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REPORT

VOLUME II

FINAL REPORT

Technical Support for

the Ohio Clean Coal

Technology Program

Volume II, Baseline of
Knowledge Concerning
Process Modification

Opportunities, Research
Needs, By-Product
Market Potential, and
Regulatory Requirements

To

Ohio Coal Development Office

CDO/R-88-LRI

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MASTER

FINAL REPORT

on

TECHNICAL SUPPORT FOR THE OHIO CLEAN COAL TECHNOLOGY PROGRAM

VOLUME II, BASELINE OF KNOWLEDGE CONCERNING
PROCESS MODIFICATION OPPORTUNITIES, RESEARCH NEEDS,
BY-PRODUCT MARKET POTENTIAL, AND REGULATORY REQUIREMENTS

to

OHIO COAL DEVELOPMENT OFFICE

August 28, 1989

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FOREWORD

This report was prepared for the Ohio Coal Development Office (OCDO) under Grant Agreement No. CDO/R-88-LR1 and comprises two volumes. Volume I presents data on the chemical, physical, and leaching characteristics of by-products from a wide variety of clean coal combustion processes. Volume II consists of a discussion of (a) process modification waste minimization opportunities and stabilization considerations; (b) research and development needs and issues relating to clean coal combustion technologies and by-products; (c) the market potential for reusing or recycling by-product materials; and (d) regulatory considerations relating to by-product disposal or reuse.

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2.0 TASK 2: BASELINE OF KNOWLEDGE CONCERNING TECHNOLOGY FOR BY-PRODUCT MINIMIZATION OR STABILIZATION

2.1 SUMMARY

The new technologies that are now at the demonstration plant level of investigation involve pressurized fluid-bed capture, in-furnace capture, in-duct capture, in-precipitator capture, catalytic reduction, adsorption/stripping, as well as various improvements to conventional wet removal, as noted earlier in this report. In this section these demonstration processes are described in more detail, and means to reduce the amounts of waste produced, to improve the efficiencies of the processes, and to produce other by-products, are discussed. Various technologies for stabilizing such wastes are also reviewed.

Typical by-product production figures for the various processes are described in several locations throughout this chapter and in Chapter 4, Table 4-2. A computer model has been generated to allow prediction of by-products as function of process variables.

It would appear that recycling of the waste products back to the processes, plus additional attention to particle size and reactivity of these reactants, are the most important research needs for the future. In terms of process modifications to produce other by-products, intensified efforts to produce construction-grade gypsum, and perhaps increased efforts to produce and/or recover SO_2 and sulfur, might be desirable. In all cases, better characterization of the wastes now expected under various process conditions during the combustion of Ohio coals, either for direct use or stabilized by various procedures, needs to be carried out.

A disadvantage of many clean coal technologies now under development within the State of Ohio is that the amount of by-product generated could increase, and possibly be of different composition than that of the by-products generated by current technology now available for the control of sulfur oxide emissions during the combustion of high-sulfur coal. A few of the new processes are capable of producing significantly less by-products in the form of elemental sulfur, but probably at an added economic penalty. Although there are several atmospheric fluidized bed combustors

being demonstrated in the United States, none yet operate with high-sulfur coal at a scale to be of interest to large power generators (i.e., 100-MW or larger). In fact none of the half-dozen or so small atmospheric fluidized bed combustors constructed in Ohio over the past decade are now operating on coal; they have either been shut down or switched to other low-sulfur fuels that are less expensive to use than is high-sulfur coal with added sulfur controls. For this reason, research on a number of innovative new technologies is being supported in attempt to find a lower-cost means of meeting SO₂ emission goals when burning Ohio coals.

Detailed operating costs on the various processes are not presented because such analysis was beyond the scope of this study.

2.2 COMPUTER SIMULATION OF BY-PRODUCT GENERATION

A simple computer simulation of by-product generation, which operates in a LOTUS® spreadsheet, has been developed for each of the clean coal technologies discussed in this chapter. To assist OCDO in examining the various technologies, a floppy disk containing these spreadsheets is included with this report. This program provides a simple means of predicting a "baseline" quantity of by-product that will be produced from the various processes. Output quantities of by-products that are calculated are not the result of rigorous material balances but rather are presented as typical by-product quantities that might be expected from the various processes described in this report.

Sample output sheets are presented in Tables 2-1 through 2-6. Process parameters are adjustable in the spreadsheet to allow the user to modify the output for specific plant conditions. Coal ash, sulfur content, and heating value can be adjusted to reflect coal variances. Boiler size and heat rate provide adjustment of plant capacity and efficiency, while calcium-to-sulfur ratio and process efficiency provide predictions of the effect of process improvements. Baseline default values in the left hand column are considered the calculation inputs and in the right hand column are the calculation outputs. Default values for calcium-to-sulfur ratio and process efficiency are based on the data obtained from the process developers or as otherwise reported. The variables then need not be adjusted unless the operator wishes. Likewise, a baseline boiler size of 100 MW and 10,000 Btu/kwh heat rate were used as default values for all of the processes except the pressurized fluidized bed. This process is somewhat unique in that only certain reactor sizes are anticipated to match currently available gas turbine sizes.

By-products produced from the processes using calcium-based sorbents will generally be coal ash diluted with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and unreacted sulfur sorbent. Calcium oxide and calcium oxide with magnesium oxide (dolomite) are the sulfur sorbents used as inputs for the processes

TABLE 2-1. PREDICTED BY-PRODUCT GENERATION RATE FOR THE E-SOX PROCESS

E-SOX PROCESS

PROGRAM INPUTS		PROJECTED WASTES Lb/hr	
FUEL:			
% ASH IN COAL	15	FLY ASH	19200
% SULFUR IN COAL	3.5	Gypsum, Other Sulfur	13169
HEATING VALUE, Btu/Lb	12500	Containing Salts	
BOILER:		Unreacted Sorbent	16275
SIZE, MW	200		
HEAT RATE, Btu/Kwh	10000	TOTAL	48644
PROCESS:			
CALCIUM TO SULFUR RATIO	2		
PROCESS EFFICIENCY, %	50		

TABLE 2-2. PREDICTED BY-PRODUCT GENERATION RATE FOR THE LIMB PROCESS

LIMB PROCESS

PROGRAM INPUTS		PROJECTED WASTES Lb/hr	
FUEL:			
% ASH IN COAL	15	FLY ASH	19200
% SULFUR IN COAL	3.5	Gypsum, Other Sulfur	13169
HEATING VALUE, Btu/Lb	12500	Containing Salts	
BOILER:		Unreacted Sorbent	24303
SIZE, MW	200		
HEAT RATE, Btu/Kwh	10000	TOTAL	56672
PROCESS:			
CALCIUM TO SULFUR RATIO	3		
PROCESS EFFICIENCY, %	50		

TABLE 2-3. PREDICTED BY-PRODUCT GENERATION RATE FOR THE HALT PROCESS

HALT PROCESS			
PROGRAM INPUTS		PROJECTED WASTES Lb/hr	
-----		-----	
FUEL:			
% ASH IN COAL	10	FLY ASH	12800
% SULFUR IN COAL	3.5		
HEATING VALUE, Btu/Lb	12500	Gypsum, Other Sulfur	13169
		Containing Salts	
BOILER:		Unreacted Sorbent	27125
SIZE, MW	200		
HEAT RATE, Btu/Kwh	10000	TOTAL	53094
PROCESS:			
CALCIUM TO SULFUR RATIO	3		
PROCESS EFFICIENCY, %	50		

=====

TABLE 2-4. PREDICTED BY-PRODUCT GENERATION RATE FOR THE LIME CHELATE PROCESS

ANL CHELATE PROCESS			
PROGRAM INPUTS		PROJECTED WASTES Lb/hr	
-----		-----	
FUEL:			
% ASH IN COAL	10	FLY ASH	12800
% SULFUR IN COAL	3.5		
HEATING VALUE, Btu/Lb	12500	Gypsum, Other Sulfur	23704
		Containing Salts	
BOILER:		Unreacted Sorbent	11935
SIZE, MW	200		
HEAT RATE, Btu/Kwh	10000	TOTAL	48439
PROCESS:			
CALCIUM TO SULFUR RATIO	2		
PROCESS EFFICIENCY, %	90		

=====

TABLE 2-5. PREDICTED BY-PRODUCT GENERATION RATE FOR THE PRESSURIZED FLUIDIZED BED PROCESS

PRESSURIZED FLUIDIZED BED

PROGRAM INPUTS		PROJECTED WASTES Lb/hr	
-----		-----	
FUEL:			
% ASH IN COAL	15	FLY ASH	84982
% SULFUR IN COAL	3.5		
HEATING VALUE, Btu/Lb	12500	BED ASH	84982
BOILER:			
SIZE, MW	680		
HEAT RATE, Btu/Kwh	8510	TOTAL	169965
PROCESS:			
CALCIUM TO SULFUR RATIO	1.6		
PROCESS EFFICIENCY, %	90		

=====

TABLE 2-6. PREDICTED BY-PRODUCT GENERATION RATE FOR THE TRW SLAGGING COMBUSTOR PROCESS

TRW SLAGGING COMBUSTOR

PROGRAM INPUTS		PROJECTED WASTES Lb/hr	
-----		-----	
FUEL:			
% ASH IN COAL	15	ASH	24000
% SULFUR IN COAL	3.5		
HEATING VALUE, Btu/Lb	12500	Gypsum, Other Sulfur Containing Salts	13169
BOILER:		Unreacted Sorbent	29969
SIZE, MW	200		
HEAT RATE, Btu/Kwh	10000	TOTAL	67138
PROCESS:			
CALCIUM TO SULFUR RATIO	3		
PROCESS EFFICIENCY, %	50		

=====

and reflected in the spreadsheet calculations. The hydrated form of calcium sulfate was used as the basis for the quantity calculations because this is the form that will be present in waste piles or landfills after disposal of the material. To provide a consistent basis for comparison, all waste products were assumed to be dry. In reality, each process waste will contain some varying quantity of water (0 to 50 percent or more) along with the solids for disposal.

By knowing the fuel ash and sulfur contents, the quantity of ash and gypsum generated by reaction can be calculated. The basic assumption made is that all of the coal sulfur is converted to sulfur oxides and the remaining sorbent exits the process.

As can be seen in the sample sheets, a large portion of the total solid by-product produced comes from two sources: the coal ash itself and the unreacted sorbent. From this simple analysis alone it becomes evident that methods for reducing coal ash prior to use can have a significant impact on the total quantity of by-product produced. Similarly, technologies that can reduce the required calcium-to-sulfur stoichiometric ratio also can have a large impact on the quantity of solid by-product produced. Such process considerations, however, must be balanced against the overall economics of the various processes.

The frame of reference for by-product minimization and stabilization with the use of high-sulfur coal is lime scrubbing, often with up to about 9 percent magnesium oxide in the calcium oxide as delivered by the supplier. A stoichiometry of 1.01 moles of calcium oxide per mole of SO_2 removed, or 1.10 moles of calcium plus magnesium oxides per mole of SO_2 removed, is typically used. The process can now meet a 90- percent SO_2 removal level when scrubbing flue gas from the combustion of, for example, a 4.5 percent, 15-percent ash, 10,700 Btu/lb (1.07×10^6 Btu/100 lb) Ohio coal. The SO_2 emissions after scrubbing are then as follows:

$$\begin{aligned}
 \text{Emissions} &= (0.10 \text{ lb SO}_2 \text{ emitted/lb SO}_2 \text{ fed}) \\
 &\times (2 \text{ lb SO}_2/\text{lb S} \times 0.045 \text{ lb S/lb coal}) \\
 &\times (100 \text{ lb coal}/1.07 \times 10^6 \text{ Btu}) \\
 &= 0.90 \text{ lb SO}_2/10^6 \text{ Btu.}
 \end{aligned}$$

The amount of reacted by-product generated would be approximately

$$\begin{aligned}
 \text{Reacted By-product} &= (0.90 \text{ lb SO}_2 \text{ removed/lb SO}_2 \text{ fed}) \\
 &\times (0.045 \text{ lb S/lb coal} \times 136 \text{ lb CaSO}_4/32 \text{ lb S}) \\
 &\times 2000 \text{ lb/ton} = 344 \text{ lb CaSO}_4/\text{ton coal.}
 \end{aligned}$$

To this calculation of reacted by-product should be added unreacted calcia and/or magnesia, which as noted above is perhaps about 10 percent additional, or about

$$\begin{aligned}
 \text{Total By-product} &= 344 \times 1.10 = 378 \text{ lb mixed SO}_2 \text{ control} \\
 &\text{by-product/ton coal.}
 \end{aligned}$$

The final combined by-product from the control process also often contains fly ash produced by the power plant, some of it possibly reacted with the SO₂, plus any chemicals used in "fixing" the combined ash and scrubber by-products for stabilization purposes. These additional solids must be included when calculating the aggregate amount of solid by-products produced.

As noted in the following sections, a number of the processes now supported by the Ohio Clean Coal effort may produce more solid by-products for disposal on a per-ton-of-coal-burned basis than conventional wet-lime scrubbing, as the trade-off under study is often one of less-expensive technology investment versus increased costs of reagents and increased amounts of solid by-products. However, as noted below, two processes are expected to produce elemental sulfur instead of gypsum, thereby significantly

reducing the volume of by-product to be generated, but probably at a cost penalty in terms of increased technology investment.

The new technologies of interest are the pressurized-fluidized project of American Electric Power, the Babcock & Wilcox E-SO_x, and LIMB injection demonstrations at Burger and Edgewater respectively, the Dravo chelated Thiosorbic® (magnesium-augmented) lime pilot-plant at Miami Fort, the TRW limestone-injection slagging combustor in Cleveland, the Columbia Gas reductive system at St. Marys, and the NOXSO alkalized-alumina pilot plant at Toronto. The major advantage of the first of these efforts, the pressurized fluidized bed system, is the fact that significantly higher efficiencies for the power generating system are expected over the use of established technologies. All the other technologies under consideration will require some power for implementation, thus causing some, but generally minor, decreases in power output as a result of use of the new control technology. The principal potential advantage of the last two processes (i.e., the Columbia Gas and NOXSO approaches) is the expected production of elemental sulfur as the by-product, which has significant commercial value and represents the smallest volume solid output of all possible process by-products. The following sections of this report describe these various new developments and then outline the possible research that is being, or might be, conducted to minimize by-product generation without a significant increase, or possibly even with a decrease, in costs.

2.3 CONTROL TECHNOLOGIES

Except for those control processes under development in the State that produce elemental sulfur as the principal by-product and, if limestone can be used as the bed material, the pressurized fluidized bed combustion process, the other new processes under study may produce more solid wastes than are produced by the conventional wet-lime scrubbing process.

Well-established, the wet-lime scrubbing process, although capital intensive, is relatively efficient in terms of reagent utilization, and hence already involves minimum solid waste production as only up to about 5 percent excess lime is used. The potential advantage of many of the other alternative new processes now under State support is the expected lower cost; however, this lower investment is generally accompanied by an increase in expected solid waste output, a fact that emphasizes the importance of optimizing these processes and of finding uses for their by-products. Chapter 4 discusses possible ways of utilizing the by-products of these new clean coal combustion technologies.

This section of the report describes the various processes in sufficient detail so that optimization recommendations can be made in terms of specific modifications to technologies currently being installed or operated for demonstration purposes in Ohio.

2.3.1 Pressurized Fluidized Bed Combustion

The pressurized fluidized bed combustion project of AEP involves the retrofit installation and operation of a 70-MW advanced combined combustion and emission control technology at the Tidd Station in Brilliant, Ohio. The process is based on the use of a combined cycle made possible by burning coal in a fluidized bed mostly consisting of calcined dolomite (high-magnesia limestone) and various combustion by-products. The process is operated at a pressure of about 12 atmospheres, and is referred to as

pressurized fluidized bed combustion (PFBC). A schematic drawing of the system is shown in Figure 2-1.

In the PFBC process, crushed coal and a sorbent (dolomite or limestone) are continuously fed into the pressurized vessel in which upwardly flowing air maintains the coal and sorbent, together with ash and sulfated product, in a highly turbulent suspended state, called fluidization. Combustion occurs in this fluidized bed of mixed solids at a relatively low temperature of about 1580 F. During the combustion process, the sulfur dioxide (SO_2) formed is absorbed by the dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) to form an inert magnesium oxide-calcium sulfate ($\text{MgO} \cdot \text{CaSO}_4$) complex. The basic chemical reactions are as follow:

The magnesium oxide-calcium sulfate complex, a dry granular by-product, when removed from the fluidized bed, can be managed more easily than the wet sludge by-product from a wet flue gas desulfurization system. This fluidized-bed process has been demonstrated through extensive pilot-plant testing to remove 90 percent of the sulfur from 4 percent sulfur coal at a Ca/S molar ratio of 1.6. Similar but, so far, less favorable reactions take place when limestone is used as the sorbent.

Because the combustion temperature is below the ash-fusion temperature of virtually all coals, the process not only allows for fuel flexibility but should also eliminate slag formation. Furthermore, the low combustion temperature should restrict the formation of NO_x to less than that of a conventional PCF plant.

In PFBC, boiler tubes submerged in the fluidized bed furnace have overall heat transfer rates of 4 to 5 times higher than in a convective furnace. The steam produced within these tubes drives a steam turbine generator to produce the bulk of the plant's electric power. High pressure in the PFBC process permits the use of a deep bed which allows high residence

FIGURE 2-1. SCHEMATIC DRAWING OF THE PRESSURIZED FLUIDIZED COMBUSTION PROCESS FOR OPERATION AT TIDD
 Source: American Electric Power (reproduced with permission)

times and thus ensures high combustion efficiency and good sorbent utilization. The deep bed also permits submerging all boiler tubes in the bed, thus taking maximum advantage of high in-bed heat transfer coefficients, leading to a very compact boiler design.

Pressurization leads to a combined-cycle configuration whereby the hot gases from the bed not only generate steam for use in driving a steam-turbine generator, but the hot gases also drive a gas turbine to provide air for fluidization and to generate additional electricity, thus resulting in a high-cycle efficiency. Before entering the combustion turbine, the combustion gases from the PFBC combustor will pass through high efficiency cyclones to remove approximately 98 percent of the solids in the gas stream. The flue gas from the gas turbine exhausts through an economizer, an electrostatic precipitator, and a stack.

