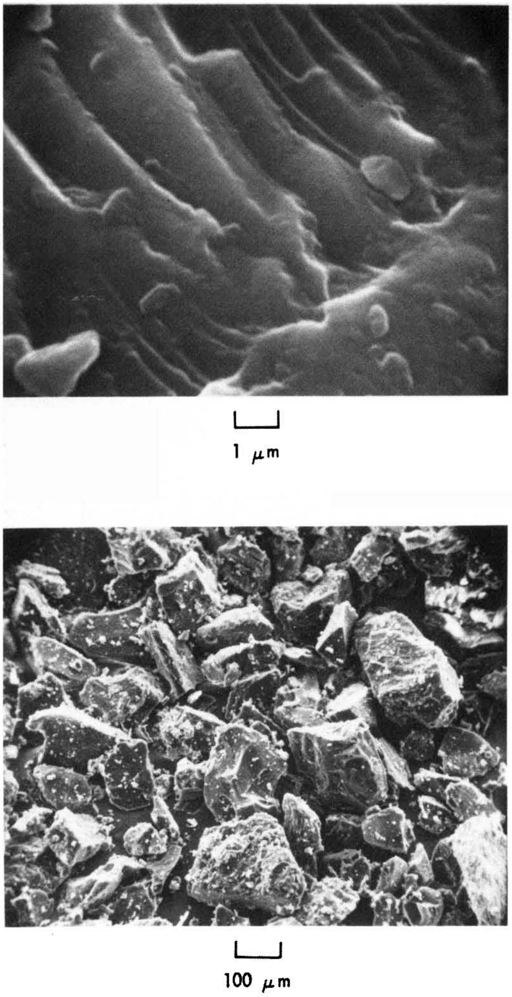


Figure 7. SEM photograph of PSOC 276 raw coal.

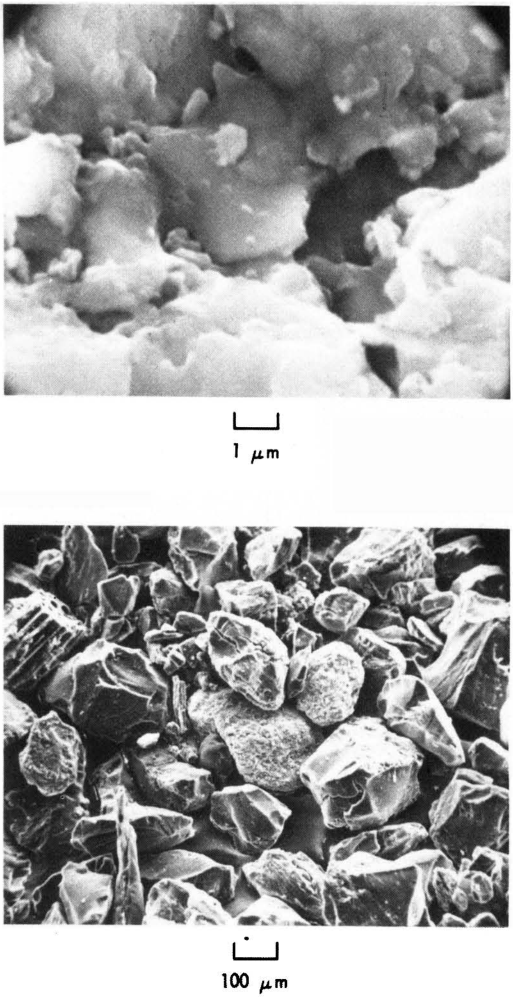


Figure 8. SEM photograph of PSOC 276 treated coal (Run No. 0046).

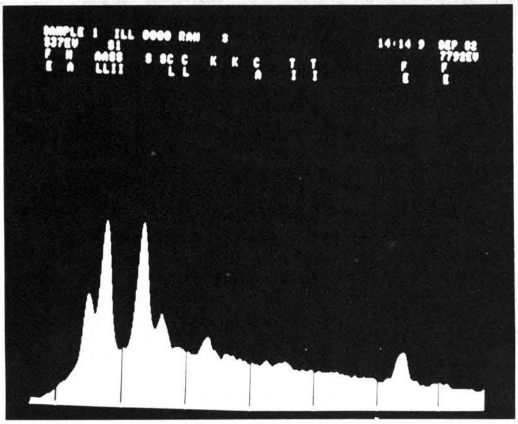
Long proximate and ultimate analyses of raw coals, chlorinated coals, and chlorinated and hydrodesulfurized coals carried out by CSMRI are presented in Table 6.

Chlorination by itself resulted in minor reductions in ash, sulfur and hydrogen contents and a considerable reduction in the heating value, whereas the chlorine content increased by almost two orders of magnitude. On the other hand dechlorination/hydrodesulfurization of chlorinated coals, besides restoring the chlorine level and heating value to those of the raw coal, resulted in marked changes in the coal characteristics. The major changes can be summarized as: ash content increased by 3-10%, carbon content increased by 10-15%, and fixed carbon increased by 45-55%; whereas volatiles content decreased by more than 80%, hydrogen content decreased by 60%, and oxygen content decreased by 70%. Nitrogen content remained essentially unchanged.

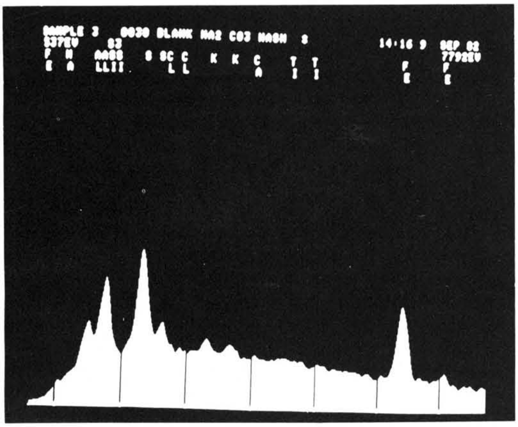
Thus, as a consequence of the desulfurization treatments, high sulfur removals were achieved which at the same time resulted in drastic reductions in the volatiles content. The latter aspect is of particular significance while assessing the suitability of the product coals as feedstocks to the existing burners. However, recent combustion test evaluations as a part of an earlier study [20] with the Penn State "Plane Flame Furnace" have shown that the low volatile highly desulfurized coals burned well to completion without serious problems.

SEM/EDAX Examination of Coal: During the desulfurization treatments, coal undergoes various chemical changes which also result in altering its gross physical structure. Relatively new techniques such as scanning electron microscopy (SEM) and energy dispersive analysis for X-rays (EDAX) are being increasingly used to assess the physical changes undergone by the coal surface. SEM photographs and EDAX spectra of raw coals and desulfurized coals from typical experiments are presented in Figures 5-11.

SEM photographs of raw coals show that the coal particles are surrounded and covered by several small particles. While the coal particles are in a size range of 50-200 μm, a majority of the small particles are of the order of 1 μm. SEM photographs of desulfurized coals show that in addition to a substantial cleaning of the coal surface, the treatments also resulted in the coal surface developing fissures and cracks. While the raw coal particle surfaces were smooth, surfaces of the desulfurized coals appear to be rough. The above features are indicative of breakdown of pore structure and loss of some portions from the coal surfaces.

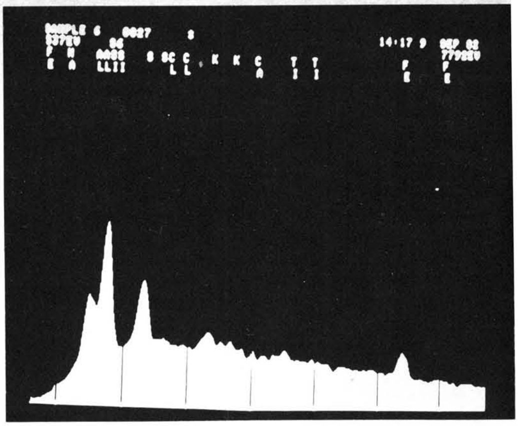


PSOC 282 RAW COAL

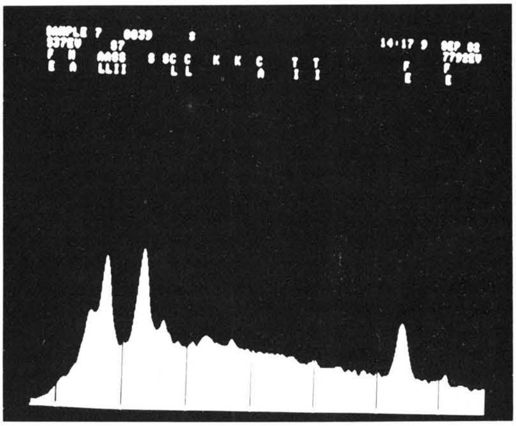


PSOC 282 COAL WASHED WITH IM Na_2CO_3 SOLUTION

Figure 9. EDAX spectrum of coal.



PSOC 282 TREATED COAL (RUN NO. 0027)



PSOC 282 TREATED COAL (RUN NO. 0039)

Figure 10. EDAX spectrum of coal.

Comparison of EDAX spectra shows that the characteristic sulfur peaks in the desulfurized coals are smaller than those in the raw coals. Some reduction in the peaks corresponding to mineral components can also be seen in the above spectra. More important, the spectra show that as a consequence of chlorine treatment, there is no enhancement in the chlorine levels in the desulfurized coals.

Simplified Low Cost Process: The reaction of pyritic and organic sulfur with chlorine in an anhydrous media favors the formation of sulfur monochloride (S_2Cl_2), and the excess chlorine the reaction goes to sulfur dichloride (SCl_2) [*19*]. Whereas, in an aqueous media, sulfur is oxidized by chlorine to sulfuric acid [*13, 17, 18, 20*]. Thus, the fluidized bed in an anhydrous media can provide chlorine savings of 60-70% over that of the aqueous coal slurry chlorination process. The use of counter current flow for regenerative heat transfer will minimize the energy requirements for dechlorination and hydrodesulfurization in a continuous flow process. Short fluidized bed reaction times with gas-solid phase desulfurization reactions should provide process cost savings over the aqueous coal slurry chlorination process.