Studies at AEP have shown that a commercial-scale PFBC plant should have the following advantages over a conventional PCF plant with a FGD system:

- Nine percent lower SO₂ emissions due to a higher generating efficiency
- Fifty percent reduction in NO_x emissions due to a lower combustion temperature.

Two types of ash will be generated in the PFBC process at Tidd, bed ash and fly ash. Bed ash, the ash removed from the bottom of the fluidized bed, is granular in form and consists of about half the calcined and sulfated sorbent mixed with coarse coal ash particles. Fly ash, the ash removed from the flue gas by the cyclones and precipitator, is a much finer material and contains about an equal portion of the finer coal ash and spent sorbent. Bed ash will be continuously removed to maintain the desired combustor bed level and will be conveyed to a dedicated ash storage silo. Fly ash from the cyclones and the precipitator will be pneumatically conveyed to a dedicated ash storage silo. From the ash storage silos, the ash will be transported by truck to a previously retired nearby fly ash pond where it will be utilized for final closure of the pond. Runoff from this pond will be discharged to a newly constructed fly ash pond for treatment.

The major variables to minimize by-product production are the nature and reactivity of the bed material. Dolomite has been selected as the bed material for initial investigation, as it has been shown to be superior for SO₂ capture at elevated pressures in pilot plant work in Sweden. On the other hand, there will be a significant amount of magnesia being transported through the system which represents an additional load on the by-product disposal system. Means to increase the reactivity of the bed are well known, including the use of finer particle sizes, the use of activators such as sodium chloride or carbonate, the selection of more reactive limestones, and so forth. Smaller particle sizes result in more losses of fine particles from the system and possibly additional loadings on the electrostatic precipitators and on the turbine. The use of sodium-based additions could result in a host of corrosion and agglomeration problems. Regenerative sorbents have been studied by others in the past, but regeneration involves additional process complexities, and eventually the SO₂ must again be converted to a waste or other low-value product at still added costs. The reactivity of various natural sorbents seems to be the key to reducing the by-product load in the future, and such studies will be undertaken in due course by AEP. On the other hand, it is desirable to use local limestone or dolomites (as is also true of coal) whenever possible.

Because the by-products contain essentially all the fly ash as well as reacted and unreacted bed material, it is not a likely source of high quality gypsum and is not considered as a candidate for use in applications requiring high purity, as noted in Section 4.4.3. However, in addition to some unreacted or reconverted carbonates, the by-products will contain significant quantities of unreacted calcium and magnesium oxides formed by calcination in the fluidized bed, and thus may have use as a liming agent or as low-quality material for construction work. The by-products from the PFBC should be especially low in sulfite content, which may be a significant advantage in disposal compared with other technical options.

Process improvements that have been considered over the years relate (1) to still greater increases in electrical generating efficiency of the process by perhaps operating at still higher pressures or temperatures,

thereby decreasing the amount of by-product solids produced per unit of electricity generated; or (2) to improvements in the utilization of the sorbent and/or ash for sulfur capture, thus reducing the amount of by-product solids being produced per unit weight of coal burned.

It is difficult to predict the degree to which further process improvements will increase efficiency and reduce solid waste production. After several decades of research, near optimum temperatures of operation have been fairly well defined. Although the electrical generation efficiency of the process will increase with temperature, the sulfur capture by the bed at temperatures above about 1652 F drops off rather abruptly because of chemical thermodynamic factors. The temperature of about 1580 F to be used at Tidd therefore represents a balance between reactivity and equilibrium considerations for SO₂ capture. An increase in pressure of operation may also have advantages, and it is planned to operate at 16 atmospheres at the newly proposed plant at the Sporn Station in West Virginia. However, the optimum pressure level is a complicated balance of considerations between increased pressure vessel-construction costs and increased air-compression requirements versus potential increases in energy releases and possible decreases in SO₂ removal.

The major chances for a decrease in solid waste production would therefore appear to be in possibly substituting limestone for dolomite, as noted previously.

2.3.2 Hydrate Addition at Low Temperature

In an effort to develop a less costly way to retrofit FGD systems onto existing utility boilers, Dravo Lime Company, with assistance from Ohio Edison Company, has developed a dry FGD process that uses existing boiler ductwork. The hydrate addition at low temperature (HALT) process removes SO₂ from flue gas by spraying atomized water into the flue gas to cool and humidify the gas and then subsequently pneumatically injecting high-calcium hydrated lime into the gas to react with the SO₂ to form a dry by-product

mixture of lime, calcium sulfate and sulfite, and fly ash. The by-products are collected in an electrostatic precipitator or baghouse.

Typical flue gas temperatures exiting the boiler air preheater are in the range of 250 F to 350 F. The flue gas is cooled and humidified with water sprays to a gas temperature of 150 F. This increases the water content of the flue gas and the SO₂ is absorbed into the liquid water droplets. Dry hydrated-lime particles are pneumatically conveyed into the duct with transport air. The hydrate reacts with the absorbed SO₂ resulting in particles that are a combination of calcium sulfite, sulfate, and calcium hydroxide. Both the spent sorbent solids and coal fly ash are collected in the particulate control device (i.e., in an electrostatic precipitator or a baghouse). The combined dry by-product solids are about double the mass of fly ash produced alone.

Work on the process was initially performed on a 300 ft³/min test facility at the Ohio Edison Company's W.H. Sammis power plant. Additional tests were conducted at the Dravo research facility on a 1 x 10⁶ Btu/hr test combustor burning Midwest high-sulfur coal.

Later, a 5-MW pilot facility, shown schematically in Figure 2-2, was operated at Ohio Edison Company's Toronto power plant. A flue gas slip stream, from either of two 65-MW boilers passed, through a 31 x 31-in. flue gas duct test section approximately 80-ft long. The system started up in November 1986 on a 24-hours-per-day and 7-days-a-week basis, and achieved 50 to 65 percent SO₂ removal efficiencies. The flue gas SO₂ levels typically ranged between 2400 to 3600 ppm coming into the test section and exited the section at 600 to 1200 ppm. The temperature of the flue gas that exited the test section was about 150 F and the particulate content was removed in either a pulse-jet baghouse or an electrostatic precipitator. The principal experimental difficulty encountered was the wetting of the duct walls and subsequent adherence of deposits during injection.

The work at Toronto showed that postcombustion injection of hydrated lime into boiler flue gas ducts is a promising process for removing SO₂ because no separate reaction vessel is needed and the process is relatively easy to retrofit. All the water spray and lime injection into the

FIGURE 2-2. SCHEMATIC DRAWING OF THE DRAVO HALT DEMONSTRATION FACILITY AT THE TORONTO STATION
Source: Dravo Lime Company

flue gas duct is downstream of the boiler air preheater before the particulate-removal device. Hence, there is no chance the FGD process will foul the boiler heat transfer surfaces and lower the boiler thermal efficiency. The FGD system performance with the HALT process should be relatively independent of the boiler system design.

The HALT process is therefore especially attractive as a viable FGD option for older coal-fired power plants. These plants may not have enough remaining years of operation to justify retrofitting higher capital cost wet FGD systems. HALT may also offer a lower cost alternative to burning low-sulfur coal at existing Midwest power plants.

The work at the Toronto station has now been terminated, but additional experimental studies are underway in a DOE-funded effort at AEP's Muskingum River Station near Beverly, Ohio. A form of the HALT process will also be tested at Ohio Edison's 100-MW Edgewater Unit 4 in Lorain, Ohio, as part of the EPA and DOE efforts, and at the OCDO LIMB project later this year.

Recycling of solids and modifications to improve the humidification systems are to be investigated in an effort to lower the Ca/S stoichiometries, and hence the amounts of by-product solids, below those levels obtained at Toronto.

2.3.3 Advanced Wet-Lime Scrubbing

The Cincinnati Gas & Electric Company (CG&E) and the Dravo Lime Company are now constructing a pilot plant to evaluate advanced magnesium-enhanced, wet-lime flue gas treatment technology at CG&E's Miami Fort Station near Cincinnati. Various modifications in process components will be tested there under OCDO support in an attempt to reduce the size and cost of a wet FGD system. In addition, some testing will be directed toward adding NO_x controls to the process based on wet scrubbing techniques, and other testing will be directed toward the possibility of providing a commercial-grade salable gypsum from the scrubber sludge by-product.

The reference technology to be used as the basis for improvement is that now employed by AEP in Conesville, Ohio, and by CG&E at the East Bend Station located on the Ohio River south of Cincinnati. The process is also to be utilized at the W.H. Zimmer Station in Moscow, Ohio. A schematic flow sheet of the process is shown in Figure 2-3. Flue gas, after particulate removal, is now passed counter-current to a flow of slurried lime in a scrubbing tower. The lime slurry is injected into this system by a series of spray headers at the top of the tower and collected in a recycle tank at the base of the tower. Slurry from the recycle tank is continuously withdrawn and returned to the spray headers by suitable pumps. A relatively small purge stream is withdrawn from the recycle tank and pumped to a thickener for partial dewatering and then to a vacuum filter for final dewatering. Makeup slurry is added to the reactor tank as needed. The wet solids from the vacuum filter are mixed with fly ash, often with a little extra lime as well, to obtain a composition that will harden with aging, and then trucked to a dedicated landfill. This technology and the similar limestone scrubbing process are the principally used methods for treating the flue gas from the combustion of high-sulfur coal in the U.S.

The pilot plant will treat a slip-stream equivalent to a 3-MW plant. The system will scrub flue gas resulting from the burning of high-sulfur ($2\frac{1}{2}$ percent plus) coal; part of this coal will be from Ohio seams 8, 10, and 11. The overall objectives are (1) to establish optimized system operation and equipment requirements that will achieve a reduction of up to 30 percent in capital cost and significantly lower the operating cost of wet flue gas systems using high sulfur coal, and improve handling and disposal of process by-product through modifications that will facilitate dewatering of scrubber sludge and increase the solids content of the by-product; (2) to verify that a low-cost technology using metal chelate additions in the scrubbing liquor can achieve significant levels (70 percent plus) of NO_x removal without adversely affecting the SO_2 removal efficiency; and (3) to determine if process modifications can convert the scrubber sludge into a commercially marketable gypsum.

FIGURE 2-3. SIMPLIFIED FGD SYSTEM SCHEMATIC DIAGRAM
Source: Dravo Lime Company

A summary of the specific cost reduction steps to be studied is provided in Table 2-7. More specific information on these studies, and how they might impact on a typical generating station, was proposed as follows:

- Demonstrate that the flue gas velocity inside the scrubber can be increased to 15 ft/sec from the present 8 to 10 ft/sec while maintaining a minimum of 90 percent SO₂ removal. The increase in velocity would enable the reduction of the number of scrubber modules from three to two for a typical 500-MW plant or a decrease in module diameter of 20 percent.
- Reduce the system's liquid-to-gas (L/G) ratio from 50 gpm/1000 acfm to 15 gpm/1000 acfm while maintaining a minimum of 90 percent removal efficiency. The L/G reduction will eliminate 50 percent of the recirculating pumps resulting in 2500 HP savings on a 500-MW size plant.
- Investigate the use of a cocurrent scrubber to remove a minimum of 90 percent SO₂ while at the same time increasing the flue gas velocity to 20 ft/sec. The use of a high-velocity cocurrent scrubber for SO₂ removal has the potential advantage of further reducing the scrubber diameter and simplifying scrubber internals.
- Investigate the reduction in height of the scrubber modules as a result of the decrease of the number of spray levels in a spray tower scrubber, the use of trays in lieu of sprays, and the use of a cocurrent scrubber as the gas slurry contactor. Such change could reduce the height of a typical scrubber from 100 to 60 ft and decrease required recycle pump operating horsepower.
- Demonstrate that the average particle size of the precipitated sludge can be increased and result in a decrease in thickener area requirements of up to 66 percent. This could result in (1) a reduced number of vacuum filter systems required, along with a smaller horsepower vacuum pump as a result of improved filtration rate; (2) a filter cake with at least 11 percent less moisture, which is expected to be obtained by improved dewatering on the vacuum filters from the present 45 percent solids content of the sludge to a minimum of 50 percent solids; and (3) a 40-percent reduction in recycle tank volume, which as an integral part of the scrubber, will decrease scrubber height by 3 ft and slightly reduce recirculating horsepower requirements.

TABLE 2-7. COST REDUCTION OBJECTIVES - ADVANCED VERSUS CONVENTIONAL WET FLUE GAS DESULFURIZATION SYSTEM

Source: Dravo Lime Company

Major Component	Conventional Wet FGD System		Advanced Wet FGD System		Reduction Objective
	Design Parameters	Typical Operating Value for 500-MW Installation	Design Parameters	Typical Operating Value for 500-MW Installation	
A. Scrubbers	Gas Velocity: 10 ft./sec.	59 ft. diam.	Gas Velocity: 15 ft./sec.	48 ft. diam.	33% area reduction
B. Recycle Pumps	Liquid to Gas Ratio: L/G = 50	82,500 gpm	Liquid to Gas Ratio: L/G = 25	41,250 gpm	50%
C. Recycle Tank	Six-hour residence time	440,000 gal.	One-hour residence time	254,000 gal.	42% volume reduction
D. Thickeners	Unit area per ton/day: 40 ft ² /ton/day	200 ft. dia.	Unit area per ton/day: 20 ft ² /ton/day	141 ft. dia.	100% area reduction
E. Vacuum Filters Residual Waste Disposal	45 wt.% Solids	1,729 tons/day	50 wt.% Solids	1,555 tons/day	11%

Among the objectives of the chelate addition studies to achieve simultaneous NO_x removal are (1) to confirm laboratory results indicating that metal chelate additives, either ferrous EDTA or HMTA, will achieve high percent NO_x removal; (2) to confirm that addition of metal chelates will not interfere with the overall system liquor chemistry required for SO₂ removal; and (3) to obtain preliminary overall costs from data such as makeup requirements, unusual production requirements, and shelf life.

The third phase of the effort is to produce a commercially attractive grade of gypsum as a possible market for the by-product of the process. Although there are now several locations in the U.S. where attempts are being made to market gypsum produced from wet scrubbers, all employ limestone, not lime, as the reagent. Thus, these studies are directed at establishing how best to modify the lime-scrubbing process to produce such a product, and also how the additives for simultaneous NO_x removal might affect the quality of the resulting gypsum. The gypsum production studies will (1) determine the efficiency with which magnesium hydroxide can be separated from gypsum and recycled to the scrubbing process, and (2) determine the quality of the gypsum produced as a function of process parameters, such as chloride, cake moisture content, etc.

The scrubbing process work proposed for study at the Miami Fort Station is mostly based on performing research related to established technology, rather than a demonstration effort of a new process. Therefore suggestions for research in addition to that proposed seem premature. In terms of impact on minimizing by-product production, no significant effects are expected, as conventional lime scrubbers already operate with high efficiencies at Ca/S stoichiometries of about 1.10. However, in terms of reduction of scrubber costs, this is an important research project. In addition, because the production of gypsum is directly related to the efforts of the State of Ohio to find alternatives to landfilling for the disposal of by-products, it might be desirable at some point in time to place increased emphasis on that phase of the effort to be conducted at the Miami Fort Station.

2.3.4 Limestone Injection in Multistage Burner

The LIMB project of B&W involves a four-year demonstration which includes the design, installation, and operation of a LIMB system at the 105-MWe Unit 4 boiler at Ohio Edison's Edgewater Station in Lorain, Ohio. This effort is a scale-up of LIMB technology to a representative full-scale, wall-fired utility boiler. The limestone is injected in the high-temperature regions of the boiler before the air heater wherein the limestone is at least partially calcined to lime and reacts with the SO_2 released from the combustion of coal.

The LIMB project also involves the retrofitting at Edgewater with XCL low- NO_x burners developed by B&W. In addition, as part of an add-on task, the Coolside process by Conoco Coal Development Company, involving the injection of hydrated lime at lower temperatures in the flue gas ducting after the air heater, is also to be demonstrated. Because the sorbent is less reactive at these lower temperatures, humidification water is added to enhance SO_2 -removal performance. The enhancement effect of adding humidification water in the flue gas ducting is also to be studied as a part of the basic LIMB project to see if it is effective with in-furnace limestone injection as well.

A schematic of the base LIMB technology is shown in Figure 2-4. Briefly, the LIMB process units consist of sorbent storage and handling equipment and feed equipment. The sorbent storage and handling equipment supplies the sorbent for the process. The sorbent is delivered by bulk transport truck in a dry state suitable for pneumatic conveying from a main storage silo to a feed silo.

The sorbent-feed equipment provides a controlled feed rate of sorbent to the injection elevations in the upper furnace of the boiler. This equipment can be utilized at any two of three injection elevations at one time. Material is conveyed pneumatically from the feed silo to distributor bottles from which the solids and air mixture enters the injection lines. At the boiler, a series of injection nozzles is provided

FIGURE 2-4. SCHEMATIC DRAWING OF THE LIMB TECHNOLOGY AT EDGEWATER
Source: Ohio Edison Company

to give the desired penetration and dispersion of sorbent into the boiler. A booster-air fan provides the energy necessary to develop the desired penetration and dispersion into the upper regions of the boiler.

Ohio bituminous coals with a nominal sulfur content of 3 percent or greater are being used to demonstrate LIMB. The goal of the project, which is cofunded by OCDO, EPA, and DOE, is to reduce SO₂ emissions by at least 50 percent, and to reduce NO_x emissions to a maximum of 0.5 lbs/10⁶ Btu, at a capital cost significantly less than that of conventional add-on FGD technology. Various technical difficulties were expected to be encountered, which is one reason for the four-year demonstration effort. These problems include slagging and fouling, changes in ash disposal requirements, and changes in particulate loading and resistivity in the flue gas. Power requirements for the LIMB equipment are relatively minor, and are mainly associated with the pneumatic conveying system. On the other hand, if the unit must be derated because of slagging or fouling, a loss-of-capacity problem, such as that encountered in earlier work at Union Electric, could be significant.