CONCLUSIONS

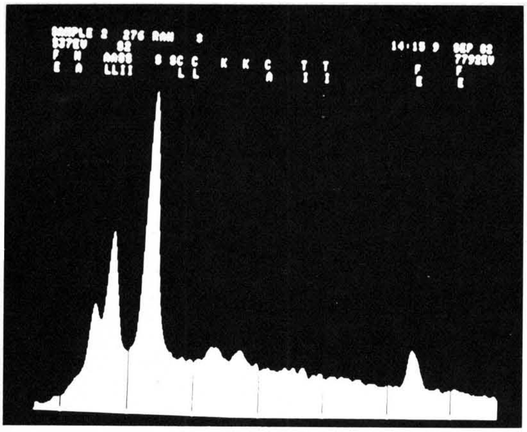
Preliminary experimental results on coal desulfurization in a fluidized bed reactor have demonstrated the potential of the process as a simple and low cost method for converting high sulfur coals to clean solid fuels.

By sequential chlorination and dechlorination/hydrodesulfurization of pulverized coal in a fluidized bed reactor it was found that desulfurization levels comparable to those in the slurry-phase process can be achieved in much shorter times of reaction.

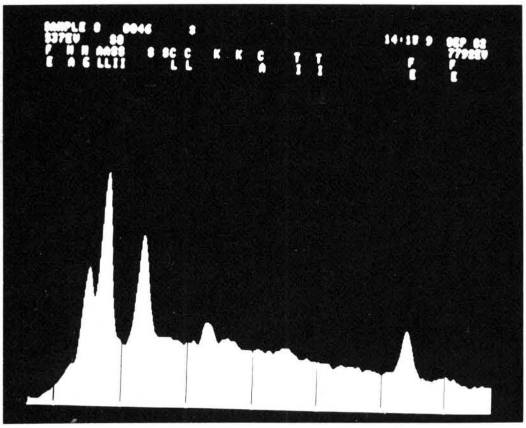
Coal chlorination appears to be a necessary pretreatment step for achieving high sulfur removals in subsequent hydrodesulfurization. Use of chlorine, however, did not result in any enhancement in the chlorine remaining in the product coals after the dechlorination/hydrodesulfurization treatment.

ACKNOWLEDGMENTS

The authors thank the Jet Propulsion Laboratory for the financial assistance from the JPL Director's Discretionary



PSOC 276 RAW COAL



PSOC 276 TREATED COAL (RUN NO. 0046)

Figure 11. EDAX spectrum of coal.

Fund, the National Research Council, and the National Aeronautics and Space Administration for awarding a Senior Resident Research Associateship to Professor M. Ravindram to support this work at the Jet Propulsion Laboratory, California Institute of Technology.

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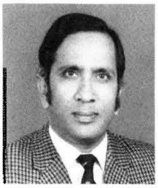

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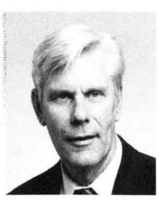

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The Electric Utility Sulfuric Acid Plant

F. G. Aragon, H. S. Taylor and J. C. Petrie

Public Service Company of New Mexico
San Juan Generating Station
Waterflow, New Mexico

San Juan Generating Station is a coal-fired power plant utilizing the Wellman-Lord SO_2 recovery process for meeting SO_2 compliance regulations. A sulfuric acid plant was designed and built for reliably producing a saleable product from the recovered SO_2. Criteria are presented to describe some of the features incorporated into the plant design to meet this unique application.

INTRODUCTION

San Juan Generating Station, operated by the Public Service Company of New Mexico, is a coal-fired power plant producing saleable sulfuric acid as a major by-product of the electric generation process. The power plant is located in the Northwest corner of the state of New Mexico and on top of one of the largest subbituminous coal deposits in the Southwest. The station consists of four operating units with a total gross generating capacity of 1800 MW and burns approximately 232 kg/s (920 tons/hr) of 0.9 wt % sulfur coal when at full load. As a result of the Clean Air Act and the additional restrictions placed on sulfur dioxide emissions by the state of New Mexico, the Public Service Company of New Mexico (PNM) was committed to producing "clean" energy with the best available technology.

After studying four different types of flue gas desulfurization systems being considered, the Wellman-Lord SO_2 Recovery process was selected as the most feasible and cost effective for the San Juan Generating Station. The Wellman-Lord process, a regenerable-type FGD system, was attractive both economically and technically because there is no significant amount of scrubber waste to dispose of, scaling is not a problem and the end product can be marketed. The end product being elemental sulfur, sulfuric acid, or liquid SO_2.

PROCESS DESIGN REQUIREMENTS

In order to operate in compliance with the environmental regulatory standards, the station must remove approximately three-fourths of the sulfur dioxide in the flue gas from the units before the gas exhausts to the atmosphere. The actual compliance requirements for the four units are the following:

	Federal	State
Unit 2 (built before 1975)	—	72% Removal
Units 1, 3, & 4 (built after 1975)	0.516 kg SO_2/GJ (1.2 lb/million Btu)	0.279 kg SO_2/GJ (0.65 lb/million Btu)
Station Average:	1.64 kg/s SO_2 (13,000 lbs/hr) maximum for all four units for any three-hour average.	

Not only must the plant be capable of recovering the SO_2 to meet these stringent standards, but it must also be capable of swinging load with the generating units as the demand for electricity can vary from day to night and weekdays to weekends. The plant also has to be reliable and produce a product of saleable quality.

PLANT CONSTRUCTION

Modern power plant construction schedules are to build the units one at a time and place them on-line as soon as possible. This was the case at San Juan. A sulfuric acid plant, designed for processing the sulfur dioxide from all four units, was added but not until the construction of the final two units. An elemental sulfur plant which had been installed for the first two units was being used to process the SO_2. However, the sulfur plant was shut down and placed on cold standby once the acid plant became available and proved to be more reliable and cost effective to operate.

The principal economic benefit realized by switching to sulfuric acid production resulted from eliminating the need for costly natural gas required as a reducing agent for the production of elemental sulfur from sulfur dioxide. Also, a sulfuric acid plant of comparable capacity costs less in capital than an SO_2 reduction unit for producing elemental sulfur.

SULFURIC ACID PLANT

The sulfuric acid plant, designed and built by Davy McKee for San Juan Generating Station, is a single absorption contact process, Figure 1. The plant is designed to produce up to 4.93 kg/s (470 ton/d) of 100% sulfuric acid with the capability to operate at very low turndown rates. This allows the plant to handle all of the sulfur dioxide from all four units at any rate of generating capacity with the maximum sulfur in the coal.

The rich SO_2 gas stream from the Wellman-Lord SO_2 Recovery process and sufficient atmospheric air to dilute the gas stream to 10.5% SO_2 are dried in separate packed tow-

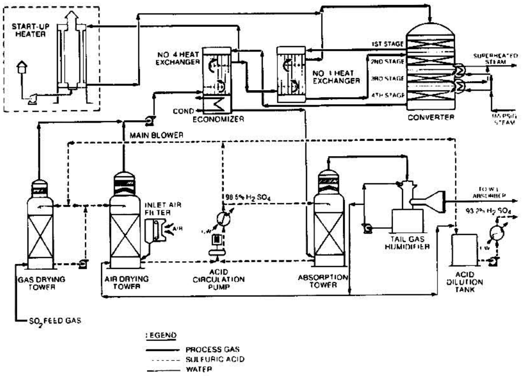

Figure 1. Sulfuric acid plant process flow diagram.

ers by direct countercurrent contact with 98.5% H_2SO_4. The two streams are then mixed and enter the main gas blower. The blower provides the suction to draw the gas and air through their respective drying towers and deliver the mixed gas through the balance of the acid plant.

After leaving the blower, the mixture of SO_2 and air passes through the shell side of the No. 4 and No. 1 Heat Exchangers where the gas stream is heated to 688.6K (780°F) before entering the converter. The gas then passes through the four catalyst beds in the converter for conversion of SO_2 to SO_3. The gas stream is cooled after passing through each bed: the gas leaving the first mass is cooled in the tube side of the No. 1 Heat Exchanger, the gas leaving the second and third masses are respectively cooled in the No. 2 and No. 3 Heat Exchangers while superheating 1221 kPa (165 psig) steam; and the gas leaving the fourth mass is cooled in the tube side of the No. 4 Heat Exchanger. Final cooling of the gas stream before entering the absorption tower is accomplished in the shell side of the economizer heat exchanger where condensate is used as the cooling fluid.

The SO_3 is absorbed from the gas in a countercurrent stream of 98.5% acid in the absorption tower. The 98.5% acid strength is maintained by the addition of water into the air drying tower and is subsequently mixed with the absorption tower acid as they pass through the common acid circulation pump.

The tail gas which leaves the absorption tower is returned to the scrubbers in the Wellman-Lord process where the small amount of unconverted SO_2 is recovered and eventually recycled back to the acid plant. For this reason, a tail gas humidifier was added to quench the gas stream leaving the absorption tower and minimize the amount of sulfuric acid carryover into the return duct and associated equipment. A stream of acid is withdrawn from the discharge of the acid circulation pump and is delivered to the acid dilution tank to produce 93.2% product acid. The product acid is then cooled and pumped to storage where it is loaded onto trucks for sale.

SPECIAL FEATURES

The high strength SO_2 gas stream available to the acid plant from the Wellman-Lord process makes possible several unique features:

Gas Strength

The recovered SO_2 gas stream is essentially 100% SO_2 on a dry basis and can be diluted with air to any SO_2 concentration desired. This provides a higher than normal O_2 to SO_2 ratio compared to the more common sulfur burning or smelter gas plants in which part of the oxygen in the air supply is consumed to produce the sulfur dioxide. For example, this plant is designed to operate with a 10.5% SO_2 gas. In a sulfur burning plant, this concentration would leave 10% oxygen in the gas stream whereas in this plant, the gas will contain more than 18% oxygen when diluted with air. This greater oxygen content enhances the conversion of SO_2 to SO_3 so that 98% conversion is readily obtained. The 10.5% SO_2 design takes advantage of the maximum SO_2 concentration which maintains conservative operating conditions in the first stage of the converter.

Acid System

This plant uses a mono acid system where a single acid concentration is used for both the drying and absorption towers. The mono acid system is used because the rich SO_2 gas can be dried separately from the dilution air and the air drying tower is used to strip the dissolved SO_2 from the small stream of acid used to dry the rich SO_2 gas. This system has several advantages over the dual acid system in which different acid concentrations are used for drying and absorption because:

a. No cross transfers are necessary to adjust concentration in two systems.
b. The acid cooling duty is reduced and simplified because good drying is achieved with 98% acid at 349.7K (170°F), instead of having to cool 93% acid to 316.3K (110°F) to accomplish the same drying.
c. A separate dilution tank is required to obtain the desired 93% product acid, but the SO_2 content of the diluted acid is much less than is normally obtained by stripping 93% drying tower acid in a dual acid system.
d. Use of the hotter drying acid preheats the incoming air and gas and reduces the acid cooling duty so that more heat is recovered as steam.
e. A single acid pump and cooler are used for the main circulation over the drying and absorbing towers.

Heat Recovery

A part of the conversion reaction heat is required to preheat the gas before it enters the converter. The balance of the heat must be removed from the gas to maintain optimum converter operating temperatures. This heat is recovered in the form of low pressure 186.85 kPa (15 psig) steam for the Wellman-Lord evaporators, Figure 2, and the heat recovery is increased by additional cooling of the gas going to the absorber which also reduces the acid cooling duty. The heat recovered as steam is more than 75% of the total conversion reaction heat.

Turndown

This was a requirement incorporated into the design of the plant making it capable of operating at rates down to 25%, and less, of design capacity. The plant has been successfully tested and operated at 25% of capacity main-

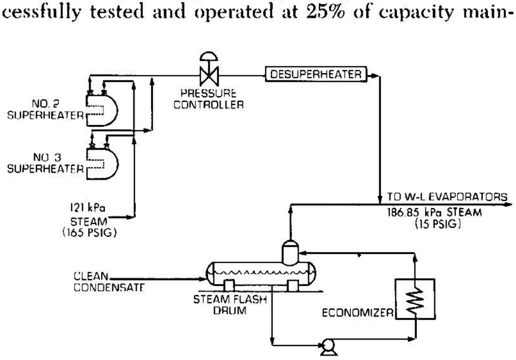

Figure 2. Heat recovery circuit.

taining "auto-thermal" conditions, i.e., no need for auxiliary heat input. Turndown rates below 25% are achieved by use of the start-up heater as an on-line process heater to help maintain the necessary heat balance.

Compact Design

This is not a unique feature resulting from the use of the Wellman-Lord process but rather because of space limitations. An isometric view of the San Juan sulfuric acid plant, Figure 3, illustrates the compact design which was necessary due to the limited area available, 512.6 m^2 (5518 ft^2), for constructing the plant. A vertical start-up heater, shown in the background, and vertical acid coolers were used to help conserve space.

There was originally some concern over safety and ease of access for maintenance because of the limited area, however, the final layout as shown has been more than adequate for safe operation and maintenance of the plant. This compact design has inadvertently resulted in lower capital requirements, i.e., less pipe, duct and structural steel, and ultimately in improved energy conservation, i.e., less heat lost through piping and ductwork and reduced fluid flow pressure drop.

OPERATING RESULTS

The sulfuric acid plant was placed on-line in July 1982 and has met or exceeded all expectations. The plant is very reliable and has had an on-stream factor of over 98% since its start-up through early 1986. The plant responds well to load changes and has met all design criteria at these varying rates. The plant has, on occasion, even been required to operate as low as 10% of capacity. The extremely clean SO_2 gas stream from the Wellman-Lord process has greatly enhanced the life of the converter catalyst and has notably contributed to the quality of the product acid. The sulfuric acid plant has consistently produced an electrolytic grade acid which has exceeded the product quality guarantee provided with the plant specifications, Table 1.

TABLE 1. SULFURIC ACID QUALITY

Specifications:	Electrolytic Grade	Guaranteed	Average Analysis
Strength, % H_2SO_4, min.	93.19	93.2	95.23
Nonvolatile Matter, ppm max.	300	Clear (free from suspended matter)	36.8
Chlorides, ppm Cl max.	10	—	<10
Nitrate, ppm NO_3 max.	5	—	—
Sulphur Dioxide, ppm SO_2 max.	40	50	<25
Arsenic, ppm As max.	1	—	<1
Iron, ppm Fe max.	50	50	10.6
Copper, ppm Cu max.	2	—	<1
Manganese, ppm Mn max.	0.2	—	<0.2
Nickel, ppm Ni max.	1	—	<1
Antimony, ppm Sb max.	1	—	<1
Zinc, ppm Zn max.	40	—	<1
Platinum, ppm Pt max.	—	—	—
Selenium, ppm Se max.	20	—	<1
Ammonium, ppm NH_4 max.	10	—	—
Organic Matter	no charring	—	—

Some improvements have been incorporated to correct problems which were discovered during the early operation of the acid plant. The two most significant changes made resulted from: 1) the entrainment of fly ash (residue from burning coal) in the air supply to the air drying tower and start-up heater and 2) the corrosion of the gas inlet nozzle to the gas drying tower. The first problem, caused by nearby ash loading and conveying systems, resulted in frequent plugging of the air drying tower mist eliminator pads and blinding of the start-up heater flame safety monitor. The oil bath filter originally supplied with the plant was not capable of removing the very fine fly ash particulate. This problem was corrected by installing a new two stage, dry-type, high efficiency filter capable of removing the very fine particulate and locating it at the north end of the chemical plant complex where the airborne particulate loading was minimal. The filtered air was then delivered to the air drying tower and start-up heater through a 1.07m (42 in.) round duct.

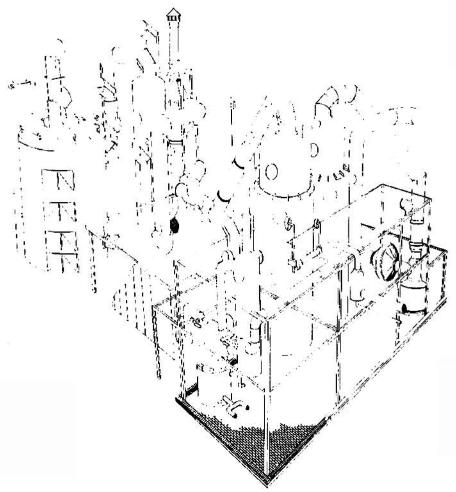

Figure 3. Isometric view of San Juan Generating Station sulfuric acid plant (shown without acid pumps and piping).

The second problem was discovered during an inspection of the gas drying tower after approximately six months of operation. The cast ductile iron thimble used for lining the inlet gas nozzle of the tower was severely corroded and close to exposing the shell of the gas drying tower to the hot circulating acid. This problem was corrected by enlarging the gas inlet nozzle and lining it with acid resistant brick and mortar. These two fixes along with other minor improvements have served to enhance the operation of the acid plant as indicated by the high availability being achieved.

IN SUMMARY

The sulfuric acid plant has proven to be a smooth operating process requiring minimal maintenance. It has become the successful "link" for helping meet station SO_2 compliance levels while producing a high quality saleable product. The high quality grade acid has been of added value since it helps broaden the market for the product and the sale of this acid helps offset some of the operating expenses for the flue gas desulfurization system. Savings are also being realized as the generating station itself consumes approximately 8% of the total production for demineralizer, cooling tower and wastewater treatment operation. This coupled with the overall availabilities and operating results being experienced at this plant are making this process a model for industry.

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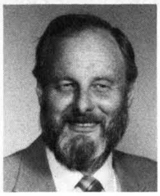

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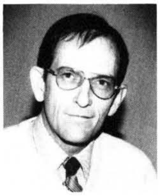

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Electrogenerative and Related Electrochemical Methods for NO_x and SO_x Control

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Electrogenerative processes can be used to reduce nitric oxide to low levels in a variety of gas streams. An approach for applying these and related electrochemical reduction processes to selectively reduce NO_x concentrations in power plant effluents is discussed. Both electrogenerative oxidation and reduction of sulfur dioxide can occur. However, oxidation of sulfur dioxide to sulfuric acid seems to be the most feasible route for incorporation into an electrochemical flue gas treatment which might also produce useful chemicals. A strategy for implementing an "electrochemical scrubbing" procedure is described.

INTRODUCTION

Greater environmental awareness coupled with increasing energy requirements in the United States have led to a Clean Air Act and Amendments mandating control of NO_x and SO_x emissions [*1*]. Subsequently the 1973 oil shortage as well as the Chernobyl disaster have brought home the fact that where flue gas treatments are involved, our concerns in the near future will have to be mainly with coal fired stationary power plants. Nitric acid and sulfuric acid plants as well as incinerator operations also will have to be operated under control. Since 1970 there has been a proliferation of treatments and strategies for removal of NO_x and SO_x pollutants as well as for limiting NO_x formation through advanced burner design [2]. Within the last two decades, a number of individual processes which may fit into emission control schemes also have been suggested by electrochemists and electrochemical engineers [3-9]. While these have been largely overlooked by mainstream investigators in the emission control area, some show promise for fitting into existing emission control schemes and possibly serving as a basis for others including an integrated "electrochemical scrubbing" process. Several possibilities are described here for further consideration and to illustrate approaches.