Sorbent injection into the boiler at Edgewater was first accomplished in July 1987. Emissions from the electrostatic precipitator increased significantly, and it was then decided to start the humidification efforts earlier than planned, not necessarily to improve SO₂ capture, but to improve precipitator capture of the fly ash and the injected and partially reacted sorbent.

The solid by-products from the process contain mostly calcium sulfate, calcium carbonate, and fly ash. Commercial outlets for this material must therefore be based on the use of this by-product as a rather low-grade source of any of its components. Disposal at present is accomplished by landfilling, and some research on this aspect of the technology is already being supported by DOE.

A major goal of the 4-year program at Edgewater is to investigate the variables that affect SO₂ removal, and thus minimize the by-product disposal requirements of the control process. Calcium to SO₂ stoichiometries of perhaps 3 to 4 may be needed for even 50 percent SO₂ removal, and thus

there is significant potential for process improvement. By humidification, an improvement of SO₂ capture efficiency by approximately 10 to 15 percentage points over the base LIMB objective (i.e., from 50 to 60-65 percent SO₂ removal) is being sought. By the use of the Coolside process, overall reductions of SO₂ may be in the 70 to 80 percent range, which would provide corresponding reductions in the amount of by-products produced.

Variables being studied include coals of various sulfur content, the location and extent of humidification, the amount, feed point, size, and the composition of the sorbent. Also being investigated is the possibility of using a solid by-product recycle system to reinject the by-products collected in the electrostatic precipitator to obtain increased utilization of the contained alkali values. This recycle system is to consist of an ash recycle storage bin, pneumatic conveying equipment, and the associated delivery piping. Although apparently a study of the means for activation of the ash before recycle at Edgewater is not yet planned, such a procedure might also prove beneficial; its cost-effectiveness would, of course, have to be determined.

To minimize by-product production, various means to activate such sorbents have been studied in the past. These involve the use of additives to the injected lime or limestone, including sodium compounds such as caustic soda, sodium carbonate, and the like; silicates and diatomaceous earths; as well as iron and chromium oxides. Fine grinding and/or steaming of the collected solids before recycling also have been found to be effective.

It has long been believed by EPA that the LIMB technology would be one of the most attractive alternatives to wet scrubbing on a cost-effectiveness basis, and the demonstration at Edgewater should provide much valuable information in this regard. The information being obtained there should also provide useful data on the amount and composition of the by-products produced and their environmental behavior.

2.3.5 Electrostatic Precipitation with Injection

The electrostatic precipitation with injection (E-SO_x) project, being conducted at Ohio Edison Company's R.E. Burger Generating Station, received its name from the principles involved. A conventional type of dust collector, called an electrostatic precipitator (or ESP), is being modified to perform double duty (i.e., removal of the oxides of sulfur [SO_x] via injection of lime and then collection of both the spent injected sorbent as well as the fly ash normally produced).

The R.E. Burger Plant is located 5 miles south of Shadyside, Ohio, across the Ohio River from Moundsville, West Virginia. The experimental E-SO_x process under construction there is designed to remove 50 percent or more of the sulfur-dioxide emissions from existing coal-fired, electric-generating stations. A schematic drawing of the facility is shown in Figure 2-5.

ESPs work on the principle of inducing an electrical charge on the dust particles, such as the fly ash emitted by a coal-fired boiler, and then collecting such particles on grounded metal plates. The first field of this ESP in a retrofit situation for the E-SO_x process would be removed to create a chamber in which a lime slurry would be injected, probably by a dual-fluid nozzle. The slurry reacts with the sulfur dioxide in the hot gas to produce a dry by-product that can be collected, along with ash, in the remaining precipitator fields. For the test at Burger, a portable research precipitator, with four "fields" of charged wires and collection plates, is to be used to process a side stream of flue gas produced by diverting about 3 percent of the flue gas emitted by one of the Burger generating units.

The concept of collecting such combined by-products, ash plus sulfur dioxide removal by-products, in a downsized precipitator is the major innovation that the E-SO_x program will test. By using another technology previously developed by EPA, involving a method of precharging dust entering the ESP fields, the handling of the larger dust load involved with the added SO₂-control system is expected to be accomplished with fewer fields.

E-SO_x CLEAN COAL PILOT PROGRAM OHIO EDISON COMPANY R.E. BURGER PLANT

FIGURE 2-5. SCHEMATIC DRAWING OF E-SO_x PILOT PLANT AT OHIO EDISON COMPANY'S R. E. BURGER PLANT
Source: Ohio Edison Company

Ground breaking for the E-SO_x project took place in April 1988, with experimental operation scheduled to begin in early 1989. Principal funding for the project is being provided by EPA and OCDO. Other participants, in addition to Ohio Edison, are B&W and SRI.

The E-SO_x process particularly needs research to optimize the variables that affect its performance in a reasonably sized demonstration unit. The lime receiving and storage and slurry-preparation equipment should be state-of-the-art items that have been used for many existing commercial scrubbers, both wet and dry, and should present no problems. On the other hand, the two-fluid nozzle arrangement requires a relatively flat and fine droplet distribution (40 to 50 μ m) for good sorbent utilization; thus this requirement needs further development to maximize SO₂ removal and minimize by-product generation. The collecting ability for the added particulate load in an ESP designed for more modest duty, at least in retrofit situations, also needs to be established. Variables affecting operation of the precharging equipment and the benefits of using larger diameter electrodes are expected to be studied. Uncertainties with regard to reagent stoichiometries, approach to saturation temperatures, and residence times, also need to be resolved from the limited laboratory-scale process data now available.

There is also concern as to whether adequate spray drying will in fact occur in the (guttled) first field of the ESP. If too much slurry is added, tenacious deposits may form in the remaining ESP equipment. ESP performance on the new types of particulate produced also needs to be established, although this may not have a first order effect on the total by-products produced by the product. Also from an operational point of view, means to discharge the added ash produced need to be demonstrated. For instance, the possible use of a delumper to prevent constrictions developing as a result of the production of oversized by-products should be considered.

However, if successful, capital costs for the E-SO_x process are expected to be significantly lower than for conventional flue gas scrubbers. Because the system is based largely on modifications to existing equipment,

it should be particularly applicable at generating stations where space limitations make conventional scrubber retrofits especially difficult.

2.3.6 Reductive Desulfurization and Denitrification

The Columbia Gas Company is now installing a pilot plant for a novel flue gas treatment (FGT) system involving reduction of sulfur dioxide to hydrogen sulfide and nitrogen oxides to atmospheric nitrogen at the municipal light plant in St. Marys, Ohio. The hydrogen sulfide would be subsequently converted to elemental sulfur. The integrated system involves the use of three separate technologies as proposed by the Ralph M. Parsons Company. Specific goals to be demonstrated at St. Marys are a minimum of 90 percent SO₂ control, a minimum of 90 percent NO_x control, and with both goals to be performed at projected competitive and viable cost levels. A schematic flowsheet for the process is shown in Figure 2-6. The three steps, each of which has been at least partially protected by patents, are as follow:

- A Beavon Sulfur Recovery (BSR) hydrogenation unit to simultaneously reduce the SO₂ to hydrogen sulfide (H₂S) and the NO_x to elemental nitrogen (N₂)
- A FLEXSORB SE* PLUS process to recover H₂S from the BSR effluent; its product is the feed stream to a sulfur production step
- A Recycle Selectox Process unit to convert the H₂S to elemental sulfur.

2.3.6.1 The BSR Hydrogenation Process

The BSR hydrogenation process was developed jointly by The Ralph M. Parsons Company and the Union Oil Company of California in the early 1970s. It is a fixed-bed catalytic hydrogenation process which is used commonly as one process step in the clean up of Claus sulfur-recovery plant tail gases. The process was originally tested in a pilot facility by Parsons/Union. Its use in more than 60 commercial plants has been reported at various locations in the world.

FIGURE 2-6. SCHEMATIC FLOWSHEET OF THE PARSONS FLUE GAS CLEANING PROCESS
Source: Ohio Coal Development Office

2.3.6.2 The FLEXSORB SE PLUS Process

The absorption of the H_2S into an amine solution has been practiced for many years. The FLEXSORB series of amine-type hydrogen sulfide removal solutions are said to have been developed by Exxon Corporation at its research facilities in Florham Park, New Jersey, and proven in commercial operation. In particular, the solvent FLEXSORB SE PLUS process is reported to have the ability to remove hydrogen sulfide to levels of less than 10 ppmv while being selective in the absorption of hydrogen sulfide from carbon dioxide.

2.3.6.3 The Recycle Selectox Process

The Recycle Selectox process was developed by The Ralph M. Parsons Company and the Union Oil Company of California in early 1980. The Recycle Selectox process was designed specifically to produce elemental sulfur from H_2S when the acid gas contains substantial quantities of carbon dioxide (CO_2) and is dilute in H_2S . The process is said to operate satisfactorily with H_2S concentrations in the range of 1 to 35 volume percent. It is a modification of the well-known Claus sulfur recovery process which operates best when the acid gas feed contains H_2S with a concentration of at least 50 volume percent. The Recycle Selectox process (which, except for the special catalyst required, is reported to be conventional Claus technology) has recently been commercialized and at present there are four units in operation, two ready for startup and the others in various stages of design and fabrication. The first commercial unit is reported to have been in operation since 1983.

2.3.6.4 Catalyst Development

This OCDO grant program for Columbia Gas also includes a research program to develop better catalysts. The OCDO catalyst research phase of the

project is being conducted in cooperation with the University of Delaware Center for Catalytic Science and Technology (DCCS) with Professor A.B. Stiles as principal investigator. The goal of this project is to develop a better catalyst for the simultaneous removal of SO_2 and NO_x in coal flue gas. Several exploratory catalysts have been made and evaluated. The most promising is a transition metal oxide on $\gamma\text{-Al}_2\text{O}_3$. This catalyst not only gives high conversions of the SO_2 and NO_x , but also converts a major fraction of the SO_2 to elemental sulfur. The influence of temperature, H_2/SO_2 ratios, and space velocity on the catalyst performance, is now being studied. The candidate catalyst can also be promoted with metal oxides, with hydrogenation functions, or with heteropoly acid components. The effects of promoters is therefore also being investigated in attempts to attain good conversions of SO_2 and NO_x at lower temperatures.

The major potential advantage of the process is the expected production of elemental sulfur as the so-called process waste product, although sulfur obviously has considerable economic value in itself. The penalty involved, however, for such an advantage is that the process requires chemical operations involving three separate processing steps. On the other hand, in terms of minimizing solid by-product production, it is one of the two prime candidate processes with such an objective (i.e., the production of sulfur) that are now under the support of the State (the NOXSO process being the other, described below).

2.3.7 Alkalyzed Aluminate Flue Gas Treatment

The NOXSO flue gas treatment process is a dry flue gas regenerative technology that can remove up to about 90 percent of the SO_2 and NO_x from the flue gas generated by coal-fired boilers. The flue gas is cleaned as it passes through a fluidized bed of solid sorbent at a temperature of about 248 F in an adsorbing reactor. The sorbent is composed of an alumina substrate on which sodium is deposited. A schematic flowsheet for the process is shown in Figure 2-7.

FIGURE 2-7. SCHEMATIC FLOWSHEET FOR THE NOXSO ALKALIZED ALUMINATE PROCESS
Source: NOXSO Corporation

Spent sorbent from the fluidized bed reactor, containing reacted and/or adsorbed NO_x and SO_2 , is regenerated for reuse by treatment with a reducing gas at a temperature of about 1112 F. This regeneration produces both SO_2 and H_2S , which can be converted to elemental sulfur or sulfuric acid. The sulfur may be sufficiently pure to be in general competition with Frasch sulfur for commercial use, or at least could probably be used for industrial-grade sulfuric acid production. The NO_xSO process is reported to generate no by-product. The adsorbed NO_x is desorbed as the loaded sorbent is heated to a regenerator temperature of approximately 1112 F with hot air, in a suitable regeneration reactor. The hot air leaving the sorbent heating operator and containing NO_x is then mixed with the combustion air fed to the boiler which the NO_xSO process is serving. The recycled NO_x is expected to suppress the production of NO_x in the coal combustor, so that the concentration of NO_x in the flue gas increases moderately and then reaches a new steady-state level.

The process itself has a relatively old history, dating back to the 1930s in England. The process has also been tested previously at a smaller scale on actual flue gas at TVA's Shawnee Steam Plant in the 1980s, and most recently at DOE's Pittsburgh Energy Technology Center (PETC) at a 0.75-MW scale of operation. It is currently being tested at PETC in a new apparatus designed to integrate all the process steps in "life-cycle" tests.

The 0.75-MW scale experiments at PETC were conducted in a fluidized bed adsorber which had a 40-in. square cross section and contained approximately 450 pounds of sorbent. The sorbent overflow pipe was adjustable to give various bed heights. The flue gas was produced by a 500 lb/hr coal combustor by burning high-sulfur coal and generating about 1500 ft^3/min of flue gas. The sorbent, containing about 4 percent sodium on the surface of a gamma alumina substrate, was provided by the Davison Division of W.R. Grace & Company.

Sorbent heating and regeneration were conducted in a single reactor consisting of a 2-ft diameter stainless steel tube inserted in a vessel which was $2\frac{1}{2}$ ft in diameter and 13 ft high. The sorbent was heated by fluidization in hot combustion gases and subsequently regenerated in a fixed bed mode with

either hydrogen, mixtures of hydrogen and carbon monoxide, or methane. Following this, the sorbent was treated with steam. After steam treatment, the sorbent was transferred to a cooling hopper and, when cool, stored in drums for subsequent reuse in the adsorber.

The PETC tests showed that scaling up the NOXSO fluidized bed adsorber by a factor of 40 from the size of the adsorber at Shawnee gave results of equally high efficiency. At an expanded sorbent bed height of 36 inches, SO₂ removal efficiency averaged 95.4 percent. In one test, at 5,000 ppm SO₂ in the flue gas inlet to the adsorber (equivalent to burning 6 percent sulfur coal), the SO₂ removal efficiency was 96 percent. This result indicates that the NOXSO process might be used on units burning very high-sulfur coal. Although in the same series of tests, NO_x removal efficiency only ranged from 71.0 to 87.5 percent and averaged 80.6 percent, subsequent tests using methane for regeneration resulted in 90 percent removal of NO_x.

In 1987 it was announced that the NOXSO Corporation and W.R. Grace & Company had signed agreements that provided for a joint research program aimed at improving the sorbent and for commercializing the NOXSO technology. NOXSO has reported that Grace funded these sorbent improvement studies, which also made Grace the preferred supplier of NOXSO sorbent in the future under a license from NOXSO. In February 1988, NOXSO Corporation joined with M.K. Ferguson and W.R. Grace to submit a proposal to DOE to build a proof-of-concept scale NOXSO system treating 5 MWe of flue gas (1,200 ft³/min) at the Ohio Edison's Toronto Station with an option on the rights to this process and would supply the sorbent used. In August 1988, a contract was awarded to build the proof-of-concept test unit at the Toronto Station under the support of OCDO.

The proof-of-concept tests are expected to take 33 months to complete. The results of the test program will then be used to design an appropriately sized system to control emissions from a full-size power plant burning high-sulfur coal and to determine the corresponding capital and operating costs.

Because the process produces no by-product (although small amounts of attrited sorbent may be generated in normal operation), research to

minimize the generation of solid by-product, at least for now (June 1989), seems premature. This aspect of the process is of course one of its principal advantages. Moreover, this is one of two FGT processes -- the Columbia Gas Company process is the other -- now being supported by the State that are designed to produce elemental sulfur as the only solid product. However, in terms of research needs not yet proposed, the recirculation of high NO_x -containing flue gas seems to be a possible additional demonstration objective.

2.3.8 Slagging Combustor with Limestone Injection

The TRW slagging combustor burner, now installed at an Argo-Tech manufacturing plant (previously owned by TRW) in Cleveland, Ohio, consists of a cylindrical downward-slanting combustion tube, somewhat like the cyclone combustor used in large electric-utility plants, affixed in the region of the burner ports on an oil-fired boiler. A schematic drawing of such an add-on combustion chamber is shown in Figure 2-8. The boiler at Argo is a 28,000 lb/hr Keeler Type CP unit, originally designed for coal firing, but converted to oil firing in recent years. Ohio coal with about 2 percent sulfur and 9 percent ash is the most frequently tested fuel.

The primary purpose of the original combustor was to remove the slag formed by the ash in the coal during combustion, and to avoid slagging and fouling that would otherwise occur when a boiler was switched from oil to coal firing. Limestone additions can also be added to the combustor or boiler by premixing with the coal or by injection at the exit of the combustor and thus reacting with at least some of the SO_2 produced to form calcium sulfate, sulfite, sulfide, and perhaps even a little elemental sulfur as well.

Nitrogen oxide reductions can be achieved by operating the slagging combustor under somewhat reducing conditions (i.e., by limiting air additions to the slagging combustor), and then by completing the combustion with additional air at somewhat lower temperatures in the boiler itself. If

FIGURE 2-8. SCHEMATIC DRAWING OF THE TRW SLAGGING COMBUSTOR BURNER

Source: TRW

another oil embargo occurred, this technology could be especially suitable for retrofit applications.

Research on the process started in 1975 and the original work was performed at the TRW test facility in Capistrano, California. The retrofit in Cleveland started up in January 1986 and more than 4,000 hours of operation have now been achieved. Ash removal of 80 to 90 percent has been demonstrated prior to injection of the combustion gases into the boiler. Limestone additions at various locations in the combustion train are to be tested in work now being supported by OCDO.

A demonstration program at the Lovett Station of Orange and Rockland in New York, funded as a replacement technology for one of the nine original award winners that did not eventually obtain the necessary private financing under the Clean Coal Technology program, is now planned. With a 2-percent sulfur Ohio coal, 50 percent capture at a reported stoichiometric ratio of 1.5, and 90 percent was reacted at a stoichiometry of about 3 to 4, in test work at Capistrano. Results at Argo were said to be less satisfactory with Ca/S ratios as high as 10 to 20 needed to provide SO₂ capture in the range of 60 to 70 percent. Maintaining good combustion conditions at such high limestone additions may be a problem, and other investigators with similar technology have had to adopt preheating or enrichment of the combustion air to solve this difficulty.