The processes discussed here are in the early research and development stage and may provide a variety of implementation paths. With this uncertainty, we can forego economic analysis for the present and concentrate on the basic concepts with illustrative results to prepare the way for future evaluation of these and related processes.

The general flowsheet for incorporation of electrochemical processing is shown in Figure 1 and does not differ from earlier ones. The approach would continue to involve a staged process where sulfur dioxide, particulates, and NO_x are removed separately although the order of particulate removal and SO_2 removal might be reversed if sulfur oxides were to be removed by an electrochemical or related route. Here we wish to explain some potential electrochemical stages, consider their integration into an overall process and present some preliminary experimental results. First, a promising electrochemical process for removing low levels of nitric oxide from diluted feed streams is described and evidence is presented for efficacy in NO_x removal from multicomponent effluent streams. Then some facets of a related process for SO_2 removal are discussed, and a possible means for implementation and integration of the two processes with suitable fuels is explained.

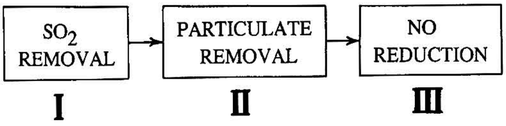

Figure 1. General flowsheet for proposed flue gas treatments.

ELECTROGENERATIVE PROCESSES

Some of the electrochemical processes which are emphasized here are novel in the sense that they are "electrogenerative" [*10, 11*]. That is, they operate in an electrochemical cell arrangement such that favorable thermodynamics can be utilized to generate a desired product from the nitric oxide reduction while byproduct D.C. electrochemical current is generated without an external power source. Some of the technology resembles that of conventional fuel cells, but electrogenerative cells are primarily electrochemical reactors which exploit favorable thermodynamic and kinetic factors. A fuel cell operation is targeted mainly toward energy generation [*12,13*] while an electrogenerative cell is one in which useful chemicals are produced or specific ones (e.g. nitric oxide here) are removed.

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This concept can be illustrated by referring to Figure 2 where an electrogenerative reactor is represented. The reactor used here incorporates two porous, Teflon-backed, gas-permeable, liquid-impermeable, catalytic platinum black-Teflon electrodes (American Cyanamid Type LAA-2) [*18, 19*] which function as anode and cathode. These are separated by a flowing acidic free electrolyte phase. The external circuit between the electrodes consists of a variable resistive load for adjusting current in series with an ammeter. As represented here, hydrogen reacts at atmospheric pressure at one electrode to produce protons at the electrode-electrolyte interface and electrons which flow in the external circuit. At the same time nitric oxide or a competitive oxidant in a gas mixture (M) reacts at the cathode with protons from the electrolyte and electrons from the external circuit to generate current. Cell voltages are determined by the reaction potential and polarization of the two electrodes. The cathode in this cell is positive relative to the hydrogen electrode. The favorable thermodynamics and the kinetics afforded by catalytic electrodes are factors which enable the electrogenerative cell to operate so that nitric oxide reacts with simultaneous D.C. current generation. These and similar reactions, as well as cell construction, have been described in a number of places [*5, 10, 11, 14-16*].

Identified overall electrode reactions for the reactant gases [*5, 6, 17*] with standard potentials (E°) can be represented as follows:

$$\text{Anode:}\quad H_2 \rightarrow 2H^+ + 2e \qquad \underline{E^\circ\ \text{(Volts)}}\ \ 0.0 \qquad (1)$$

H^+ transported through the electrolyte
Electrons transported through external circuit.

With nitric oxide in the cathode compartment,

$$\text{Cathode:}\quad 2NO + 2H^+ + 2e \rightarrow N_2O + H_2O \qquad 1.59 \qquad (2)$$

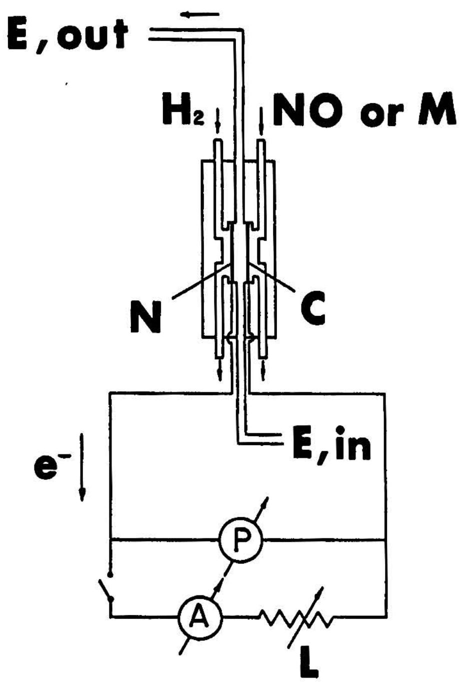

Figure 2. Schematic representation of operating components of electrogenerative cell for nitric oxide reduction. Cathode (C) and anode (N) separated by flowing electrolyte (E). Inlet gas to cathode compartment is NO or gas mixture (M) (see text). P - potentiometer; A - ammeter; L - variable resistive load.

$$2NO + 4H^+ + 4e \rightarrow N_2 + 2H_2O \qquad 1.68 \qquad (3)$$

$$2NO + 6H^+ + 6e \rightarrow 2NH_2OH \qquad 0.38 \qquad (4)$$

$$2NO + 10H^+ + 10e \rightarrow 2NH_3 + 2H_2O \qquad 0.73 \qquad (5)$$

$$2H^+ + 2e \rightarrow H_2\ \text{(concentration cell)} \qquad (6)$$

If there is a flue gas-type mixture in the cathode compartment, the following reactions might also occur,

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad 1.229 \qquad (7)$$

$$SO_2 + 4H^+ + 4e \rightarrow S + 2H_2O \qquad 0.45 \qquad (8)$$

Reactions (or Equations) (2) and (3) at a cathode remove nitric oxide to produce nitrous oxide (laughing gas) and nitrogen in the effluent gas stream. Equations (4) and (5) represent the formation of ammonia and hydroxylamine which are soluble in the acid electrolyte as salts (e.g. ammonium and hydroxylammonium sulphate). The former is useful in fertilizer and the latter in formation of caprolactam, a nylon-type precursor. The gaseous components of the chemical production from the cell can be monitored using gas chromatography. Electrolyte-soluble products (NH_2OH and NH_3) can be determined colorimetrically [*17*].

NO_x CONTROL

To demonstrate the characteristics of the nitric oxide cell, we can limit our initial discussion to nitric oxide cathode feed streams (concentrated or diluted with nitrogen) free of other flue gas constituents. The variation of cell voltage with current as the external load is decreased (the polarization curve) is shown in Figure 3. The decrease in cell voltage with increasing current is a result of activation polarization, cell resistance and loss due to depleted reactant (nitric oxide) concentration at the electrode. The polarization curve is corrected for cell voltage resistance loss which is a function of configuration.

Figure 3 shows a comparison between the polarization curves for concentrated (curve A) and nitrogen diluted (curve B) nitric oxide cathode feeds. They can serve as a basis for understanding the overall operation of nitric oxide electrogenerative cells. Both the pure and dilute (5.6% NO in nitrogen) feed curves display a sharp drop in cell voltage between 0.6 and 0.4 volts. Analysis of effluents passed over catalytic platinum electrodes showed that nitrous oxide formation (Reaction 2) predominates above 0.4

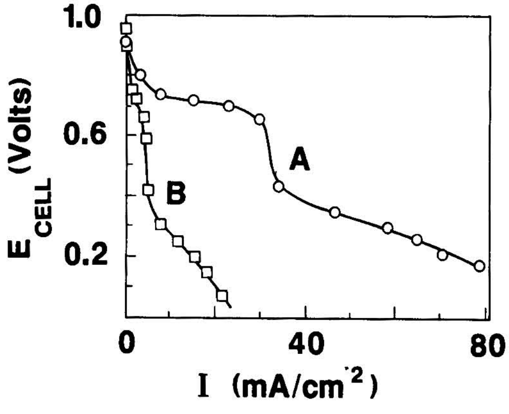

Figure 3. Polarization curve for a nitric oxide-hydrogen electrogenerative cell with perchloric acid electrolyte. Platinum black-Teflon cathode and anode, 2M $HClO_4$ aqueous electrolyte. Curve A (○) pure nitic oxide feed at 2.5 cm³/min. Curve B (□) nitrogen with 5.6% NO feed at 4.2 cm³/min. Cell voltage values are IR corrected. Cell internal resistance 0.38 ohm.

volts while the other reduction products are formed with varying selectivity below this voltage. The drop in voltage generally accompanies a change from nitrous oxide production to electrolyte soluble products or nitrogen. The important feature however is that with a low external load (a cell voltage below 0.4 volts) initial experiments indicate more than ninety-seven percent of the nitric oxide is removed from the feed stream of the cell.

Sulfur dioxide or sulfur are well known inhibitors for the oxygen electrode reaction which is the cathode reaction of hydrogen-oxygen fuel cells and is represented by Equation (7). Now it is conceivable that sulfur dioxide or sulfur from reduced sulfur oxide in a flue gas mixture also might severely inhibit or alter the nitric oxide reduction reaction. The results of a preliminary study of the effect of the presence of sulfur dioxide are shown in Figure 4 for a cell with sulfuric acid electrolyte. The upper curve shows results from cell operation with a nitrogen feed containing 2.4 percent nitric oxide using an American Cyanamid LAA-2 porous, Teflon-platinum black cathode. The dashed curve shows the cell performance with the same feed mixture at a cathode which was soaked overnight in contact with aqueous sulfuric acid-sulfur dioxide solution. The electrode and any adsorbed sulfur dioxide was pre-reduced with hydrogen as part of the activating procedure before polarization data were obtained. It can be seen that current generation (equivalent to nitric oxide reduction and removal) is affected significantly only at higher currents. Most important, complete nitric oxide conversion is achieved on the sulfur dioxide treated electrode. With prolonged cell operation the sulfur-derived layer appears to be eventually removed. It can, however, be renewed.

The electrogenerative reduction of nitric oxide primarily with hydrogen has been illustrated. However, other reductants can be employed at the anode including scrap metals (e.g. iron). Synthesis gas routes can serve as a source of hydrogen at power plants.

Further possibilities for electro-reduction of dilute nitric oxide in the presence of other gases with a platinum cathode are illustrated with the data of Table 1 where operating details are also given. Some typical industrial stationary power plant flue gas compositions before treatment are: 180-240°C, 15 mg/m^3 dust, 9% moisture, 13% O_2, 9% CO_2, 20-60 ppm CO, 3-7 ppm hydrocarbons, and 180-240 ppm (0.018-0.024%) each NO and SO_x [*20*]. NO_x and SO_x may be much higher depending on fuel constituents and pretreatment [*21*]. Actual operation of the electrogenerative cell with these low levels of NO, CO, and SO_2 or other effluent mixtures was not possible in the preliminary study because the gas mixtures had to be prepared manually by bleeding various gases into the cathode stream with needle valves. The results in Table 1 are presented in terms of generated current together with chemical conversions of nitric oxides. Although many constituents are more concentrated than in flue gas, these experiments illustrate the attractive possibilities for reduction and removal of nitric oxides in power plant effluent streams.

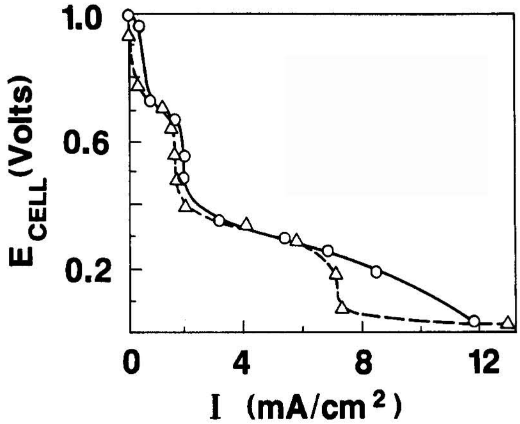

Figure 4. Polarization curve for a NO-H_2 electrogenerative cell: 3*M* sulfuric acid electrolyte and platinum black electrodes. Effect of reduced SO_2 at the cathode on cell performance. Cathode feed is nitrogen with 2.4% NO at *ca.* 5 cm^3/min. (○) untreated platinum cathode. (△) Platinum cathode with reduced SO_2 products (see text). Cell internal resistance is 0.26 ohm.

Using many of the techniques described earlier, it was found that most of the generated current in reducing the nitrogen oxides at low potentials resulted in formation of ammonia and hydroxylamine [*17, 23*] in the electrolyte. While ammonia formation is strongly favored in nitrogen diluent alone, there is a trend toward hydroxylamine formation in the presence of carbon monoxide or sulfur dioxide. Some selectivity studies in these reductions also have been described earlier [*17*].

It has already been shown that even when nitric oxide is at low concentration, its strong adsorption characteristics on noble metal catalysts such as platinum can bring about high conversion (>97%) of the NO, primarily to ammonia. The positive potential at the cathode under these conditions also will result in some hydrogen transfer because of

TABLE 1. ELECTROGENERATIVE CELL DATA FOR NITRIC OXIDE REDUCTION IN MIXTURES
(DATA FROM REFERENCES 6, 23 AND 27)

(Pt Black Cathode and Anode; 5 cm^2, 3*M* H_2SO_4 Electrolyte, Hydrogen Anode)
[Ambient temperature operation]

Experiment (a)	Cathode Feed Rate, cc/min	Measured Cell Potential volts	Current Density, mA/cm^2	Current Fraction, %		NO Conversion Before Cell, %	NO Conversion Through Cell, %	Overall NO Conversion % (b)	Overall O_2 Conversion %
				NO_x Reduction	O_2 Reduction				
1	4.5	0.112	24	13.5	86.5	97.2	>82.1(d)	>99.5	83.5
2	4.8	0.029	7.0	33.3	66.7	93.7	46.0	96.6	14.7
3	5.6	0.083	28(c)	5.8	0.8	92.5	60.0	97.0	1.3

(a) Experiment	Feed Composition (vol. %)
1	1.9% NO, 8.6% O_2, Bal. N_2
2	1.9% NO, 9.2% O_2, 1.4% CO, Bal. N_2
3	1.6% NO, 5.3% O_2, 18.3% SO_2, Bal. N_2

(b) Overall NO conversion to NO_2, HNO_3 and electrogenerative cell products (mainly NH_3 and NH_2OH).
(c) Substantial SO_2 reduction at the cathode formed sulfur (solid) and H_2S (g).
(d) Final NO concentration in product gas stream was less than 100 ppm (limit of GC detectability here) after single pass through cell.

electrochemical concentration cell effects as illustrated by Equation (6). This accounts for some current not used in nitric oxide reduction.

In Experiment 1 of Table 1, where the feed consisted of dilute NO with 8.6% oxygen, considerable competitive reduction of the oxygen is observed. Most important, however, is that nitric oxide is removed with considerable selectivity, apparently because it is adsorbed preferentially and reduced with removal at the platinum cathode. The nitric oxide concentration was reduced from 1.9% in the feed to less than 100 ppm (0.01%) in a single pass (greater than 99.5% conversion). Those familiar with flue gas reactions will recognize that the high NO conversion also involved considerable nitric oxide oxidation to NO_2 with oxygen in the feed stream before the cell. Electrogenerative reduction of NO_2 also occurs together with remaining NO to give ammonia. The fuel cell reaction involving oxygen reduction to water (Equation (7)) also contributed to the overall current. When this same feed mixture passed through the cell at open circuit where no electrochemical reaction could occur, nitric oxide concentration was not reduced below 1,100 ppm by oxidation with O_2 even when sampled further downstream. Nitrogen dioxide is also quite soluble in aqueous electrolyte with formation of nitric acid which is reduced readily to ammonia in electrogenerative cells of the type described here [22].

With the results of Table 1, it is difficult to perform exhaustive material balance calculations because of the nitric oxide oxidation to nitrogen dioxide in the dilute feed stream before and after the cell as a result of the presence of oxygen. However, analyses by gas chromatography for oxygen and nitric oxide before and after entering the cathode compartment of the electrogenerative cell are quite feasible [*17, 23*].

Experiment 2 illustrates the inhibiting effect of carbon monoxide on the platinum catalyzed reduction reactions of NO/NO_2 and O_2. The inhibition of oxygen reduction is significantly greater although it is not readily quantified with respect to carbon monoxide concentration. Extrapolating from the relatively high levels of CO in this experiment (Experiment 1 at 1.4% CO) to the low level of CO normally found in flue gas (typically as low as 60 ppm), however, suggests that selective, high conversion of NO might be realized in the cell while the oxygen reduction reaction might be inhibited by other flue gas constituents. Carbon dioxide can also compete for adsorption on the platinum catalyst. In other preliminary experiments it was found that it has little effect on the nitric oxide reduction while the oxygen reduction is inhibited.

Experiment 3 involved a mixture of 1.6% NO in the presence of 5.3% oxygen and 18.3% sulfur dioxide. The high feed level of SO_2 occurred because of limited flow control with the SO_2 feed needle valve. This experiment, although obviously at a much higher level of SO_2 than usually observed in flue gas, shows significant conversion of the nitric oxide as we might have anticipated from the experiment of Figure 4. Substantial SO_2 reduction to elemental sulfur and odoriferous hydrogen sulfide occurred at the cathode while sulfur dioxide reduction nearly completely halted oxygen reduction. The large amount of sulfur deposited (indicated by a yellow solid buildup) could eventually have covered all the platinum surface. In power plant effluent streams, sulfur dioxide concentration can be controlled by well known processes. The electrochemical reduction of sulfur dioxide also has been studied by White and Winnick [7] who recognized situations where this reaction might be useful for SO_2 removal.

The results above indicate that electrogenerative systems may represent a viable alternative for NO_x abatement. Very high conversion of dilute NO can be maintained in the presence of competitive oxidant gases such as O_2 and SO_2. The inhibiting effects of CO and SO_2 on the oxygen reduction are advantageous since these can still permit selective reduction of the nitrogen oxides, making the electrogenerative system more electrochemically efficient for NO_x removal (less hydrogen is consumed for non-NO_x reduction). Electrogenerative NO_x removal also appears compatible with high temperature incineration where considerable nitric oxide formation can occur.

With these experimental results, it becomes possible to visualize how an electrogenerative nitric oxide reduction operation would fit into the emission control scheme of Figure 1 using conventional methods in Stages I and II. In managing effluent gas streams, efforts could be directed toward controlled removal of sulfur dioxide without restricting NO_x formation during combustion since such gases can be readily reduced and removed in the types of cells being considered. There are options in the choice of electrolyte [*17*], which might be processed for recovery of ammonia and hydroxylamine, both of which have commercial value. In effluent streams from nitric acid production it might be possible to arrange for selective removal of nitric oxide through the use of carbon monoxide or electrolyte control.

SO_2 EMISSIONS

There are other possibilities with regard to control of sulfur dioxide emission when high sulfur coal or oil fuels are employed. Sulfuric acid is a preferred electrolyte constituent in the nitric oxide control scheme described here and it can be prepared in an electrogenerative cell. The electrogenerative process is attractive because of a favorable free energy relationship, and the feasibility of electrocatalysis. Electrogenerative production of sulfuric acid conceivably could be combined with pollution control of stationary power plant or copper smelting effluent streams [*3, 4, 11*].