The intent of the work now under support of the State is to further investigate the variables that affect performance at Argo when using low-, medium- and high-sulfur Ohio coals. Improvements in nozzle design are being studied to obtain improved sorbent injection. Recycling the slagged solid products to improve limestone utilization will also be studied.

In terms of minimizing the by-product solids load, TRW is already studying means to improve limestone utilization by adding the limestone at various regions downstream of the combustor, by recycling the by-products for improved utilization, and by adding a spray-dryer reactor between the boiler and a retrofitted baghouse. This latter approach is shown schematically in Figure 2-9. A Joy Manufacturing Company spray-dryer system, which was said to have demonstrated greater than 90 percent capture when operated with

FIGURE 2-9. SCHEMATIC REPRESENTATION OF TRW PROCESS DEVELOPMENT PLANS

Source: TRW

slaked lime, is apparently being installed at Cleveland. This step is expected to demonstrate high SO₂ capture in the spray dryer with the lime produced by calcination in the boiler of the injected limestone. At Lovett, plans are to use extension solids sampling to determine the reactivity of the products of such limestone calcination in order to verify that a spray dryer could provide the desired SO₂ capture.

2.4 STABILIZATION PROCESSES

The use of coal ash and fly ash has been of interest for some time. Several processes have been developed to stabilize these by-product materials so they can be utilized as raw materials. Common end uses of coal by-product materials range from road aggregate materials to use as mineral wool. In general, the end use of the by-product materials corresponds directly with local markets for the materials. This results in generally small volume end uses for the large volume by-products.

Even though several end uses for ash exist, there are relatively few processes that can be considered coal by-product stabilization processes. Most processes actually use fly ash or scrubber sludge as an agent to stabilize other materials. In this case, the total utilization of the coal waste products is quite small in relation to the quantities produced. Technologies evaluated during this task study cover only those processes identified that stabilize coal combustion by-products themselves, rather than utilize coal combustion by-products as a stabilizing agent.

To provide a consistent basis for comparison, it was assumed that stabilized wastes would be disposed of in an on-site landfill. As a result, no avoided costs or process costs need be included in the process description below.

2.4.1 Approach

A literature search was conducted to identify activities on coal by-product stabilization processes. Although several activities were identified relating to uses for coal combustion by-products, only a few of these actually relate to stabilization of coal combustion by-products. Stabilization technologies were then reviewed as to their applicability to Ohio clean coal combustion by-products. These technologies are discussed below.

2.4.2 Stabilization Technologies

Five stabilization technologies have been identified that may be applied to Ohio clean coal combustion by-products. These are as follow:

- Calcilox® Process
- I.U. Conversion systems Poz-0-Tec Process
- Enviroclean Process
- Terra Crete Process
- Ames Granulation/Sintering Process.

A brief description of each of these stabilization processes is presented in Sections 2.4.2.1 through 2.4.2.5.

2.4.2.1 Calcilox® Process

This process consists of using a dry powder additive to improve the handling and land disposal characteristics of coal combustion (calcium-based) by-products. The Calcilox® material is hydraulically active and when used results in a cement-type process.

About 5 to 15 percent of dry slurry weight of the additive is mixed with the by-products. Dewatered by-products (55 to 70 percent solids) use slightly less, while materials with a lower solids content require slightly more of the additive. Leaching tests show reduced leach rates compared with raw sludges. Typically, a 1 to 2 order of magnitude reduction has been reported.

The additive is a product of the Dravo Lime Company of Pittsburgh, and has been used primarily at Pennsylvania utility sites. No cost data were available on this technology (Landreth, 1982).

2.4.2.2 Poz-0-Tec Process

The Poz-0-Tec process uses fly ash and additional additives. Two chemical reactions take place simultaneously in the by-product, one between

soluble salts in the fly ash and unreacted lime and alumina, and a slower reaction between silica and lime. The second reaction is a pozzolanic reaction and takes several months to complete. Several million tons of SO₂ scrubber sludge are treated annually by the process. The process essentially encapsulates leachable components of the by-product to stabilize them and render them nonleachable.

Cost of treatment by the Poz-O-Tec process are reported to be in the range of \$0.30 to \$2.20 per cubic foot of sludge. Specific costs of treatment depend on such variables as total by-product quantity, water content of the sludge, toxicity, equipment redundancy desired, and operational methods chosen.

The physical and environmental properties of the stabilized sludges improve with time as the pozzolanic reactions proceed. A monolithic mass of low permeability subject only to surface leaching is formed. Structural data for a typical stabilized material are found in Table 2-8.

TABLE 2-8. PROPERTIES OF POZ-O-TEC STABILIZED SLUDGE

Wet Density	85 to 100 lb/ft ³
Dry Density	65 to 85 lb/ft ³
Moisture Content	25.5%
Cohesion	>2,000 lb/ft ²
Unconfined Compressive Strength	>25 lb/ft ²
Permeability Coefficient	10 ⁻⁶ to 10 ⁻⁸ cm/sec
Allowable Bearing Capacity	3 tons/ft ²
Stable Fill Slope	2 horizontal to 1 vertical
Saturation	Incomplete

The stabilized sludge may occupy more volume than the unstabilized sludge, but this is offset by the weight reduction resulting from the dewatering of the material, and the greater stacking heights achievable with the stabilized sludge (Landreth, 1982).

2.4.2.3 Enviroclean Process

The Enviroclean process utilizes either portland cements, lime and pozzolans, or cement and lime and pozzolans as stabilization agents depending on desired results and/or local availability of materials. By-product stabilized by the process has a soil-like consistency and gradually over a period of years becomes a concrete-like mass. The process developer, Industrial Waste Management, Inc., emphasizes the use of the material for roadways, parking lots, and walkways.

Cost of the stabilization process is about \$0.50 to \$0.80 per cubic foot of sludge not including removal or hauling charges. As with other processes, costs vary with water content, volume, and chemical composition of the sludge to be processed.

The initial strength of the stabilized by-product is 15 to 40 lbs/ft². This increases to 74 to 400 lbs/ft² in 3 to 6 months and further increases to 300 to 700 lbs/ft² in 2 years. Permeabilities of 10⁻⁷ to 10⁻⁸ cm/sec were said to be achieved in one month. An increase in volume of 1.1 to 1.6 over the raw materials results from the addition of materials (Landreth, 1982).

2.4.2.4 Terra Crete Process

The Terra Crete process is a "self-cementing" process based on the production of a cement-like material from calcium sulfite hemihydrate or calcium sulfate. A portion of the sulfite/sulfate sludge stream is dried and calcined to produce a cementing agent. This material along with other additives as needed are introduced into the by-product stream and form a hard, low-permeability mass from the sludge. Projected processing costs in the range of \$2.25 to \$3.00 per ton of sludge have been claimed.

The compressive strength of the stabilized sludge depends on the amounts of additive used, but typical strengths of 200 to 12,000 lbs/ft² have been measured. Reported permeabilities are usually in the 10⁻⁶ to

10-7 cm/sec range. The process developer is Sludge Fixation Technology, Inc., of Orchard Park, New York (Landreth, 1982).

2.4.2.5 Ames Granulation/Sintering Process

In this stabilization process, by-products are pulverized when necessary and residual carbon in the by-products is used as an energy source to sinter the materials in to hard nonleachable materials. A schematic of the process is found in Figure 2-10. Unlike the other processes discussed, this process is still under development. Thus far testing at the University of Iowa has focused primarily on the production of granules from the raw by-products. Granules are formed in a rotary pan agglomeration device and are referred to as "green" granules. Particle size of the feed material, moisture content, and residence time in the agglomerator all have an effect on the size of the green granules. Some additional water is used as a binding agent.

Green granules are then fired in a sintering furnace at temperatures of 1652 F to 2192 F for 1 hour. This temperature is sufficient to ignite the carbon present in the granules. Measurements made on sintered granules showed that those processed at a temperature of about 2012 F had the greatest strength. Higher processing temperatures resulted in slag-covered surfaces but soft granule interiors, while lower temperatures were not sufficient to sinter the materials. The temperature at which the highest-strength sintered granules were produced varied slightly with the composition of the green granules. No cost data of processing were reported (Burnet et al., 1988).

FIGURE 2-10. THE AMES GRANULATION/SINTERING PROCESS
 Source: Preprints 1988 ACS National Meeting,
 Burnet, G., et al. (reprinted with permission)

2.5 BY-PRODUCT PRODUCTION

In principle, it is possible to produce various sulfur- containing chemicals or products of industrial importance from the SO₂ removed by flue gas control technology. (The markets for these materials are discussed in Chapter 4 of this report.) The most common by-products of such processing are solid calcium sulfate and incompletely oxidized calcium sulfite. Calcium sulfite has very limited commercial importance, but can be readily oxidized to calcium sulfate with a relatively minor, but also a slightly more costly, modification to conventional wet scrubbing and dry injection systems. Calcium sulfate, in the form of its dihydrate which is known as gypsum, is extensively used as a construction material. However, gypsum is also widely available as a naturally available material and is relatively inexpensive.

Often there are stringent demands on the properties of gypsum used for construction, especially for use in wallboard manufacture. Factors that affect the properties of the casting slurry or the finished board must be carefully controlled. Among these properties are the calcining characteristics that affect slurry properties such as flow characteristics and setting rate, and impurities that could cause poor bonding of the paper, reduced strengths, and efflorescence and discoloration. Important properties of the gypsum itself include the particle size, which determines the slurrying properties, and the presence of soluble salts, even at low levels. Wallboard manufacturers control raw gypsum properties to some extent by selective mining and blending. They also have extensive experience in the use of additives to modify the effects of gypsum properties. Fortunately, the specifications for use of gypsum in the cement industry are generally not as strict with regard to the level of impurities allowed and the use of this by-product for such purposes might involve little variation in current practice.

The level of chlorides and other impurities in the fuel, in the makeup water to the FGD system, and in the lime or limestone used, will affect the purity of the by-product gypsum. In order to obtain high-purity

gypsum, there must be an efficient particulate collection device ahead of the FGD system. Also, there should be a separate prescrubber loop to remove impurities, and/or the gypsum should be washed. A separate prescrubber loop allows the particulate collection device to be less efficient because removal of residual particulates can be accomplished in the prescrubber. However, a bleed stream from the prescrubber must be discharged to the environment. If the gypsum is washed and the FGD system is operated with a closed water loop (no discharge), then the impurities build up in the scrubbing slurry. At some point, it is necessary to blow down the system to keep these impurity concentrations within limits. Chloride is a particular problem with regard to its effect on both SO_2 removal efficiency and corrosion. In addition, permits to discharge either a prescrubber bleed stream or an FGD blowdown may be difficult to obtain in some locations.

FGD by-product gypsum can be dewatered in continuous vacuum belt filters (rotary or horizontal) or in continuous or batch centrifuges. Belt filters allow for easy washing of the gypsum but require primary dewatering in a thickener or hydroclone. Continuous centrifuges may or may not require primary dewatering. Batch centrifuges do not require primary dewatering and yield a product with the least amount of surface moisture. Further drying of the gypsum may increase its marketability because of reduced handling problems and shipping costs. However, the drying step can add significantly to the processing cost.

FGD by-product gypsum is usually the dihydrate form of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum users may prefer different chemical forms such as α or β hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) crystals, called plaster of paris, that can be produced by calcining the dihydrate. The β form can be produced only by thermal calcination and is the main raw material for wallboard. The α form, which has special uses, can be produced under less energy intensive conditions by heating gypsum in water or in a steam atmosphere. It might be possible to use the α hemihydrate to control mine subsidence.

In addition to the technical difficulties in producing gypsum of commercial interest, there is the problem of developing a dependable market and of continuing to produce an acceptable gypsum after the market is

developed. If selling the gypsum would eliminate the cost and operating problems of solid by-product disposal, the situation would be different. However, there is still the ash to dispose of, the amount of which may be approximately equal in volume to that of the sludge being produced or several times greater. Moreover, it would be necessary to provide sludge disposal facilities even if the gypsum were sold, so that power production could continue if the market failed.

All FGD processes that produce other sulfur compounds, especially elemental sulfur, hydrogen sulfide, and sulfur dioxide, could be modified to produce calcium sulfate, but such directly produced sulfur-containing compounds generally have higher commercial values than the sulfate; thus such further chemical processing is considered undesirable. Likewise calcium sulfate can be converted to sulfur, sulfide, and/or sulfur dioxide, but only by other relatively expensive additions to the already complex equipment used to recover the flue gas SO_2 values as calcium sulfate. For such reasons it is prudent to utilize the sulfur-containing product of a given control process in the form that it was designed to be produced. Such a process was originally conceived as being the most cost-effective means for producing a given by-product, and further chemical processing only increases the overall cost of the operation as well as the cost of the ultimate sulfur-containing chemical produced.

As noted previously, Chapter 4 reviews the market potential for these by-products, especially with regard to commercial opportunities in the State of Ohio.

2.6 REFERENCES

Most of the information concerning the process descriptions was obtained from proposals submitted by the proposers to the Ohio Coal Development Office, as well as from the following specific references:

- Burnet, G., et al, "A Granulation/Sintering Method for the Codisposal of Solid Residues from Coal Conversion Processes," American Chemical Society, Division of Fuel Chemistry Preprints, Vol. 33, No. 2, June 5-10, 1988, pp. 103-111.
- Landreth, R. E., Guide to the Disposal of Chemically Stabilized and Solidified Waste, USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH, Report SW-872, September, 1982a, pp. 77-87.
- Rosenberg, H.S., "Byproduct Gypsum from Flue Gas Desulfurization Processes," I&EC Product Research & Development 1986, 25, pp. 348-355.

3.0 TASK 3: BASELINE OF KNOWLEDGE
CONCERNING RESEARCH AND DEVELOPMENT NEEDS/ISSUES
PERTAINING TO THE DISPOSAL OR REUSE OF COMBUSTION BY-PRODUCTS

3.1 INTRODUCTION

The objectives of this task were to identify and evaluate baseline needs for research and development that may assist in fostering the safe reuse and/or increase the ease of disposal of clean coal technology combustion by-products. These research and development needs have been described in each of the other four tasks in this project, namely

- Task 1 on by-product characteristics
- Task 2 on clean coal technology process modification opportunities
- Task 4 on the market analysis for the reutilization of by-products
- Task 5 on regulatory requirements and considerations.

The data needs and unresolved issues are summarized below, organized by task, and are briefly listed in Table 3-1. They are presented in a format that gives a brief definition and scope of key technical issues, the development timing and general estimate of costs (in terms of person-years) to resolve these issues. This information and the associated background in each chapter can be used by OCDO to develop a detailed plan of research, development and advocacy for data-based clean coal combustion by-product disposal and reuse options.

TABLE 3-1. SUMMARY OF R&D NEEDS/ISSUES PERTAINING TO DISPOSAL OR REUSE OF OHIO CLEAN COAL COMBUSTION PRODUCTS

Task	R&D Needs/Issue
Task 1: By-Product Characteristics	<ul style="list-style-type: none"> • Site-specific characterization data • Data from metal chelate systems • Data quality and analytical methodology • By-product variability • By-product stabilization • Long-term stability
Task 2: Process Modification Opportunities	<ul style="list-style-type: none"> • Means to increase limestone reactivity • Activation of by-products for recycling • Process optimization
Task 4: Market/Reuse Potential	<ul style="list-style-type: none"> • Production of higher value by-products • Forced oxidation of calcium sulfite • Definition of parameters for synthetic gypsum production • Road aggregate • Agricultural use • Reclamation applications • Concrete products • Landfill uses
Task 5: Regulatory Evaluations	<ul style="list-style-type: none"> • Quantification of fate and effects • Reuse policy • Level of performance disposal criteria • By-product reuse legislation • Multistate symposium

3.2 TASK 1: BY-PRODUCT CHARACTERISTICS

3.2.1 Site-Specific Characterization Data

Scope and Key Technical Issues: Data on the physical, chemical, and leaching characteristics of by-products from the clean coal demonstration projects in Ohio are generally not yet developed, and those that exist were obtained primarily from bench-scale (as opposed to pilot or full-scale) experiments. The effect of variable amounts of sulfite and sulfate seems to be an especially important parameter to be studied. Also, leaching data are needed as a basis for whether by-products can be used or disposed in the environment without prior stabilization.

Some of the general by-product characteristics can probably be approximated from existing data for similar desulfurization technologies demonstrated previously, particularly those using high-sulfur bituminous, preferably Ohio coals. However, the characteristics of by-products resulting from ongoing or planned desulfurization demonstrations in Ohio, as listed in Table 1-1, will not clearly be known until site-specific data are available. Most of the individuals associated with the various projects indicated that data are either in the process of being generated or will be collected in the near future. Thus, an annual review of the updated data base for the next several years would probably be useful. This data is necessary to support the recommendation in Chapter 5 regarding determination of the environmental impact of the by-products and their associated land disposal and reuse control requirements.

Development Time and Estimated Costs (person-years): This recommendation is allied with that made in Sections 3.4.8 and 3.5.1: 1-1/2 person-years over 1 year.

3.2.2 Characterization of the By-products Produced upon Use of Chelates in Scrubbing Systems

Scope and Key Technical Issues: At present it is known that the metal chelate systems for combined NO_x/SO_x removal will produce various nitrogen-sulfur streams but of poorly defined composition and of uncertain concentrations. Both the Japanese and Germans have investigated the chelate process in the past, but commercialization has never been completed, partially because of effluent problems. Newly available data, combined with previous results, should be reexamined and perhaps supplemented with additional research in an attempt to predict the environmental impact of the by-products from the use of such technology.

Development Time and Estimated Costs (person-years): 1/4 person-year over 1/2 year.

3.2.3 Documentation of Data Quality and Methodology

Scope and Key Technical Issues: This is an extension of the need for site-specific data, Recommendation 3.2.1. Care must be taken in the reporting of analytical data to describe or at least cite the analytical methodology used. Differentiation between sulfite and sulfate or the degree of hydration of the calcium sulfate phases, for example, is not straightforward, and proper interpretation of the analytical data requires knowledge of the analytical methodology used. Also, more data are needed on the identification and composition of the solid phases, as opposed to strictly elemental data which do not identify the solid phases. These data are important because they are vital input to the assessments of reuse and/or disposal alternatives, which may be inaccurate if the analytical data are ambiguous or incomplete.