Using concentrated reactants the sulfur dioxide-oxygen electrogenerative cell can operate with the following electrode reactions:

$$\text{Cathode:}\quad 0.5\,O_2 + 2e + 2H^+ \rightarrow H_2O \qquad \underline{E^\circ\ \text{(volts)}}\ \ 1.229 \qquad (9)$$

$$\text{Anode:}\quad SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e \qquad 0.17 \qquad (10)$$

to give the overall reaction

$$SO_2 + 0.5\,O_2 + H_2O \rightarrow H_2SO_4 \qquad (11)$$

Thus, sulfur dioxide is removed with reaction at the anode producing sulfuric acid and generating D.C. current. Polarization curves similar to Figure 3 have been obtained for cells of this type [*11*]. Dr. P. W. T. Lu of Westinghouse who has been particularly interested in Reaction 10 in another context has provided several suggestions for operation of these cells [*24*]. Using these and other developments from our laboratories [*15, 25*], we have been able to assemble electrogenerative sulfur dioxide-oxygen cells which perform well with current as high as 200 milliamperes/cm^2 with concentrated reactants. Sulfur dioxide is quite soluble in the electrolye phase. It is so strongly adsorbed on catalytic surfaces that it can inhibit the oxygen reaction at the catalytic cathode. Thus a membrane separator should be used to separate anode and cathode compartments in the analogous SO_2-O_2 cell.

The consequence of strong adsorption of sulfur dioxide actually can be advantageous. This is illustrated with curve A in the polarization data represented in Figure 5. The performance here is for an anode stream of 18.5 percent SO_2 with 17.1 percent oxygen in nitrogen [*25*]. The cathode stream is oxygen. Substantial currents are generated in the presence of anode oxygen with sulfur dioxide removal. The presence of oxygen has been found to have only a slightly deleterious effect on the magnitude of the generated current.

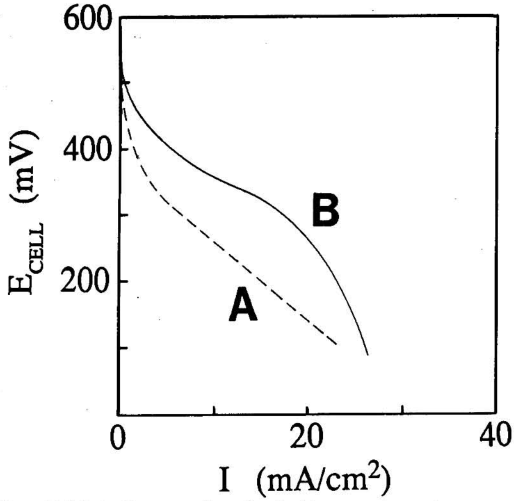

Figure 5. Polarization curves for sulfur dioxide-oxygen ion-exchane membrane divided cells. Cathode is a flowing oxygen electrode. Curve A, 4.5M sulfuric acid electrolyte, anode gas: 18.5 percent SO_2, 17.1 percent O_2 with nitrogen (flow 104 cm^3/min); curve B, 1.5M sulfuric acid flowing electrolyte at the anode saturated with sulfur dioxide. Gas diffusion electrode. No vapor phase sulfur dioxide is present.

Means for removing and concentrating sulfur dioxide from flue gas appear to be at hand including the Bergbau-Forschung (BF) and Wellman-Lord processes [26]. The latter involves sodium bisulfite decomposition [25] while the former involves sulfur dioxide sorption on treated porous coke followed by a thermal regeneration step. For incorporation of the BF process into the electrochemical scheme envisioned here Stages I and II would be interchanged so that particulate removal takes place first. The flue gases would then be conveyed to an adsorber-reactor stage at 130°C where sulfur dioxide is removed on activated coke together with any remaining dust. The sulfur dioxide can be oxidized further to sulfuric acid in the coke pores in the presence of oxygen and moisture.

The coke adsorbent with sulfuric acid and SO_2 is then charged to a regenerator with hot sand so that it is at about 650°C. Under these conditions, the sulfur trioxide generated from sulfuric acid decomposition is reduced by the coke to sulfur dioxide. The gaseous SO_2 is fed to an electrogenerative cell for the preparation of aqueous sulfuric acid while the activated coke and sand are separated using a vibrating screen. The activated coke after subsequent cooling with water to below 140°C can be returned to the flue gas treating area to adsorb sulfur dioxide again. The hot sand can be heated and recycled.

The sulfur dioxide generated in the BF process can be dissolved in sulfuric acid for conversion to sulfuric acid in accord with Equation (11). The polarization performance of an electrogenerative cell with saturated sulfur dioxide in sulfuric acid anode electrolyte and a gaseous oxygen cathode is represented in Figure 5. While the concept needs development, from an optimistic viewpoint the sulfuric acid electrolyte for electrogenerative nitric oxide removal in Stage III could be prepared by an electrogenerative operation in a new Stage II or an equivalent stage using another burner operation with a high sulfur fuel.

A different electrochemical approach was envisioned by Maget [9]. His process involved adsorption of sulfur dioxide from flue gas onto activated carbon which was subsequently conducted to an electrolysis cell where the SO_2 containing sulfuric acid slurry reacted at an anode to give additional sulfuric acid as represented by Reaction 10. However, the cathode reaction is changed to

$$2H^+ + 2e \rightarrow H_2 \qquad E^\circ = 0.0\ V \qquad (12)$$

The electrochemical cell now would consume some energy while hydrogen which can be utilized in another electrogenerative stage is produced. The electrode compartments of the electrolysis were separated with an ion exchange membrane. The washed reprocessed carbon can then be dried for subsequent sulfur dioxide adsorption.

The sulfur dioxide obtained from either the BF process or Maget approach could contain nitrogen dioxide formed in a cooling effluent stream originally containing nitric oxide in the presence of oxygen. In the SO_2 adsorbing operation, some nitrogen dioxide would be dissolved with the SO_2 into the working solution. The chemistry is again complex but some nitric acid would appear in the sulfuric acid electrolyte. Fortunately, this too can be reduced through an electrogenerative process to ammonia and hydroxylamine.

Electrochemical removal of sulfur dioxide can now be added for consideration to existing processes for sulfur dioxide removal including wet scrubbing, dry scrubbing and spray drying. For a 15 MW burner using high sulfur oil an estimated 43.3 kg SO_2/hr (95.4 lbs SO_2/hr) are emitted [21]. This amount represents 677 gmol SO_2/hr. For a 2-electron reaction at an optimistic current of 200 mA/cm^2 about 18 square meters of electrode would be required. While this is a large electrode area, it is not unreasonable considering the process opportunities which are created.

AN INTEGRATED ELECTROCHEMICAL SCRUBBING PROCESS

An implementation scheme for incorporating electrogenerative NO_x removal into an overall electrochemical scrubbing process is represented in Figure 6. Sulfur dioxide is removed for further oxidation using sorption technology and either electrolysis or electrogenerative processing. Nitric oxide can be removed in an electrogenerative process to produce ammonium sulphate which can be used for fertilizer and hydroxylamine which can be used to produce caprolactam. Mixed acid and sulfuric acid are other potential products. Other possibilities not discussed in detail here are reduction of sulfur dioxide to sulfur and oxidation of nitric oxide to nitric acid.

Assuming electrochemical processing is technically feasible there are still special problems in implementing the approach described here. These include choice of materials to handle strong acid solutions the composition of which must be determined. Even if supported on graphite or other materials platinum and related noble metal catalysts would be expensive. There are good possibilities, however, that they can be supplanted with less expensive, effective electrocatalysts. While model cells are discussed here, further developments should lead to improved configurations and refined electrochemical cell components.

ACKNOWLEDGMENT

We thank Mr. John Card for special help and support as well as many undergraduates who participated in this work. We thank the National Science Foundation and the

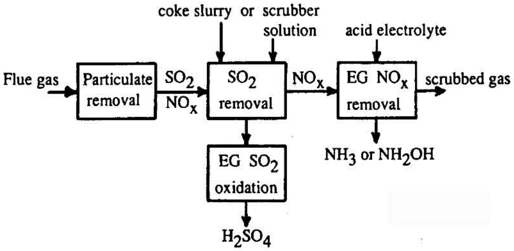

Figure 6. A proposed electrochemical flue gas scrubbing procedure incorporating electrogenerative nitric oxide removal.

University of Wisconsin for support over many years. All patent rights on electrogenerative reduction are assigned to the Wisconsin Alumni Research Foundation.

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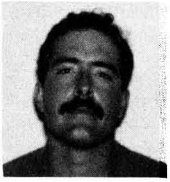

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Automation of an Electrolytic Cell for the Treatment of Oily Wastewater

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An automatic control system was installed and evaluated on a pilot plant for the electrolytic treatment of oily wastewater which was in operation at an automotive transmission plant. In this continuous process, the wastewater passes through a porous iron chip bed anode where the oil emulsion is demulsified by electrolytically dissolved iron, forming an oil-rich floating sludge and oil-free water. The control system maintains a low effluent oil concentration by adjusting the anode current—and hence the amount of iron dissolved—in response to deviations from a set-point of effluent oil content, as sensed with an in-line turbidimeter. The current automatically assumes the newly demanded value within about 6 to 10 minutes of a step increase or decrease in effluent turbidity. The system controlled the treatment of the widely varying plant wastewater continuously for 30 days, with no intervention or control adjustment and with a minimum of daily maintenance.

INTRODUCTION

Oily wastewaters generated in metal working plants are generally treated in a batch chemical process that consists of pH adjustment and the addition of polymeric flocculating agents and/or an iron or aluminum salt that forms a flocculant precipitate onto which the chemically demulsified oil is sorbed. This method yields water of good quality, but greatly increases dissolved solids and generates a voluminous sludge containing only 5% oil. Further processing of the sludge increases the oil content to about 30%. Improvements have been made in batch chemical treatment processes to reduce the sludge volume, but the treatments still increase dissolved solids and require pre-testing of each batch of wastewater to determine the concentrations and ratios of chemicals to be used. For a small-to-medium size machining plant to install a new waste treatment facility based upon batch chemical treatment, limitations on space for treatment tanks and for storage of chemicals and generated sludge are apt to present a major problem. An electrolytic process has been developed to overcome some of these limitations. It is a continuous process which introduces much less dissolved solids, produces less sludge with a higher oil content, and is readily adaptable to complete automation. Also, the process requires much less space and there is no need of storage facilities for acid or caustic.