Development Time and Estimated Costs (person-years): In conjunction with Recommendation 3.2.1.; 1/2 person-year over 1 year.

3.2.4 By-product Variability as a Function of Source Coal and Process Parameters

Scope and Key Technical Issues: By-product characteristics may vary significantly as a function of coal type and/or process variables. For example, metal content varies widely from seam to seam, and this variability should be reflected at least to some extent in the composition of the desulfurization by-products as well. Process parameters such as temperature and oxygen content would be expected to have an effect on phase composition. The effects of these parameters should be determined in order to define the variability of the chemical, physical, and leaching characteristics of the resulting by-products.

Development Time and Estimated Costs (person-years): 1/2 person-year over 1/2 year.

3.2.5 By-product Stability Versus System Efficiency and the Need for By-product Stabilization

Scope and Key Technical Issues: When lime, limestone, or other sorbent is used in excess of what is necessary for sulfur removal, free sorbent will be present in the by-products. Lime is one of the chemicals that is frequently used to stabilize hazardous wastes, particularly metal-bearing wastes. Excess limestone would also tend to keep wastes from becoming acidic. Therefore, the presence of unreacted sorbent would seem to be beneficial in terms of metal leach rates, because of the somewhat alkaline environment that it creates. In other words, by-products containing free sorbent should be somewhat self-stabilizing.

This subject needs to be studied further. Critical issues are

- (a) whether metal leaching is an issue in desulfurization by-products;
- (b) whether the presence of unreacted sorbent reduces metal leaching; and
- (c) whether extremely efficient desulfurization systems are undesirable because they remove too much reagent, thus rendering the by-product less stable.

Development Time and Estimated Costs (person-years): 1 person-year over 1 year.

3.2.6 Long-Term Stability of By-products in the Environment

Scope and Key Technical Issues: In order to fulfill Chapter 5's recommendation to determine environmental impact of by-products and ascertain the proper level of land disposal protection required for these materials, regulatory authorities will most likely require a demonstration that ground-water resources will not be adversely affected by leaching of target compounds. Therefore, data on long-term stability (i.e., pertaining to the leaching behavior of by-products over a period of time in the environment) will likely be needed. The EPA has developed a test, the Multiple Extraction Procedure (SW-846 Method 1320), for assessing long-term stability. No such data were identified on clean coal combustion products in this study and should be obtained on selected by-products.

Development Time and Estimated Costs (person-years): 1/2 person-year over 1 year.

3.3 TASK 2: PROCESS MODIFICATION OPPORTUNITIES

3.3.1 Means to Increase Reagent Reactivity

Scope and Key Technical Issues: Any process that uses limestone as the sorbent for SO₂ capture, or would benefit by its use, is generally at a disadvantage from a solid waste disposal standpoint because of the low reactivity of limestone compared with that of lime or dolomite, for instance. It is now believed that very small particle-sized limestone might be sufficiently reactive to be of interest in several control processes, but this needs to be verified and a low-cost means of obtaining small particle-sized limestone is necessary. In-situ comminution in the fluidized bed process is one variant that should be considered as a long-range possibility. Methods to increase the reactivity of limestone, such as steam activation, chemical promoters, and so forth, also need to be examined.

Development Time and Estimated Costs (person-years): 4 person-years over 2 years.

3.3.2 Recycle of the By-product Solids After Suitable Activation

Scope and Key Technical Issues: Comminution of the by-products solids for duct-injection systems has been found by researchers at the University of Lund to have potential for higher utilization upon recycle, and steam activation has been studied at the University of Graz and found to also impart improved reactivity to the by-products solids upon furnace reinjection. The variables involved in these treatments need to be defined and experiments carried out with Ohio coals and sorbents to determine the cost-effectiveness of such activation treatments.

Development Time and Estimated Costs (person-years): 3 person-years over 2 years.

3.3.3 Process Optimization

Scope and Key Technical Issues: To design a system that can effectively minimize waste production, more detailed descriptions of each process are needed from the various developers and manufacturers. For example, an effort was made in this study to determine ways of minimizing reagents used in the various clean coal combustion processes. Insufficient process information made these calculations difficult. Future work should focus on developing more detailed process information so that process modifications could be made to minimize reagent usage, if possible, given the current degree of uncertainty regarding the efficiency of demonstration systems relative to tradeoffs in investment costs; also, more information is need on the unknowns, such as the amount of environmental stability provided by sorbent in the by-product (Recommendation 3.2.5, above).

Development Time and Estimated Costs (person-years): 2 person-years over 1 year.

3.4 TASK 4: BY-PRODUCT REUSE POTENTIAL

3.4.1 Processes to Produce High Value By-products

Scope and Key Technical Issues: Gypsum, sometimes mixed with calcium sulfite and sometimes mixed with fly ash, is produced by most of the advanced and existing clean coal combustion technologies that could be used in Ohio. Although large-volume, low-value uses such as in road base may avoid the cost of disposal, it is desirable to find a method for converting sulfur-bearing calcium compounds into higher value products. One possible option is to convert the material to sulfuric acid or sulfur for sale, and lime for recycle to scrubber units.

Sulfuric acid is used widely and in large volume but is hard to store and expensive to ship; sulfur, on the other hand, can be easily stored and shipped. Sulfuric acid is quite corrosive; sulfur can burn. Either is a useful and valuable product, but in the absence of a nearby customer, sulfur would be more desirable. If an acid user is nearby, sulfuric acid would be attractive.

Processes to produce sulfuric acid and road aggregate are known. The Davy McKee Company has started up a demonstration unit in Louisiana. However, lime for reuse in scrubbers might be of more value to Ohio utility companies. There are proprietary efforts in industry to develop new processes for producing both higher value calcium products and higher value sulfur products, but none is commercial. These represents a possible research opportunity for OCDO.

Development Time and Estimated Costs (person-years): Proof of concept: 2 person-years over 2 years.

3.4.2 Forced Oxidation of Calcium Sulfite in Chelated Systems

Scope and Key Technical Issues: Calcium sulfite, the first product formed in scrubbing flue gas with lime or limestone, can be converted to calcium

sulfate dihydrate (gypsum), which is a useful product. The specifications require nearly pure calcium sulfate with only small amounts of calcium sulfite and small amounts of fly ash present. Thus, to utilize the calcium salts in scrubber sludge it is necessary to convert as much of the calcium sulfite as possible to calcium sulfate.

In some processes the oxidation (termed "forced oxidation" to distinguish it from the small amount of oxidation that occurs under normal conditions) can be done in the scrubbing system itself. However, the only process under consideration in this study that yields calcium salts not contaminated by large amounts of fly ash may involve chelated-lime scrubbing. This process requires that the level of sulfite be kept high. Therefore to produce gypsum of high quality, a postscrubbing forced-oxidation step must be used. Several postscrubbing processes have been developed, but how well they would work with the chelated lime scrubbing process is unknown. Research to find and perfect a postscrubbing forced-oxidation process optimized to the chelated lime process might make the economics of that scrubbing process more attractive.

Development Time and Estimated Costs (person-years): 2 person-years over 1-1/2 years.

3.4.3 Definition of the Parameters Associated with Synthetic Gypsum Production for Wallboard Manufacture

Scope and Key Technical Issues: Although wallboard production is a major potential outlet for FGD by-products produced by the more conventional scrubbing processes, it is also an industry that has developed more on art than on first principles. It is therefore very difficult to predict the properties of synthetic gypsum that would be either desirable or detrimental for use in established wallboard processing operations. Such variables as chloride content, crystal morphology, sulfite levels, ash contamination, and use of additives, are at best poorly defined, and usually have an essentially unknown effect on the synthetic gypsum. Significant bench-scale research is needed to study how these variables affect set time, water

retention, paper bonding, board strength, and density of the products manufactured from synthetic sources of gypsum.

Development Time and Estimated Costs (person-years): 1-1/2 person-years for preliminary research over 1 year; 1-1/2 person-years for production trials over 1 year.

3.4.4 Road Aggregate

Scope and Key Technical Issues: Fly ash mixed with a variety of calcium salts is the principal by-product from several of the clean coal technologies under consideration, for example, HALT, LIMB, and PFBC. Some evaluation of the products as gravel for road beds has been done, but data are limited and generalizations cannot be made. Data with by-products from Ohio coals are believed to be non-existent. Research that provided head-to-head comparisons of the various products would be helpful in gaining the acceptance of private users and in qualifying products for public use. Such research, in conjunction with the characterization and environmental impact studies recommended under Chapter 1, would also provide the basis for advocating regulatory change to promote the beneficial reuse of the by-products, as recommended in Chapter 5.

Development Time and Estimated Costs (person-years): 5 person-years over 3 years.

3.4.5 Agricultural Use

Scope and Key Technical Issues: Lime, limestone, and gypsum have proven useful as soil-neutralizing and soil-stabilizing material. Fly ash can add valuable trace elements for growing crops. Because the by-products of the clean coal processes have combinations of lime, limestone, gypsum, and fly ash, agricultural utility is likely in areas that have certain nutrient deficiencies. Research or demonstrations in multiple counties reflecting the diversity of soil types and crops grown in Ohio would help to gain acceptance

of these materials by farmers. The demonstrations should use the material from all the candidate processes and should involve the Agricultural Extension Service, because many farmers turn to their County Agent as their primary source of information. Some of this data may be covered in recent proposals to OCDO by Ohio State University and the U.S. Geological Survey.

Development Time and Estimated Costs (person-years): 10-15 person years over 5 years (could be phased by region).

3.4.6 Reclamation Applications

Scope and Key Technical Issues: Currently, at least one utility in the State has developed a wetlands restoration system consisting of a clay lining and a nutrient system of earth, fly ash, lime, and perhaps scrubber by-products, to permit the growth of a natural ecosystem that detoxifies acid mine drainage. The by-products from injection processes, because of low conversion levels and high levels of lime, might conceivably be suitable for such applications.

Development Time and Estimated Costs (person-years): 2 person-years over 2 years.

3.4.7 Concrete Products

Scope and Key Technical Issues: Because most of the processes under study by the State produce solid by-products that contain excesses of alkalinity, they may be especially suitable for use in the manufacture of cement-type products. The fly ash content of many of these by-products is also not necessarily a detriment, as ash frequently contains compounds with pozzolanic activity useful for concrete manufacture. Outlets for the concrete so produced might be in roadway bases, asphalt aggregate, block and bricks, and in underground coal-mine operations (i.e., pillars, rail ties, etc.). Much work has been done in this area using plain fly ash, thus the methodology for the research and the test methods to be used are well worked out. The properties needing investigation include strength development rate, ultimate

strength, and mechanical properties such as freeze-thaw resistance and effect on air entrainment. A major effort in this regard is recommended since users will need to be persuaded to abandon currently successful systems.

Development Time and Estimated Costs (person-years): 4-1/2 person-years over 3 years.

3.4.8 Landfill Uses

Scope and Key Technical Issues: Clean coal combustion by-products have been investigated as liners and caps for ash pits. Further work, sponsored jointly with the Ohio Environmental Protection Agency (OEPA) if possible, would help to gain acceptance of these materials for these applications, as well as in waste landfills, and perhaps in hazardous waste landfills. A permeability of no more than 10^{-7} cm/sec is desirable for liners. Admixtures of one residue with cement come close to the desired value. More detailed research to evaluate this application of using by-product and admixtures with by-products is desirable, if not for its economic benefit, then because success would allow companies to reuse the by-products in their own operations. This recommendation should be considered concurrently with Sections 3.1, 3.2, and 3.5 recommendations.

Development Time and Estimated Costs (person-years): 1 person-year for preliminary research and 2 person-years for demonstration and cooperation of a power company over 3 years.

3.5 TASK 5: REGULATIONS ON CLEAN COAL COMBUSTION BY-PRODUCTS

3.5.1 Quantification of Fate and Effect of By-products in the Environment

Scope and Key Technical Issues: Develop a specific data base for decision making. Sponsor in-field research of coal combustion by-products generated from Ohio coals (a) to better understand and quantify the leach rate, fate and transport of sulfates, and trace metals; and (b) to demonstrate the level of protection necessary to build public acceptance of disposal at land-based facilities.

Development Time and Estimated Costs (person-years): This recommendation ties in directly with those made in Sections 3.1, 3.2, and 3.4: 10 person-years over 3 years.

3.5.2 Encourage Reuse Policy

Scope and Key Technical Issues: Sponsor environmental impact studies of by-product applications described in the recommendations of Chapter 4. This impact data will provide a rational base from which to evaluate reuse options and encourage policy analysis by the State of existing regulations that impede or do not facilitate adoption of such options.

Development Time and Estimated Costs (person-years): 3 person-years over 1-1/2 years.

3.5.3 Develop Level of Performance Disposal Criteria

Scope and Key Technical Issues: Develop a permit for placement of low toxicity by-products that includes location criteria and level of performance measures to meet existing water quality standards. Promote the environmentally acceptable placement of this material in such locations as road

embankments, structural fills, mine backfill, and road bases. This recommendation complements those of Chapters 1 and 4.

Development Time and Estimated Costs (person-years): Recommended for OEPA: 5 person-years over 2 years.

3.5.4 Encourage By-Product Reuse Legislation

Scope and Key Technical Issues: Encourage enactment of legislation or regulatory change to facilitate options for greater incentives for reuse and recycling of coal combustion by-products.

Development Time and Estimated Costs (person-years): 1 person-year over 2 years.

3.5.5 Sponsor Multistate Symposium

Scope and Key Technical Issues: The State should sponsor a multistate symposium of representatives from midwestern coal-producing states and generators to address common regional issues and to focus on individual differences in each State's approach to reuse/disposal problems. Proceedings should be published for use as information in other research/recommended action areas.

Development Time and Estimated Costs (person-years): 1/2 person-year over 9 months.

4.0 TASK 4: BASELINE OF KNOWLEDGE CONCERNING THE MARKET POTENTIAL FOR RECOVERABLE COMBUSTION BY-PRODUCTS

4.1 SUMMARY

The disposal of by-products from clean coal combustion and scrubbing processes not only can impose an additional burden on the environment but also can add to the overall cost of the combustion process. This task looks at the possibility of utilizing the by-products directly as useful products or indirectly as raw materials for making such products. The analysis was confined to the by-products of the processes funded by the OCDO and considers the unique chemistry of each. In accordance with the scope of this study, by-products of precombustion cleaning processes and conventional fly ash were not considered.

A list of potential markets was developed and these markets were screened for technical fit with the chemistry of the processes being considered and the size of the market relative to the production expected from an 800-MW generating unit. For those markets passing this original screening, and the several that were added during the investigation that were attractive, a subsequent market study was done which considered demand, supply, pricing, and other relevant factors.

Most potential markets of reasonable size are currently supplied by low cost materials of acceptable purity. Some of the material are by-products of other processes, such as fly ash, refinery produced sulfur, and smelter produced sulfuric acid. Mined gypsum and limestone also are available at low costs. This will make market penetration using clean coal combustion by-products difficult except at a low price, comparatively. However, a number of markets appear attractive; these are sulfur, sulfuric acid, gypsum, agricultural liming, and road base material. The fit with individual processes is shown in Table 4-1. In order of decreasing market size, these uses are as follows:

- Scrubber sludge, from processes that generate calcium salts, can be mixed with fly ash for road base. This use can

TABLE 4-1. MATCH BETWEEN PROCESSES AND USES

Uses	PFBC	LIMB	HALT	Coolside	NOXSO	Columbia Gas	E-SO _x	Chelated Lime Process	TRW Slagging Combustor
Sulfur					Good Direct	Good Direct			
Sulfuric Acid					Good Direct	Good Direct			
Gypsum								Good Indirect	
Ammonium					Some Indirect	Some Indirect			
Alum					Poor Direct	Poor Direct			
FeSO ₄					Poor Indirect	Poor Indirect			
Road Building	Good Direct	Good Direct	Good Direct	Good Direct			Good Direct	Some Indirect	Good Direct
Agriculture	Good Direct	Good Direct	Good Direct	Good Direct			Moderate Direct	Poor Direct	Good Direct

utilize all of the potential output from Ohio power plants but competes with local limestone priced at \$3.50/ton FOB the mine.

- Agricultural use can command a price 2/3 that of limestone and could use half of the potential output from Ohio.
- Gypsum use for non-fly ash by-products is smaller than the preceding market size, but the FOB mine price is about \$7/ton.
- Sulfur or sulfuric acid, from processes that do not produce a sludge, has modest markets locally but could compete in the big Florida market if the price was low enough.

4.1.1 Sulfur and Sulfuric Acid

The sulfur and sulfuric acid markets in Ohio are really the same market and would be satisfied by a plant having about 1,000 MW of capacity and operating half the hours of the year. Sulfur production would have the advantage of easy storage and shipment. It would be competing with out-of-state sulfur. Sulfuric acid production would compete with established plants located in Ohio and on the Ohio River in Kentucky. Large amounts of Ohio produced sulfur or sulfuric acid could compete in the big Florida fertilizer market if the price were low enough to compete with by-product sulfur from Alberta and Wyoming.

4.1.2 Gypsum

As many as four 800-MW generating units producing gypsum by the chelated lime process followed by forced oxidation can be supported by the market in Ohio. The market would be almost entirely for wallboard. Production would compete with a mine in Ohio and mines in Michigan and Indiana. The average 1988 price for the U.S. was \$7.00/ton FOB the mine.

4.1.3 Agricultural Lime

Agricultural liming uses in Ohio could account for about half of the maximum potential by-product production if flue gases from all of the

coal burned in Ohio were scrubbed by those processes that yield residue with excess lime or limestone. Five of the processes yield by-product that could be used for liming soil and could command a price (before transportation) of as much as two-thirds that of ground limestone, or about \$2.70 per ton.

4.1.4 Road Base

The by-product material probably will be suitable for road base and fill but not for surfacing unpaved roads or for use as aggregate in concrete or asphalt paving. Road base and fill use of crushed rock and gravel are estimated to be about 16 million tons per year, roughly equal to the 14 million tons of by-product that would be produced if all Ohio power plants used calcium-based processes that include fly ash in the by-product. This is a good fit with the potential market, but the by-product will have to compete with limestone at about \$3.50 per ton.

4.2 INTRODUCTION

As indicated throughout this baseline study, the various clean coal combustion and flue gas cleaning processes being funded by OCDO frequently create significant quantities of solid or liquid by-products. The disposal of these by-products is not only a significant challenge to the producers, but can also add to the overall cost of the clean coal combustion process.

Tasks 1 and 2 of this study provided the available, but limited baseline of knowledge on clean coal combustion by-product characteristics, some research suggestions regarding by-product minimization and details on alternative demonstration processes, and methods for the stabilization of solid by-products in disposal sites. This task looks at the possibility of utilizing the by-products either directly as useful products or indirectly as raw material for making such products.

4.2.1 Scope

The by-products under study are related to the OCDO's research on clean coal combustion, such as pressurized fluidized bed combustion, or new flue gas cleaning technologies. New approaches to cleaning of the coal prior to combustion, such as biological pretreatment, are not part of the scope of this study. Likewise, uses for traditional fly ash and bottom ash from coal combustion are not covered, except where there is direct competition with the by-products from clean coal combustion technologies. The fly and bottom ash are already utilized to some extent, and there are many research and development projects underway aimed at new uses.

The processes included in this study are

- Pressurized Fluid Bed Combustion (PFBC)
- Limestone Injection Multistage Burner (LIMB)
- [Lime] Hydrate Addition as Low Temperature (HALT)
- Coolside
- NOXSO
- Columbia Gas Catalytic Reduction

- ESO_x
- Chelated Lime Scrubbing
- TRW Slagging Combustor.

These processes were described in Chapter 2.

4.2.2 Approach

A variety of chemicals and materials potentially can be produced from the by-products of clean coal combustion processes. The first goal in by-product utilization is the production of a high volume, high value product but, unfortunately, such products are hard to find. When one plots the logarithm of the price of chemicals or minerals per unit versus the logarithm of the annual volume, a downward sloping, more-or-less straight line is obtained (Schuman, 1960; Lund, 1969; Sheppard and Lopinsky, 1977; Gilman, 1987). In other words, the reality of the marketplace is that only a modest price can be expected when dealing with a large volume by-product.

A second goal in utilizing by-products is to match the amount that might be produced by Ohio power plants with the likely total consumption within a reasonable shipping radius. For example, using a coal with 12,500 Btu, 3.5 percent sulfur, and 90 percent recovery at a heat rate of 10,000 Btu/kWh, an 800-MW generating unit operating half the hours of the year would yield 44,000 short tons of elemental sulfur.* If the markets for a particular derivative of sulfur are much smaller than this amount, it is not considered attractive. The amount of by-product from a single 800-MW generating unit under standard conditions is used throughout the initial screening in judging whether there is a good match between potential production and the market size.

 * Note: Sulfur statistics are usually given in long tons, 2,240 pounds, or in metric tons, 2,205 pounds; however, in this report all data reported as tons will be short tons, 2,000 pounds. These conditions plus the specification of 15 percent ash will be referred to in this text as "standard conditions" for the sake of conciseness.

In the analysis that follows, the current prices of chemicals and materials are cited as benchmarks. If huge amounts of material were priced very low, local markets for the material would be captured, export markets could be developed, and new uses could be developed. The ultimate limit might be the cost of transportation. In fact, because there is a disposal cost for the clean coal combustion by-products, it is conceivable that the generator would be willing to pay a subsidy to the user, reducing the delivered price to less than the cost of transportation while also reducing the cost of any remaining by-product disposal. This study has looked at current price and demand and has not addressed the question of elasticity of demand, since the investigation was designed to see where, given typical sales arrangements, there is a potential fit. The concept and analysis of subsidies is a topic for a separate study.

4.2.2.1 Initial Screening

Before examining the properties of clean coal combustion technology by-products, a list of potential products was drawn up for initial screening. These were

- sulfur
- sulfuric acid
- gypsum
- ammonium sulfate
- alum
- sulfur dioxide
- ferrous sulfate.

An initial screening of this list was conducted by estimating the market sizes in Ohio and yields from a typical plant to see if further investigation was justified. A literature search aimed at reviewing what has been done to utilize by-products was also conducted.

4.2.2.2 Final Analysis

The by-products that fit well with the market size and other economic factors were subjected to more intensive study. The present and future market sizes were estimated, transportation costs were estimated, and the potential for competition with existing suppliers and potential suppliers using clean coal combustion technology in nearby states was assessed. Some new opportunities not included in the initial list were identified and explored. Finally, telephone interviews with current producers, potential future consumers, and government agencies were conducted.

4.3 INITIAL SCREENING

Table 4-2 lists the clean coal combustion processes considered, the type of by-products produced, their typical composition, and yield. The composition and percent distribution of the products were based on data from Tasks 1 and 2 and judgments as to the chemistry involved. (Available data were limited on the physical and chemical characteristics of by-products from clean coal demonstration projects in Ohio. See recommendations in Section 3.2.) The percent distribution is based on total by-product produced. Where fly ash is obtained separately, it is not included in the total. The calcium oxide equivalent, which is used in evaluating the agricultural liming power, is calculated from the limestone, hydrated lime, quicklime, and magnesium oxide in the by-product. Two of the processes, the NOXSO and Columbia Gas processes, are expected to yield sulfur or sulfuric acid that is free of impurities. The chelated lime process yields calcium sulfur compounds that can be converted to gypsum by straightforward processes. The other processes all yield calcium salts mixed with varying amounts of fly ash.

4.3.1 Sulfur

Sulfur can be produced from the products of both the NOXSO process and the Columbia Gas catalytic reduction process. Both of these processes produce hydrogen sulfide gas and the NOXSO process also produces sulfur dioxide gas in a separate stream. Existing technology can easily convert the gas stream(s) to elemental sulfur as long as the molecular ratio of hydrogen sulfide to sulfur dioxide is 2:1 or more. The purity of the sulfur produced is not reported, but by analogy with sulfur recovery at petroleum refineries and natural gas processing plants, it should be at least standard acid-making grade, which constitutes more than 90 percent of the market.

One 800-MW generating unit under standard conditions would, as specified above, yield 44,000 tons per year of sulfur. The sulfur consumed in sulfuric acid plants in Ohio, if operated at nameplate capacity, is on the order of 112,000 tons per year (SRI International, 1988). In addition,

TABLE 4-2. TYPICAL BY-PRODUCT YIELDS BASED ON 15.0 PERCENT ASH, 3.5 PERCENT SULFUR
AND 12,500 BTU/LB COAL

Process	Process Type	By-Product Type	Chemical Nature	Tons per Ton of Coal	Percent Distribution
Pressurized Fluid Bed Combustion	Fluid Bed Dolomite	Ash plus spent sorbent (Fly ash and bottom ash)	Aluminosilicates and iron oxides	0.128	36.12
			MgO	0.056	15.83
			CaSO ₄	0.114	32.24
			CaCO ₃	0.044	12.47
			CaO	0.012	3.34
			Total	0.353	100.00
			CaO equivalents	0.114	32.32
LIMB	Dry Injection Limestone	Fly Ash plus spent sorbent	Aluminosilicates plus iron oxides	0.120	41.96
			CaSO ₃	0.052	18.26
			CaSO ₄	0.022	7.65
			CaO	0.092	32.13
			Total	0.286	100.00
			CaO equivalents	0.092	32.13
HALT	Dry Injection Lime (hydrated) Water spray	Fly Ash plus spent sorbent	Aluminosilicates plus iron oxides	0.120	30.28
			Ca(OH) ₂	0.121	30.64
			CaSO ₄ · $\frac{1}{2}$ H ₂ O	0.021	5.20
			CaSO ₃ · $\frac{1}{2}$ H ₂ O	0.052	13.18
			CaCO ₃	0.082	20.70
			Total	0.396	100.00
			CaO equivalents	0.138	34.78

TABLE 4-2. TYPICAL BY-PRODUCT YIELDS BASED ON 15.0 PERCENT ASH, 3.5 PERCENT SULFUR
AND 12,500 BTU/LB COAL (Continued)

Process	Process Type	By-Product Type	Chemical Nature	Tons per Ton of Coal	Percent Distribution
Coolside	Dry Injection Lime NaOH or Na ₂ CO ₃ Water after collection	Fly Ash plus spent sorbent	Aluminosilicates plus iron oxides	0.120	29.66
			Ca(OH) ₂	0.121	30.01
			CaSO ₄ ·2H ₂ O	0.021	5.09
			CaSO ₃ ·½H ₂ O	0.052	12.91
			CaCO ₃	0.082	20.28
			Sodium salts	0.008	2.05
			Total	0.405	100.00
			CaO equivalents	0.138	34.07
NOXSO	Dry Na Aluminate Spent sorbent	Sulfur Compounds	SO ₂ H ₂ S	0.032 Sulfur equivalents	100.00
			Elemental Sulfur	0.032	100.00
Columbia Gas (Parsons)	Dry Catalytic	Sulfur			
E-SOx	Dry, Injection of Hydrated Slurry	Fly Ash plus spent sorbent	Aluminosilicates plus iron oxides	0.120	50.82
			CaSO ₃ ·½H ₂ O	0.021	8.73
			CaSO ₄ ·½H ₂ O	0.032	13.71
			Ca(OH) ₂	0.011	4.63
			CaCO ₃	0.236	100.00
			Total CaO equivalents	0.031	12.97

TABLE 4-2. TYPICAL BY-PRODUCT YIELDS BASED ON 15.0 PERCENT ASH, 3.5 PERCENT SULFUR
AND 12,500 BTU/LB COAL (Continued)

Process	Process Type	By-Product Type	Chemical Nature	Tons per Ton of Coal	Percent Distribution
Chelated Lime Process	Wet Scrubber Chelate plus Lime	Calcium salts	$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	0.109	78.56
			$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.023	16.80
			$\text{Ca}(\text{OH})_2$	0.004	2.91
			CaCO_3	0.002	1.73
			Total	0.139	100.00
			CaO equivalents	0.004	3.17
TRW Slagging Combustor	Injection of Limestone into Combustor	Fly ash plus spent sorbent	Aluminosilicates plus iron oxides	0.030	11.72
			$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	0.052	20.40
			$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	0.021	8.05
			$\text{Ca}(\text{OH})_2$	0.153	59.83
			Total	0.256	100.00
			CaO equivalents	0.116	45.27

other uses, such as rubber compounding, consume higher grade sulfur. Thus the potential output meets the market-size criterion. Therefore sulfur passes the initial screening.

4.3.2 Sulfuric Acid

Sulfuric acid is not yielded directly by any of the clean coal combustion processes but can easily be made from sulfur or sulfur dioxide by widely used commercial processes. In addition, calcium sulfate and sulfite, which are produced by the lime- and limestone-based processes, can be used as raw material for production of sulfur by known processes, although the economics of these processes have not been demonstrated in the U.S. (McGinty, 1987).

An 800-MW generating unit under standard conditions would produce about 135,000 tons of sulfuric acid per year. Ignoring acid sludge processing, which merely recycles spent sulfuric acid, the capacity for making sulfuric acid in Ohio is about 330,000 tons per year (SRI International, 1988). Therefore sulfuric acid passes the initial screening.

4.3.3 Gypsum

None of the proposed clean coal combustion processes yields gypsum (calcium sulfate dihydrate) in pure form. However, the wet lime process yields mixed gypsum and calcium sulfite hemihydrate, which can be upgraded to nearly pure gypsum by using forced oxidation which is a well-developed process. Excess lime or limestone can be converted to gypsum by adding sulfuric acid. The other calcium-based processes yield material containing large amounts of fly ash and are not suitable for existing applications for gypsum.

An 800-MW generating plant using a chelated lime process and a unit using forced oxidation of the collected residue would yield about 240,000 tons per year of gypsum. U.S. consumption in 1988 has been estimated as 25 million tons (Davis, 1989). Because the principal uses are for making wallboard and as a cement additive, usage is distributed roughly according to population. Assuming gypsum use is distributed on per capita basis,

1,100,000 tons is consumed in Ohio. Therefore gypsum passes the initial screening.

4.3.4 Ammonium Sulfate

Some processes use ammonia as part of the scrubbing process and can yield ammonium sulfate, a useful fertilizer. However, none of the Ohio clean coal combustion processes now under support use ammonia. Ammonium sulfate could be made by adding ammonia to the sulfuric acid that is made directly or indirectly from those processes, but there is little economic advantage to doing so.

The ammonium sulfate made from the sulfur obtained from an 800-MW generating unit would amount to 180,000 tons per year. Total U.S. consumption is on the order of 2.2 million tons per year, obtained almost entirely as a by-product of making caprolactam and scrubbing coke oven off-gases (SRI International, 1988). There is sufficient demand, if the price is low enough, to support the production of ammonium sulfate, but because its current price is at a level that just barely permits disposal of by-product ammonium sulfate, there is no economic incentive to make it on purpose. Small amounts produced by scrubbing ammonia fumes can be considered a downstream market for sulfuric acid. Therefore ammonium sulfate fails the initial screening.

4.3.5 Alum

Alum, or aluminum sulfate, is commonly used in paper sizing and potable and wastewater treatment. (Strictly speaking, the term alum refers to hydrated aluminum potassium sulfate; however, common commercial usage of the word denotes aluminum sulfate with 18 waters of hydration, which is the usage adopted here.) Commercially, alum is made by treating bauxite, clay, or hydrated alumina with sulfuric acid followed by purification. None of the Ohio clean coal combustion processes generate alum directly; however, it might be made by digestion of fly ash-containing residues with sulfuric acid, followed by extensive clean up. Making it from fly ash or fly ash-containing residues would be much more complex and expensive than treating clay because the iron found in the high-sulfur coals would make the clean up especially

difficult. Alum made by digestion of fly ash with sulfuric acid produced from the by-products of the NOXSO or Columbia Gas processes would be a downstream use of sulfuric acid.

Alum produced using the sulfur from an 800-MW generating unit would amount to about 300,000 tons per year. The U.S. production of alum is about 1.4 million tons from 88 plants, 6 of which are in Ohio (SRI International, 1988). A single dedicated plant of the size indicated would produce too much for local consumption. Therefore, alum fails the initial screening.

4.3.6 Sulfur Dioxide

Sulfur dioxide is the pollutant produced directly in the burning of high sulfur coal, however, none of the Ohio clean coal combustion processes trap sulfur dioxide as such. It can be made easily by the burning of sulfur in air, and, in fact, this is the first step in the commercial conversion of sulfur to sulfuric acid. In principle, sulfur dioxide could be released from sulfite-containing sludges by acidification with sulfuric acid, but this approach is not economically feasible.

The use of sulfur dioxide both directly and in making nonsulfuric acid derivatives is small. U.S. commercial demand for sulfur dioxide, all shipped as a liquid, is about 180,000 tons per year. Capacity is about 262,000 tons, 13,000 of which is in Ohio (SRI International, 1988). An 800 MW generating unit would produce sulfur sufficient to make 88,000 tons of sulfur dioxide, more than could be used in Ohio or adjacent states. Therefore, sulfur dioxide fails the initial screening. However, its use as an intermediate in sulfuric acid production should be borne in mind.

4.3.7 Ferrous Sulfate

Ferrous sulfate, a useful animal feed supplement, water treatment chemical, and soil amendment, is usually made by the reaction between sulfuric acid and either iron metal or ferrous compounds. The traditional sources have been spent pickle liquor, the result of removing scale from steel with sulfuric acid, and the sulfate process for making titanium dioxide, which yields ferrous sulfate as a by-product. None of the Ohio clean coal combustion processes yield ferrous sulfate directly; however, it

could be made using sulfuric acid produced as a by-product. Since the iron in the fly ash and fly ash-containing residues is not entirely in the ferrous state, digestion of these materials with sulfuric acid would not be an economically reasonable approach. Pickle liquor use or digestion of ferrous scrap would be technically feasible, but steel pickling is being switched to hydrochloric acid, which is recyclable, and the treatment of scrap is too expensive.

The sulfuric acid from an 800-MW generating unit would be equivalent to 380,000 tons of ferrous sulfate heptahydrate, the usual commercial form. Total U.S. production is about 250,000 tons, with large additional amounts of material imported (Anonymous, 1988c). Although supplies in early 1989 are reported to be tight, more domestic plants are being constructed. A dedicated plant based on the output of an 800-MW generating unit is too large for the markets in Ohio or adjacent regions. Therefore, ferrous sulfate fails the initial screening.

4.3.8 Other Opportunities

In the course of the literature search on opportunities to utilize by-products, two large volume uses that are potentially viable were uncovered. These are road building base material and similar construction uses and use as an agricultural soil amendment. These uses will be covered in the detailed analysis sections that follow. Other uses that were uncovered but which failed to meet either the volume or technical specifications were portland cement making, ash pit linings and covers, and as an aggregate for concrete or asphalt. In some of these markets, coal ash, especially fly ash, is well established. Because clean coal combustion by-products are likely to be less homogeneous from plant-to-plant and over time, they would have trouble competing even at low or zero cost. Further research in this area, however, might still be warranted.

4.4 POTENTIAL OPPORTUNITIES

The attractive opportunities are sulfur, sulfuric acid, gypsum, construction uses, and agricultural uses. Each of these is described below.

4.4.1 Sulfur

4.4.1.1 Demand

Sulfur is used in the following manner: making sulfuric acid (80 percent), exports (12 percent), agriculture (4 percent), and other uses (4 percent) (Anonymous, 1988e; Mansville, 1985). The miscellaneous use category includes vulcanizing rubber, supplementing recycled kraft pulping chemicals, and making chemicals such as carbon disulfide. Demand for sulfur in all categories was estimated to be about 13.9 million tons in 1988.

Sulfuric acid manufacture is described in detail in the following section of this chapter; it is important to note that the chief use of the acid is for making fertilizer, done mostly in Florida.

Sulfur is used in agriculture as a nutrient for sulfur-deficient soils and as an agent to neutralize soils that are too alkaline. Agricultural usage is not an important factor in Ohio.