In the electrolytic cell, shown schematically in Figure 1, the wastewater flows horizontally through a porous iron chip bed anode. When a potential is applied between the anode and a screen cathode, ferrous ions form at the anode and hydroxyl ions are generated at the cathode. The ferrous ions react in a complex manner with the emulsifying agents, freeing the oil and producing an oil-rich iron hydroxide sludge and oil-free water. The oily sludge floats to the surface where it is skimmed and the water can be directly discharged.

The flow diagram for the electrolytic process is shown in Figure 2. A receiving or flow equalization tank (not shown) serves to minimize surges in oil concentration to

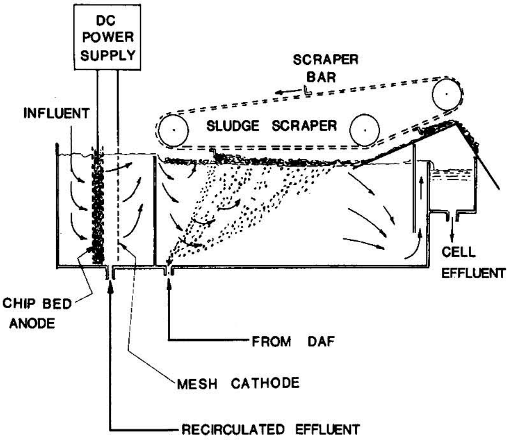

Figure 1. Schematic diagram of the electrolytic cell.

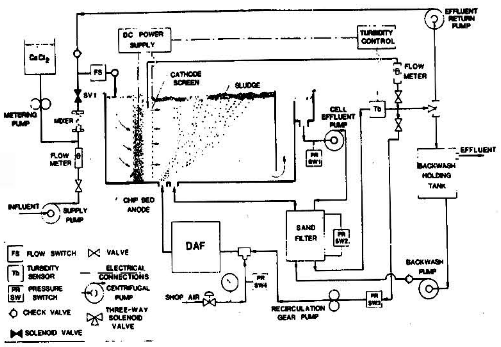

Figure 2. Electrolytic cell control system schematic.

TABLE 1. ELECTROLYTIC CELL INTERLOCK SYSTEM OPERATION

- Mushroom head pushbutton to shut down entire system.
- Chloride metering pump operates in parallel with supply pump to provide constant flow.
- Flow switch—flow rate must be above the pre-set minimum for the electrode power supply to be energized.
- Pressure switch No. 1 must be actuated for the cell effluent pump to be operated.
- Pressure switches No.'s 1, 4 and 5 must be actuated for the re-aeration and high pressure recirculation pumps to be operated.
- Over limit on turbidity causes the three-way valve to divert effluent flow to recirculate through the electrolytic cell, actuates the effluent return pump, closes the main cell supply valve (SV1) and turns off the chloride metering and main supply pumps.
- Return from overlimit on turbidity de-energizes the three-way valve (TWV3), opens solenoid valve SV1, stops the effluent return pump and starts the supply and chloride metering pumps.
- Pressure Switch No. 3, on exceeding the set pressure, three-way valves TWV1 and TWV2 are energized to divert cell effluent flow from Sand Filter 1 to Sand Filter 2, the backwash pump is started and solenoid valves SV2 and SV4 are energized. Sand Filter 1 is backwashed for five minutes, after which the backwash pump and valves SV2 and SV4 are de-energized.
- Pressure Switch No. 2, on exceeding the set pressure, the three-way valves TWV1 and TWV2 are de-energized to divert cell effluent from Sand Filter 2 to Sand Filter 1, the backwash pump is started and solenoid valves SV3 and SV5 are energized, Sand Filter 2 is backwashed for five minutes, after which the backwash pump and valves SV3 and SV5 are de-energized.
- Solenoid valves SV2 and SV4 can be energized only when three-way solenoid valves TWV1 and TWV2 are energized.
- Solenoid valves SV3 and SV5 can be energized only when three-way solenoid valves TWV1 and TWV2 are not energized.

the electrolytic cell. Free or suspended oil and particulates can also be removed from the system in the receiving tank. From the receiving tank, the wastewater is pumped to the electrolytic cell where it passes through the anode and into the mixing/flotation section of the cell. A dissolved air flotation unit (DAF) is used to enhance flotation of the oil-rich sludge. The effluent from the cell passes through a sand filter to remove any residual suspended iron and through an in-line turbidity sensor.

The water stream is then divided into three equal flows. One portion is recirculated to the space between the anode and cathode to reduce sludge build-up on the face of the anode. Another is diverted to the DAF unit where it is saturated with air and then re-injected into the cell, whereupon the dissolved air is released in a myriad of tiny bubbles, which greatly enhance flotation of the sludge. The remaining water flow passes to an effluent holding tank, from which it is finally discharged. Additional details of the process are described elsewhere [*1-6*].

Since the earlier pilot scale operations and projections to larger scale systems have indicated the automatic electrolytic process to be practical and economically attractive, a control scheme was designed and developed to determine the viability of continuous "hands-off" operation for the process. The control system was installed and evaluated on the pilot treatment plant which was in operation at the Livonia Transmission Plant of the Ford Motor Company [*6*].

AUTOMATIC CONTROL SYSTEM

The main function of the control system is to maintain the desired water quality in terms of the remaining oil content of the effluent. The quality of the effluent stream is monitored with an in-line turbidimeter. This instrument senses the stream turbidity level (a measure of the oil content) by measuring the intensity of forward scattered light. The signal from the turbidimeter provides the basis for regulating the rate of iron dissolution to obtain the selected level of oil concentration in the system effluent.

In addition to the controller, the system has an extensive interlock system to permit safe, unattended operation. These interlocks, which are described in detail in Table 1, protect the system from damage due to insufficient liquid flow, control the addition of calcium chloride or another salt when needed to obtain adequate conductivity, prevent discharge of inadequately treated water and provide for valving and back washing of the sand filters.

CONTROL EQUIPMENT AND SELECTION

Previous experiments had indicated that the cell effluent turbidity level would provide a suitable parameter upon which to base an automatic control system. A dependable, sensitive transducer for sensing turbidity level was needed to provide a signal which could be used as a control parameter. Two units were obtained for evaluation of their ability to dependably perform the required measurement and signal conditioning. The first unit tested was a Model B, Jacoby-Tarbox Corp., full stream nephelometric turbidimeter with a transverse flow cell. A schematic of the flow cell is shown in Figure 3. It was found

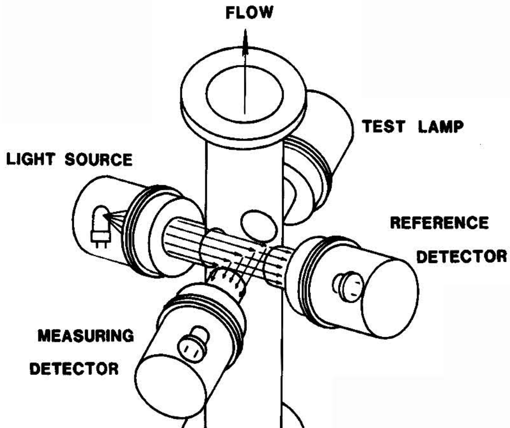

Figure 3. Schematic diagram of the Jacoby-Tarbox transverse flow cell.

necessary to install Kel-F liners on the four windows to prevent their rapid fouling. After installation of the liners and recalibration of the unit, the turbidimeter was relatively free of fouling problems. The second unit tested was a Monitor Technology, Inc. Monitek Turbidimeter, Model 210-130. A schematic diagram of the sensor is shown in Figure 4. The windows are covered with Kel-F liners to minimize fouling by material in the flow stream. Window cleaning jets also are incorporated into the sensor housing for flushing of the windows with either clear water or a solvent or detergent solution. This unit was calibrated in Formazine Turbidity Units (FTU). A correlation was established between Nephelometric Turbidity Units (NTU) and the concentration of Freon extractables and between FTU and Freon extractables. After a short trial with the Monitek unit, both units were installed in series in the electrolytic cell effluent stream for a direct performance comparison. The electrolytic cell was run for more than two months with this arrangement. Both instruments were quite stable and calibration was maintained until excessive fouling of the windows occurred. During this period, the Jacoby-Tarbox turbidimeter windows were much more subject to fouling than those of the Monitek unit. Therefore, the Monitek unit was selected for use in all future tests with the electrolytic cell. Both units generated output signals which were proportional to the electrolytic cell effluent turbidity and would serve as the control signal. Thus, when the effluent turbidity is above the set point, current to the electrode is increased, increasing the rate of iron dissolution which in turn reduces the oil content of the water and brings the turbidity level back to the set point.

The signal output from the turbidimeter was amplified, passed through a variable attenuator and integrating circuit, and then fed through a second amplifier to the programming terminals on a programmable power supply. A series of experiments were run to determine the time dependence of the system. A batch of wastewater being put through the electrolytic cell was diluted with clear water to cause a rapid drop in effluent turbidity. The control system responded as shown in Figure 5, and in about six minutes after detecting a change in turbidity level, the electrode current had been reduced to near the final level. In a subsequent experiment with the cell stabilized at a very low effluent turbidity, soluble oil was added directly to the electrolytic cell immediately following the electrodes. The turbidity reading began increasing rapidly six minutes later and was at maximum scale value after an additional four minutes. Electrode current commenced a rapid rise some six minutes after the soluble oil was added, exhibiting a system time constant of approximately six minutes as shown in Figure 6. The response rate of the control system could be varied with the attenuator between the amplifiers since it contained additional capacitance which could be switched into or out of the control circuit.