Of the chemical uses, making carbon disulfide is probably the most important. Carbon disulfide is used primarily for making carbon tetrachloride, rayon, cellophane, rubber processing chemicals, and pesticides. Demand in 1988 was about 200,000 tons of carbon disulfide, requiring a net 168,000 tons of sulfur. There are no plants in Ohio making carbon disulfide, but one of the four U.S. plants is in New Martinsville, West Virginia. It has a capacity of 30,000 tons per year, out of a national total of 350,000 tons. The principal uses for carbon disulfide are declining nationally, but Ohio sulfur producers would be well located to supply the West Virginia plant. However, the decline in carbon disulfide usage is due to a shift in its markets and probably would not be stopped by a decrease in sulfur prices.

As discussed in Section 4.3.1, sulfur can be made into sulfur dioxide, which is then used in making other sulfur chemicals and in pulp and paper, corn wet milling, metal ore refining, and oil refining operations.

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Municipal wastewater treatment is a growing market for sulfur dioxide. U.S. sulfur dioxide production in 1988 was 180,000 tons, which represents a 90,000 ton-per-year market for sulfur.

Vulcanized rubber contains roughly 3 percent sulfur, although hard rubber products contain considerably more. Rubber products are still important in the economy of Ohio although not nearly as important as in the past. A special, finely divided grade of sulfur is used for rubber compounding. It is not clear whether sulfur from the NOXSO and Columbia Gas processes is suitable for this application.

4.4.1.2 Supply

Sulfur is obtained from three principal sources: Frasch mines, by-product recovery from natural gas processing, and by-product recovery from petroleum refining. A plant designed to obtain sulfur from gypsum was constructed in Texas during the 1960s but never operated; however, similar plants are operating in Austria and South Africa.

Frasch Mining. The Frasch process involves injecting superheated steam into underground sulfur domes, which melts the sulfur and brings it to the surface. The economics of a Frasch mine are highly dependent on energy (natural gas) prices. In recent years, as gas prices have risen and by-product recovery has increased, many Frasch mines have been shut down. Part of the decline is due to the exhaustion of existing reserves, but Freeport-McMoRan reports finding a new 55 million-ton deposit off the Louisiana coast (Anonymous, 1989d). Frasch mines now account for about one-third of domestic sulfur production. The mines, located onshore and offshore of the Louisiana and Texas coasts, are well situated for transporting their product to Florida and export markets. Since by-product sulfur production is beyond the control of the producer and most producers ship the product as soon as produced, the Frasch mines act as discretionary sources, increasing or decreasing production as the market demand requires.

Petroleum Refining. Crude oil contains varying amounts of sulfur, which must be greatly reduced in the production of refined products. The only markets left for high sulfur products are residual oil for ships' bunker

fuel and petroleum coke for export; these markets are limited. In a petroleum refinery, sulfur is recovered from various processes as hydrogen sulfide and then converted to elemental sulfur. There are four refineries in Ohio that have a sulfur-producing capacity of about 120,000 tons per year; production in 1987 was 46,000 tons (Morse, 1988). These refineries and their respective capacities are as follows:

- Ashland, Canton, 40,000 tons
- BP America, Lima, 14,000 tons
- BP America, Toledo, 47,000 tons
- Sun, Toledo, 20,000 tons.

The capacity in Detroit (Marathon) and Catlettsburg, Kentucky (Ashland) is an additional 110,000 tons per year (SRI International, 1988). These refineries have a high rate of capacity because they were engineered to be able to use much higher sulfur crude than they are using now. In the future, a higher sulfur content in crude oil is expected as the supplies of light, sweet crudes are used up. In addition, there is a redundancy of sulfur units so that the whole plant is not shut down if a unit is taken out of commission for repair. A typical refinery might have three sulfur units, each capable of handling 50 percent of the maximum potential sulfur output.

Natural Gas Processing. Natural gas can contain hydrogen sulfide in amounts ranging from a fraction of a percent to more than 75 percent of the total. To avoid corrosion of the gas transmission and distribution system, the sour gas is scrubbed with an amine solution to reduce the sulfur content to acceptable levels. The hydrogen sulfide is stripped from the scrubbing solution and processed in a recovery plant, which yields elemental sulfur. Large amounts of by-product sulfur is produced from gas wells in the Gulf Coast states, Wyoming, and Alberta, Canada. Although markets in Alberta are limited, producers there have elected to store their excess production rather than dump it on the market. At one time supplies there equaled one year's consumption in the U.S., which is about 14 million tons.

4.4.1.3 Pricing

The price of sulfur is controlled by the fact that there is one large dominant market, located in central Florida, and a huge supply

available in Alberta, Canada. Transportation costs from Alberta to Florida determine the cost at all intermediate points. The prices published for May 5, 1989 (Anonymous, 1989b) show the following (mined sulfur commands a premium over recovered sulfur, partly because production rates and quality can be more closely controlled by the producer):

- Tampa, \$128 per ton
- Port Sulphur, LA, \$106 per ton (mined)
- New Orleans, \$97 to \$105 per ton (recovered)
- Alberta, \$54 to \$58 per ton.

The price reported for Louisiana by the Bureau of Mines for 1987 was \$87 per ton; for Ohio it was \$83 per ton, with most production being in the Toledo area. The local price is related to bringing competing material from Alberta. If a large excess were produced and shipped out of state, it would compete with Alberta sulfur at intermediate points along the way to Florida. Barge shipment of (molten) sulfur is roughly half the cost of shipment by rail per ton mile. An Ohio shipper barging sulfur to Florida would be at a disadvantage relative to a producer in Louisiana and probably would have to accept a FOB price of roughly \$95 per ton rather than about the \$120 per ton obtainable in local Ohio markets, assuming the Louisiana producer did not fight back by lowering prices.

4.4.1.4 Outlook

Using 90 percent of the capacity of sulfuric acid plants in Ohio as a proxy for the market size in Ohio, estimated demand would be roughly 101,000 tons. Local production is about 46,000 tons, leaving 55,000 tons to be supplied from outside the state or by new plants using the NOXS0 or Columbia Gas processes. Since an 800-MW generating unit would supply 44,000 tons per year, a total of 1,000 MW could be installed without creating an excess that would have to be shipped long distances by barge or rail to the Florida market. The supply and demand situation in nearby states does not change the outlook substantially. Du Pont's large sulfuric acid plant in Wurtland, Kentucky has a consumption about equal to the Catlettsburg refinery's output. The other nearby acid plants produce by-product sulfuric acid and are not potential customers for Ohio sulfur. On the other hand, all the coal burned in Ohio in 1987, 47 million tons, would yield 1.1 million

tons of sulfur, about 7.8 percent of total U.S. usage, assuming the state-wide average of 2.7 percent sulfur content in the coal burned (OCDO, 1989) and 90 percent recovery.

It is clear that there is a modest market for sulfur for making sulfuric acid in the Ohio region at roughly current prices. Large amounts could be sold in Florida, but because of shipping costs, the net return to local producers would be reduced. If local producers cut their prices, the local refineries would have to follow suit since their production is "fated" by the crude they refine. At a low enough price, Ohio sulfur, shipped by barge, could be cheaper in Florida than sulfur from Wyoming and Alberta because of their higher shipping price (at least some of the shipping would be by rail from those locations), even if the selling price out of Wyoming and Alberta. Such a low price would probably not be needed in order to sell 1.1 million tons of sulfur, but the equilibrium price is a matter of speculation and beyond the scope of this study.

4.4.2. Sulfuric Acid

Because sulfuric acid can be produced from by-products from lime- and limestone-based processes as well as from sulfur obtained from the NOXSO and Columbia Gas processes, a separate analysis is included here. In the latter case, the markets for sulfur, described above, and sulfuric acid overlap and should be considered together to avoid double counting.

4.4.2.1 Demand

Although sulfuric acid is the most commonly used acid in the chemical industry, its use in making phosphate fertilizer dominates. Between 60 and 70 percent of sulfuric acid produced is used in fertilizer making; in 1988 it was estimated as 68 percent. Other uses are petroleum refining, 7 percent; ore leaching, 4 percent; industrial organic chemicals, 3.5 percent; synthetic rubber and plastics, 2.5 percent; pulp and paper, 2.5 percent; and miscellaneous uses, 9 percent (Anonymous, 1988d).

The starting point for phosphatic fertilizers is phosphate rock, which is nearly insoluble calcium phosphate, found principally in Florida, North Carolina, and Idaho. To make it more soluble, the rock is treated with

sulfuric acid, which converts it to what is termed "calcium superphosphate." This material contains not only the solubilized fertilizer but also calcium sulfate formed by the reaction. To increase the amount of active ingredient and also reduce shipping costs, a two-step process is commonly used. Calcium phosphate is treated with a large quantity of sulfuric acid so as to form phosphoric acid and calcium sulfate. The acid is separated from the calcium sulfate and used to acidulate phosphate rock. The superphosphate thus formed has no contaminating gypsum and is known as "triple superphosphate." Triple superphosphate capacity is about three times that of normal superphosphate. An alternative is to treat phosphoric acid with ammonia to make diammonium phosphate.

Sales of phosphatic fertilizer depend on two factors: purchases by U.S. farmers and exports. The former, in turn, depends on weather, acreage allotments, and farm exports. Exports of fertilizer depend to an important extent on the relative value of the dollar.

Altogether, the other uses of sulfuric acid constitute a good economic indicator of the health of the chemical industry in general. The future outlook is for all but one of these uses to grow with the chemical economy. The exception is the production of titanium dioxide, where the chloride process is replacing the sulfate process. In the petroleum industry, the sulfuric acid process for making alkylate gasoline is being replaced by the hydrofluoric acid process when plants are expanded but there is no rush to replace existing units in spite of energy savings offered by the hydrofluoric acid process. In any case, the hydrofluoric acid is made by treating calcium fluoride with sulfuric acid. The use of sulfuric acid for pickling operations, the descaling of iron and steel prior to coating, is being replaced by hydrochloric acid pickling. In recent years there has been a rapid expansion in the use of sulfuric acid for the leaching of low grade metallic ores. This use, which frequently is in locations near where by-product acid is produced, is said to be approaching maturity and is not likely ever to provide a market for all of the by-product acid available in areas such as Arizona and New Mexico.

Total demand for sulfuric acid in the U.S. was estimated as 38.5 million tons in 1988. Overall growth through 1992 has been forecasted as 1 percent per year (Anonymous, 1988d).

4.4.2.2 Supply

Sulfuric acid produced in the U.S. is made in three ways. The first process is by burning elemental sulfur, as described in the section on sulfur; second, by processing petroleum refinery acid sludges; and finally, by roasting sulfide ores. About 90 percent of capacity is based on sulfur burning, yielding what is termed "virgin acid." The balance is termed "by-product acid." In Canada and Europe sulfuric acid is also made intentionally by roasting iron pyrite. Imports, mostly by-product acid from Mexico and Canada, are about 4.2 percent of the U.S. total consumption. Freeport-McMoRan is now starting up a pilot plant in Louisiana to evaluate a process that will produce sulfuric acid and aggregate from phosphogypsum (McGinty, 1987).

Considering the U.S. and Canada together, demand in 1987 was 40.9 million tons, 85 percent of which was from elemental sulfur, 12 percent by-product acid, 2.7 percent from iron pyrite, and 0.5 percent imports of by-product acid from Mexico. In the next few years several large by-product acid plants will come on stream in Ontario and Quebec to control smelter gas emissions and much of this by-product acid will be marketed in the U.S. (Anonymous, 1989a).

4.4.2.3 Pricing

As is the case with sulfur, the price of sulfuric acid varies by region, perhaps even more than with sulfur, since it is more difficult to store, weighs three times as much as the equivalent sulfur, and is more expensive to ship. In looking at prices, it is important to compare on constant terms since spot prices can be very different from long-term contract prices and contract terms can vary widely. The Table 4-3 reflects the pattern of regional variation.

TABLE 4-3. PRICE OF SULFURIC ACID IN VARIOUS LOCATIONS

Location	\$/ton
<u>Virgin, 100%, at works</u>	
East Coast	71.75 to 95.90
Gulf Coast	75.00 to 86.40
Southeast	68.15
Midwest	80.25
West Coast	85.00
<u>Smelter, 100%, tanks, at works</u>	
Gulf Coast	48.00 to 52.00
New Mexico	20.00 to 25.00
Southeast	63.15
<u>Smelter, 93%, tanks, delivered</u>	
Northwest	60.00 to 65.00

Source: Anonymous, 1989b

Although the price in the Midwest is currently near the highest in the country, production of larger amounts of sulfuric acid than can be utilized would cause the price to drop to the levels found now in the Southwest. The price would be related to the cost of shipping by barge or rail to market. It is difficult to get precise shipping costs but for distances of 100 to 200 miles, rail costs are \$11 to \$12 per ton.

4.4.2.4 Outlook

Ohio sulfuric acid plant capacity in Ohio is shown in Table 4-4.

TABLE 4-4. SULFURIC ACID PLANTS IN OHIO AND NEARBY AREAS

Company	Location	Capacity	Source (Tons)
Armco	Middletown	8,000	Coke Oven
Coulton Chem.	Oregon	200,000	55 % Sludge 45 % Elemental
Cairo Chem. (Sub.)	Cairo	60,000	Elemental
Du Pont	North Bend	167,000	Elemental
OHIO TOTAL (not including sludge-based)		325,000	
Du Pont	Wurtland, KY	200,000	Elemental
Horsehead Ind.	Monaca, PA	110,000	Smelter
Rhone-Poulenc	Hammond, IN	350,000	60% Sludge 40% Elemental

Source: SRI International, 1988.

ASARCO's plant in Columbus, which formerly roasted zinc sulfide and produced by-product acid, has been shut down. PVS Chemicals recently announced that it would cease production in Copley and instead the site will be a distribution center for Canadian by-product acid.

One 800-MW generating plant could produce 135,000 tons of sulfuric acid per year and 1,900 MW of generation capacity could replace all of the virgin acid capacity in Ohio. On the other hand, all the coal burned in Ohio in 1987, 47 million tons, would yield 3.4 million tons of sulfuric acid, about 9 percent of total U.S. usage, assuming the statewide average of 2.7 percent sulfur content in coal burned and 90 percent recovery.

It is clear that there is a modest market for sulfuric acid in the Ohio region at roughly current prices. As is the case with elemental sulfur, large amounts could be sold in Florida, but because of shipping costs, the net return to local producers would be much reduced.

4.4.3 Gypsum

Strictly speaking, gypsum is the dihydrate of calcium sulfate. It can reversibly lose water of hydration on heating to form plaster of paris, the beta form of calcium sulfate hemihydrate. This material also is called "stucco." Heating gypsum in water in an autoclave gives rise to the alpha form of the hemihydrate. Heating above 325 F yields calcium sulfate with no water of hydration, which is known as soluble or insoluble anhydrite, depending on how strongly it was heated. As frequently is the case in commerce, the definition of gypsum is somewhat blurred. Some use the term to cover all species of calcium sulfate. In this discussion the more precise definition, calcium sulfate dihydrate, will be used.

Of the Ohio clean coal combustion processes under consideration, only the chelated lime process yields calcium sulfur products not mixed with considerable amounts of fly ash. PFBC, LIMB, HALT, Coolside, ESOX , and the TRW slagging combustor give calcium sulfate and sulfite with various waters of hydration, unreacted lime or limestone, and considerable amounts of fly ash. The NOXSO and Columbia Gas approaches do not use calcium chemicals.

In the case of the chelated lime process, the product is a mixture of mostly calcium sulfite hemihydrate (78 percent), gypsum (17 percent), unreacted lime (3 percent), and calcium carbonate (2 percent). The scrubbing solution is a red aqueous liquid containing iron EDTA salts. The solid can be washed clean and the sulfite oxidized to sulfate using air, a process known as "forced oxidation." Excess lime and calcium carbonate can be converted to gypsum at the same time by adding small amounts of sulfuric

acid. In some scrubbing processes it is possible to do the forced oxidation in the scrubber itself, but in the chelated lime scrubbing process it is necessary to maximize the amount of sulfite present to get efficient scrubbing. This means the forced oxidation must be a separate step, requiring extra equipment and extra capital equipment. However, better control of the operation is possible, so that a product better suited to the utilization of the gypsum is obtained.

4.4.3.1 Demand

Gypsum is principally used in making plaster and wallboard. Other uses are as a set retardant for portland cement, as a soil conditioner, and as filler for paints and caulks.

Wallboard. The chief use of gypsum is in the making of wallboard, which used about 20 million of the 25 million tons of gypsum consumed in 1988 (Davis, 1989). The gypsum is calcined, mixed with water, and allowed to set between paper sheeting. It is then dried and cut. There are 72 production plants in 29 states; 3 plants are located in Ohio (Prusser, 1987):

- Celotex, mine and plant, Port Clinton
- National Gypsum Co., plant, Lorain
- USG Corp., plant, Gypsum, Ottawa County.

Calcined gypsum produced in Ohio in 1987 amounted to 460,000 tons, 2.6 percent of the national total, with a reported value of \$23.60 per ton.

There is no ASTM standard for gypsum for wallboard, although there is one for wallboard itself. Specifications for gypsum for use in making wallboard vary from company to company, as shown in Table 4-5, and are related to the details of the process and equipment employed. The size of particle preferred is greater than 100 microns, with a stubby shape. Fines content, that is particles less than 150 microns, should be low. The specifications for soluble salts, especially chlorides, are critical for each company's design, since soluble salts hold moisture and make adherence

TABLE 4-5. COMMERCIAL GRADE GYPSUM SPECIFICATIONS

	National Gypsum	Georgia Pacific	USG Corp.	Domtar Canada	Japanese	German(c)
Gypsum Content	94.0% min.	94% min.	95.0% min.	95.0% min.	95%	95% (if impurities inerts-80%: min.
$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	0.5% max.	NS	2.0% max.	0.5% max.	0.25% max.	0.25%(SO ₂) max.
Total Water- Soluble Salts	NS	NS	600 ppm max.	NS	less than 1000 ppm	NS
Na	250 ppm max.	200 ppm max.	75 ppm max.	75 ppm max.	NS	600 ppm max.
Cl	400 ppm max.	200 ppm max.	120 ppm max.	75 ppm max.	NS	100 ppm max.
Mg	250 ppm max.	NS	50 ppm max.	100 ppm ax.	NS	1000 ppm max.
Free Water	10-15%	10%	10% or less	10% or less	10% or less	10% or less
pH	6-8	3-9	6.5-8.0(a)	6.5-8.0	6.0-8.5(b)	5-9
Particle Size (micron)	xy = 2000 sq.	NS	20 (mass mean)	4000 cm ² /g(d)	max 50x150 min 10x50	NS
Inerts %	3.0% max.	NS	1% max. fly ash	5% max.	NS	NS

NS = Not specified

(a) 10 grams gypsum/100 ml H₂O(b) 1 gram gypsum/500 ml H₂O

(c) Requirements (for FGD gypsum use in wallboard) established in 1984 by the Federal Association of Gypsum and Plaster Board Industries e.V. (West Germany), which also specified that color should be a level of white no less than 80 percent, odor should be neutral, and toxic components should be none.