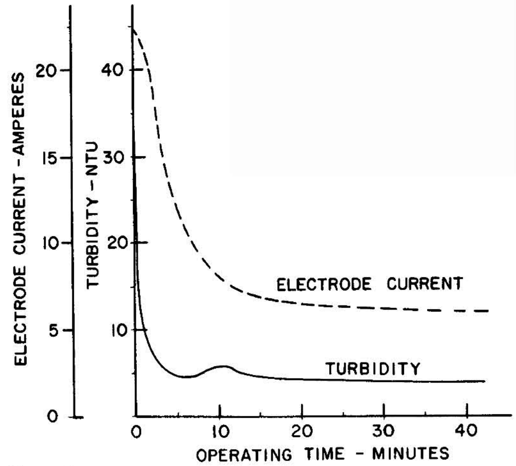

Figure 5. Electrolytic cell effluent turbidity and electrode current vs. operating time with a step decrease in turbidity.

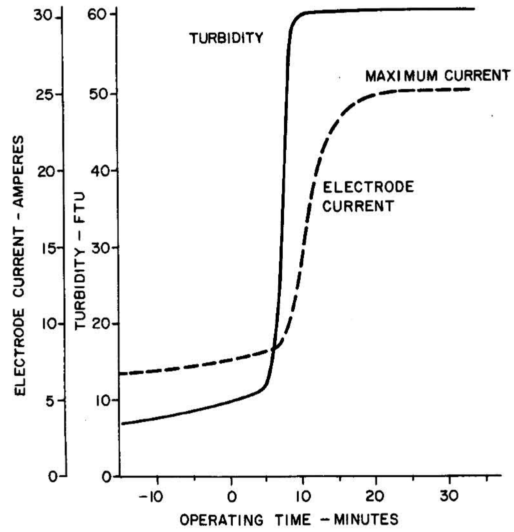

Figure 6. Electrolytic cell effluent turbidity and electrode current vs. operating time with a step increase in turbidity.

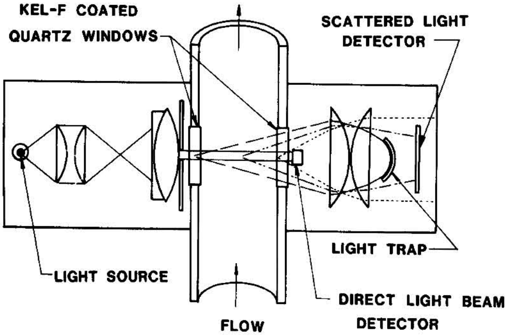

Figure 4. Schematic diagram of the Monitek forward scattered light flow cell.

CONTINUOUS AUTOMATIC SYSTEM OPERATION

Based upon the response curves and automation scheme described, the electrolytic cell was set in a fully automatic mode with control settings from 5 to 60 FTU. At readings below the setting the current would automatically be reduced to dissolve less iron; with readings above the setting, current would be increased with a corresponding increase in voltage and greater iron dissolution. The results of a 30-day run with influent consistent of the actual plant wastewater with its widely varying composition are shown in Table 2. The control was set to maintain the effluent turbidity between 10 and 20 FTU. The system ran

Table 2. Test Results Automated Electrolytic Cell

	Influent		Electrode		Effluent		
Run No.	Freon Extr (mg/L)	pH	Volts	Amps	FTU	Freon Extr (mg/L)	Sludge % Oil
19	1488	8.5	22	32	26	15.5	—
20	1488	8.5	22	29	—	12.7	—
21	3524	8.9	17	28	14	23.0	—
22	3128	8.9	22	21	34	42.0	—
23	2824	7.5	16	17	3	23.9	40
24	2388	8.8	17	21	8	—	63
25	2667	8.6	16	13	6	20.7	—
26	2623	9.0	22	13	—	—	52
27	2638	10.4	16	33	8	5.9	24

continuously as expected with a minimum of daily maintenance and without control adjustments.

The cell maintenance that was necessary during the 30-day run was a daily routine of brushing between the anode and cathode to remove accumulated sludge not swept away by the recirculated water and the periodic mixing of the calcium chloride feed solution. The system operated with no major problems and is being scaled up to a full size paint capable of handling 25,000 gals/day [7].

ACKNOWLEDGEMENT

The authors would like to thank R. L. Forgacs for his design of the electrical interlock circuitry.

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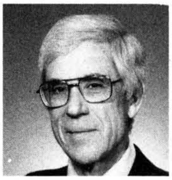

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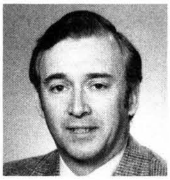

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1986 *ENVIRONMENTAL PROGRESS* READERSHIP SURVEY

The first *Environmental Progress* Editorial Advisory Board held in Chicago at last year's annual AIChE Meeting mandated that readership survey be conducted among the members of the Environmental Division of AIChE. The results of this survey will be most useful providing valuable information about the reader audience in terms of their educational background, job function, level of responsibility, and involvement in environmental specialties. The survey addresses the readers attitudes concerning the format, structure and topics of *Environmental Progress* as well as stressing directions of involvement as seen to be needed by the reader audience. This survey was developed largely through the efforts of Dr. Robert W. Peters of Purdue University and Dr. I. Atly Jefcoat of the University of Alabama. The results of this survey will be published in the February issue.

1. I am a member of AIChE. Yes ☐ No ☐

2. I am a member of the Environmental Division (Group 9) of AIChE. Yes ☐ No ☐

3. My main job function is:

Research and development ☐
Design or application ☐
Manufacturing/plant operations ☐
Marketing ☐
Sales ☐
Teaching, education ☐
  University Professor ☐
  Graduate student ☐
  Undergraduate student ☐
  Post doctoral student ☐
  Other, please specify: ____________________

Environmental Engineering ☐
Consultant/consulting engineering firm ☐
Operator/laboratory technician ☐
Government ☐
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4. My level of responsibility is:

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Management other than engineering ☐
Engineering and scientific management ☐
Engineer/scientist/chemist/physicist ☐
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Other ____________________

5. Environmental specialties which I am involved with (check all that apply):

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Water ☐
Wastewater ☐
Solid wastes ☐
Hazardous wastes ☐
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Other, please specify: ____________________

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20-29 years ☐
30-39 years ☐
40-49 years ☐
50-59 years ☐
60 years and over ☐

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Major	B.S.	M.S.	Ph.d.	Other
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Chemistry				
Environmental/ Civil Engineering				
Other (Please Specify)				
Not Applicable				

8. I am a regular reader of *Environmental Progress*. (I read at least 3 of the 4 quarterly issues a year).
☐

I am an occasional reader of *Environmental Progress*.
☐

9. Comment on the coverage of the various topical areas of articles in *Environmental Progress* listed below:

Area	Excellent Coverage	Adequate Coverage	Inadequate Coverage	Excessive Coverage
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Air				
Solid/Hazardous Wastes				
Water				

10. I find *Environmental Progress's* technical level of presentation (check all that apply):

Appropriate ☐
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Too technical ☐
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Commentaries ☐
Legislation action summaries ☐
System design ☐
Industrial pollution ☐
Atmospheric pollution ☐
Editorials ☐
Advanced/innovative technology ☐
Historical reviews ☐
Career development ☐
Legal decisions/relevance ☐
Other: ______________________

12. Please list specific articles, special reports, or issues since November 1985 which you found to be particularly interesting or effective:

a. ______________________
____

b. ______________________
____

c. ______________________
____

d. ______________________
____

13. In terms of the quality of publications, I would rate *Environmental Progress* in comparison with the other environmental engineering journals listed below:

Publication	Better Quality	Equal Quality	Poorer Quality	No Basis For Opinion
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Environmental Science and Technology				
Journal of Air Pollution Control Association				
Journal of the American Water Works Association				
Journal of the Environmental Engineering Division (ASCE)				
Journal of Hazardous Materials				
Journal of the Water Pollution Control Federation				
Pollution Engineering				
Science				
Water Research				

14. Please check any of the following areas that you find interesting and informative:

Editorial ☐
Applications ☐
Environmental Shorts ☐
Book list ☐
The cover picture ☐
Case histories ☐
Washington Environmental Newsletter ☐
Scientific/technical papers ☐
Fundamental papers ☐
Other: ______________________
____

15. Please check any of the following categories that you feel should be added to *Environmental Progress:*

Book reviews ☐
Call-for-Papers for environmental meetings ☐
New and recent AIChE publications ☐
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16. I find the illustrations in *Environmental Progress* (check as many as apply):

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About the same ☐
Improved, but still in need of improvement ☐
Worse ☐

17. My issue of *Environmental Progress* usually arrives (check any that apply):

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Late ☐
Occasionally late ☐
In good condition ☐
Damaged ☐
Occasionally damaged ☐
I live outside the United States ☐

18. With regard to *Environmental Progress,* I'd like to see special issues devoted to a particular topical area (such as groundwater, treatment of hazardous wastes, heavy metal separations, innovative technology, multidisciplinary environmental research, etc.):

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  AIChE ☐
  Other, please specify: ________________
Purchased or read a book discussed in *Environmental Progress* ☐
Contacted an advertiser ☐
Learned more about my specialty ☐
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Became active in AIChE and/or the Environmental Division ☐
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Changed jobs ☐
Changed assignments ☐
Been promoted ☐
Other, please specify: ________________

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21. Please use this space to comment on changes in format or content that you'd like to see implemented. Use extra sheets if necessary.

22. If you have been a contributor to *Environmental Progress,* comment on the following:

The turnaround time is:
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  Too rapid ☐
  Satisfactory ☐
The reviews are:
  Informative ☐
  Satisfactory ☐
  Critical ☐
  Lacking in substance ☐

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Dr. Robert W. Peters
Environmental Engineering
School of Civil Engineering
Purdue University
West Lafayette, IN 47907

Thank you for your time and assistance.

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