(d) Blaine Specific Surface Area.

Source: compiled from New Frontiers for By-product Gypsum, Conference Proceedings, Ortech International, November 3-4, 1988, Mississauga, ONT, pp. 28, 96, 154, 166.

of the liner paper difficult. If coals high in chloride are treated to generate gypsum, prescrubbing might be required. The magnesium limit also is critical, meaning the use of low magnesium limestone or lime is required. The low level of sulfite also is important but this level can be met by existing forced oxidation processes.

Building Plaster. Plaster is also prepared by the calcining of gypsum, and the same specifications apply except, perhaps, those for soluble salts. Total U.S. consumption in 1988 was 680,000 tons, 2.7 percent of the total use of gypsum.

Concrete Additive. Gypsum is used without calcining with portland cement as set retardant since it helps to reduce what is termed "flash setting." Total U.S. consumption in 1988 was 4.6 million tons, 18 percent of the total use of gypsum. The specifications are a maximum of 3 to 4 percent calcium sulfite and a low fines content. For FGD gypsum to be acceptable, it must be briquetted, which is an added expense. On a per capita basis, Ohio would consume 200,000 tons of gypsum in this application. This is slightly less than the 240,000 tons that would be produced by a standard 800-MW generating unit. Market performance shows, however, that attempts to sell briquetted by-product gypsum in Florida in competition with imported Spanish gypsum have not been successful. (Ortech, 1988).

Since fly ash can be used in concrete, one might think that the mixture of gypsum plus fly ash from clean coal combustion could be utilized directly. In reality, however, the cement industry has well worked out formulations and procedures and a consulted industry expert felt that the industry would prefer to buy pure gypsum and well characterized fly ash separately.

Agricultural Use. In 1988, 1.4 million tons of gypsum were used in agriculture, primarily in California and the Southeast. Gypsum helps in salt removal from soils and is useful as a source of calcium and sulfur as nutrients without changing the pH of the soil. The latter is important for citrus crops.

Fillers and Miscellaneous. Uncalcined gypsum also is used as a filler in paints and caulks, as a filter material for beer, and as a stabilizing agent in baked goods, etc. Consumption amounted to 301,000 tons for the U.S. in 1987.

Possible Uses of the Alpha Hemihydrate. The alpha form is more complex to make than the beta, but it has certain desirable characteristics. For example, the alpha form gives plaster a greater compressive strength, allowing the making of a thinner board or shapes that are not held together by a liner. It requires less water to make a slurry of the correct consistency, thus reducing the energy requirements for drying. However, the maximum amount of alpha form that can be used in wallboard is 60 percent. At present the alpha form production is only 1 percent of the gypsum calcined.

4.4.3.2 Supply

There are 62 gypsum mines in the U.S., located in 21 states. Most of these are open pit mines. About half of the mines have associated wallboard plants. Total U.S. mined-gypsum production in 1988 was about 14 million tons. There is one mine in Ohio, operated by Celotex in Port Clinton, with a wallboard plant at the same site. Production in Ohio is not published but the amount mined for calcining is probably on the order of 0.20 to 0.25 of the amount of calcined material produced, or about 100,000 tons, based on employment and product mix at the three Ohio wallboard plants (Harris, 1988). Additional amounts may be mined for use in cement making. In any case, Ohio's production is in the bottom 5 or 6 of the 21 states with mines.

The leading producing states are Texas, Michigan, Iowa, Oklahoma, California, Nevada, and Indiana. In 1986, Michigan produced 2.0 million tons, ranking second in the nation. Indiana ranked seventh but no tonnage figures are available (Davis, 1988).

Since few gypsum mines are located on the seacoasts, imports play an important role. Imports in 1988 were 9.5 million tons, about 38 percent of U.S. consumption. Most of this is from Nova Scotia, going to the East Coast (65 percent). Imports from Mexico (21 percent) to the West Coast, and Spain (10 percent) to Florida, also are important. Imports from Spain are

used as ballast on barges returning from hauling phosphate rock from Florida to Europe and hence are transported at almost no cost.

Use of by-product gypsum in 1988 was 900,000 tons, according to the Bureau of Mines (Davis, 1989). There are a number of by-product sources available. The largest and most concentrated source is the by-product of phosphoric acid production for fertilizer manufacture in Florida. The material, usually referred to as phosphogypsum, contains phosphate residues, fluoride, and uranium and its radioactive daughter products. Other by-product sources are the residues from the neutralizing of spent acid from making hydrofluoric acid (fluorogypsum) and titanium dioxide pigment (titanogypsum). Gypsum also is produced in more limited quantities in the manufacture of citric acid, the plastic Kevlar, and other organic chemicals (Ortech, 1988).

Wallboard is currently being produced from by-product gypsum in a number of countries. Japan, which has no domestic gypsum mining industry, has a well developed by-product utilization industry. Roughly 6 million tons per year of by-product gypsum, including 2.2 million tons of FGD, were used for making wallboard, plaster, etc. In West Germany, government policy against "throwaway" scrubbing has led to extensive production of wallboard from FGD by-product gypsum in spite of the existence of a gypsum mining industry.

Utilization in the U.S. is starting in a modest way. USG Corp. at its Galena, Texas wallboard plant uses about 120,000 tons per year of FGD gypsum, between 50 and 85 percent of the plant's feed. Windsor Gypsum Company at Tatum, Texas has a new plant with 250,000 ton capacity using 100 percent FGD feed. Georgia-Pacific will start operations in 1989 at Drakesboro, Kentucky using 300,000 tons per year of FGD gypsum from TVA's Paradise power plant. Celotex in Jacksonville, Florida is reported to be making arrangements to buy FGD gypsum from two nearby power plants. Florida Mining Company in Ruskin, Florida is starting operations to pelletize 60,000 tons per year of FGD gypsum from the nearby Tampa Electric Company power plant for use in cement making. Half of the raw material used at the USG Corp. wallboard plant in Baltimore is titanogypsum, using between 120,000 and 250,000 tons of by-product material (Ortech, 1988). Fluorogypsum from Du Pont's La Porte, Texas hydrofluoric acid plant is now being utilized as road building base material and as a result has been reclassified as a co-product,

not a waste product under Texas's waste disposal regulations (Anonymous, 1989c).

Much work on the utilization and reuse of phosphogypsum has been done by fertilizer companies, engineering firms such as Salzgitter Industriebau GmbH, and the Florida Institute of Phosphate Research. Currently, a pilot plant to use phosphogypsum, pyrite, and high sulfur coal to produce sulfuric acid and road aggregate at Freeport-McMoRan's fertilizer plant in Louisiana is in the start-up phase (McGinty, 1987).

4.4.3.3 Pricing

The reported value of gypsum at the mine for the U.S. and Ohio is shown in Table 4-6.

TABLE 4-6. VALUE OF GYPSUM, UNITED STATES AND OHIO

	\$ Per Ton FOB				
	1984	1985	1986	1987	1988
	<u>Current Dollars</u>				
Crude, United States	7.94	7.76	6.46	6.85	7.00
Calcined, United States	20.75	23.53	18.19	18.28	19.00
Calcined, Ohio	23.32	23.14	20.16	23.63	NA
	<u>Constant 1988 Dollars</u>				
Crude, United States	9.02	8.51	6.82	7.13	7.00
Calcined, United States	23.56	25.80	19.20	19.02	19.00
Calcined, Ohio	26.48	25.38	21.28	24.59	NA

Source: Davis, 1986; 1988; and 1989.

Prices have been more or less stable in recent years in nominal dollars with a downward trend. When they are transformed into constant 1988 dollars using the Consumer Price Index, a pronounced downward trend can be seen. Prices not only depend on the state of the housing market, the big

user of wallboard, but also on the degree of aggressiveness in pricing by the few companies that have most of the business. Typical costs for trucking are reported to be \$3 to \$22 per ton, depending on distance.

A wallboard company typically will not pay the price for by-product gypsum that mined material commands in the open market. For example, Georgia-Pacific in Grand Rapids, Michigan has been paying \$1.00 per ton for 20,000 tons per year of gypsum cake, FOB the Grand Haven Light and Power plant (Ortech, 1988).

4.4.3.4 Outlook

The amount of gypsum brought into Ohio for calcining is roughly 360,000 tons and additional unreported amounts are used in cement making. If the 25 million tons consumed nationally is distributed in the same proportion as the population, the total net imports (use minus local mining) would be 1,000,000 tons per year. Since an 800-MW generating unit would produce about 240,000 tons per year, the gypsum market might accommodate the output from as many as four such units. Out-of-state markets are probably small since Michigan and Indiana have well-established gypsum mining industries and a new, large FGD gypsum plant will start up soon in Kentucky. The populous East Coast is currently supplied by imported gypsum, which can be transported cheaply by water. The Pittsburgh area is a possibility, but it is likely that scrubber-based plants there will preempt that market.

It is important to remember that the dominant wallboard producers are highly integrated. They own mines, operate wallboard plants, which are often adjacent to the mines, and have regional and local distribution centers for their products. A utility would need to establish a working relationship with one of the active producers rather than try to enter the market on its own. Of course, the wallboard company will want the scrubber managed so as to optimize the quality of the gypsum, which may be in conflict with the desire of power plant operators, who wish to run the scrubber operation to minimize emissions, maintain reliability, and minimize direct generating costs.

4.4.4 Agriculture

This section discusses potential uses of by-products of clean coal combustion processes as sources of calcium or alkalinity for several agricultural applications. There is also the possibility that by-products may contain trace nutrients needed for crop growth or for farm animal nutrition as well as the possibility of toxic heavy metals. For the most part, the by-product material appears to be suitable for agriculture, based on the Task 1 data; i.e., it does not contain excessive amounts of heavy metals.

In Ohio, the chief micronutrient problem is with manganese deficiency, principally with soybeans and especially in western Ohio. Other problems are boron deficiency with alfalfa and zinc with corn. Copper deficiency may occur with organic soils. Because these markets are specific to the particular soil and crop, these possibilities will not be discussed in detail. Complicating the analysis is the nonuniformity of the by-products and the difficulty of getting data on current market demand for trace nutrients. Manganese applications are typically 1 to 6 pounds per acre; with by-product residues containing 500 ppm, this would be 0.1 to 0.6 tons per acre. If the residue contained only 50 ppm, 1 to 6 tons per acre would be required. No evaluations of the availability of the manganese in by-product were found. Agronomists have found that manganese oxide must be finely ground to be available to the plants (Hall, 1989).

Some research has been done on the impacts of the use of by-products as soil amendments for improving pH and adding calcium, mostly looking at any adverse effects that the crops grown on treated soil might have on livestock or laboratory animals due to the uptake of toxic metals. This work is discussed below. Work has also been done on the use of by-products as a source of calcium in poultry feed. AFBC residue was not significantly different from limestone when used as a calcium source for broilers and broiler breeders (Merkley, 1987). Although AFBC residues are not explicitly included in the scope of this OCDO study, the results are reported because, in many respects, the properties relevant to agriculture are similar to by-products that are part of the study.

4.4.4.1 Demand

Calcium-containing materials are used in agriculture for pH adjustment, poultry grit, mineral food, and other uses. The U.S. Bureau of Mines' publications often are the best source of statistics on which materials are used for various applications, but often report substantial amounts (up to 50 percent) attributed to "other unspecified uses." The problem is caused by production or consumption estimates that lack a breakdown by end use and to estimates of likely sales by nonrespondents to biennial questionnaires from the Bureau of Mines. Therefore, adjustments to statistics have been made here by assuming that these unspecified uses are distributed proportionately among the end uses that are accounted for.

The sources of calcium or alkalinity used by farmers include crushed limestone (calcium carbonate), crushed dolomite (calcium carbonate and magnesium carbonate), hydrated lime (calcium hydroxide) or quicklime (calcium oxide). Disaggregated data on specific end use consumption of these four materials are not available for agricultural applications for the U.S. or Ohio. For both the U.S. and Ohio, limestone makes up about 94 percent of the limestone-dolomite total.

Adjusting the pH of agricultural soils by using either quicklime or hydrated lime decreased at an average annual rate of 7.5 percent per year between 1959 and 1983, and the downward trend is probably continuing, despite the fact that these sources offer about twice the fertilizer value per ton, in the case of unslaked lime, and are faster reacting than pulverized limestone. However, the high cost of these energy-intensive materials, \$40 to \$50 per ton versus \$5 to \$6 per ton, has persuaded most farmers to substitute pulverized limestone for counteracting excess soil acidity. As seen in Table 4-7, soil pH adjustment for the U.S. as a whole accounted for hydrated lime and quicklime consumption of 100,000 tons (Ober, 1988), compared with 30,200,000 tons of crushed stone, most of it as limestone (Tepordei, 1988). Comparable figures are not available for Ohio.

Poultry grit and mineral food end uses accounted for 3,000,000 tons of crushed stone, most of it as limestone (Tepordei, 1988). Other agricultural uses required about 600,000 tons of limestone.

Also shown in Table 4-7 is the aggregated agricultural data for Ohio indicating that pH adjustment, poultry grit and mineral food, and

TABLE 4-7. AGRICULTURAL USES OF LIME OR CRUSHED STONE SOLD OR USED
IN THE UNITED STATES AND OHIO, MILLION SHORT TONS, 1987

Application	Lime		All Crushed Stone	
	U.S.	Ohio	U.S.	Ohio(a)
pH adjustment	0.1	NA	30.2(b)	NA
Poultry grit	-	-	3.0(b)	NA
Other	-	-	0.6(b)	NA
TOTAL	0.1	NA	30.4	1.4

(a) In Ohio total includes limestone (93.4%), dolomite (6.2%) and sandstone (0.4%).

(b) Data adjusted for substantial amounts (32 to 50%) of crushed stone listed as "other unspecified uses," based on the assumption that these unspecified uses are distributed among all applications in proportion to their share of the total.

Sources:

Ewell, M., U.S. Bureau of Mines, personal contact, "Ohio: Crushed Stone Sold or Used by Producers in 1987," March 1989.

Ober, J. A., "Lime," preprint from 1987 Minerals Yearbook, U.S. Bureau of Mines, Washington, D.C., 1988.

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Tepordei, V. V., "Sand and Gravel," 1986 Minerals Yearbook, U.S. Bureau of Mines, Washington, D.C., 1987.

miscellaneous agricultural uses combined required 1,400,000 tons of crushed stone, almost all of which was limestone (Ober, 1988; Ewell, 1989).

4.4.4.2 Supply

Six companies are listed as the principal suppliers of crushed stone in Ohio (Prosser, 1987). These six companies have 32 plant and/or operations located in 24 counties, while a total of almost 2,500 limestone and 119 dolomite quarries are found across the U.S. Ohio has nine lime-producing plants and is the country's leading lime producer. However, no data were found identifying the product from the Ohio crushed stone operations or whether lime is imported from or exported to neighboring states. Clean coal combustion by-product should not be considered as competition for Ohio limestone and lime kilns. On the contrary, using the calcium-based clean coal combustion processes, followed by use of residues for agricultural or road base applications, represents a new market that might be lost to noncalcium processes without the added value obtained for the by-products.

4.4.4.3 Pricing

According to the Bureau of Mines, the value of Ohio agricultural limestone averages \$4.47 per ton compared with a \$5.82 average for all grades of crushed limestone (Tepordei, 1988). Transportation cost is in addition and is comparable for the coal by-product material. The price of lime in Ohio in 1986 was \$49 per ton (Prosser, 1987). The lowest price at which farmers could obtain the by-product would be the cost of transportation and handling, roughly \$3 to \$10 per ton. Alternatively, power plants could charge as much as 60 percent of the agricultural limestone price, or \$2.70 per ton plus transportation, for coal by-product containing on the order of 30 percent unslaked lime because this form of lime has roughly twice the neutralizing power of limestone.

4.4.4.4 Outlook

It has been recently reported that Minnesota alfalfa farmers have found that a paper company's ash from burning wood, wood waste, and coal was useful in neutralizing acid soil; 2.5 tons of ash were equivalent to 1 ton of lime (Anonymous, 1988a). It also was stated that each ton was "worth" \$24 to the farmer.

Extensive work has been done to evaluate liming using AFBC by-product, a material not within the scope of this study. AFBC by-product, which is high in calcium oxide, was found to be an adequate source of liming, as good or slightly better than agricultural lime (Carlson, 1988a). Soil conductivity, an indication of salinity, was increased but no adverse effects were observed. An adverse effect on apples was observed at levels eight times the liming requirement (Korcak, 1980). Rats (Carlson, 1988b), sheep (Reid, 1988), and cattle (Fontenot, 1987) showed no adverse effects after being fed on crops raised on soil treated with AFBC residues. However, pigs showed a decrease in body weight and increased nitrogen retention (Carlson, 1988c). These results need to be confirmed and extended to the residues covered by OCDO research before firm conclusions can be drawn. Tentatively, however, it appears that the residues with free lime and limestone can be used as agricultural soil amendments.

The various clean coal combustion processes yield varying amounts of calcium sulfite and sulfate, calcium carbonate, hydrated and quicklime, and magnesium oxide. The first two have neutral or slightly acidic pH and therefore are not sources of alkalinity for pH adjustment, the largest agricultural end use; therefore they are ignored. The remaining materials account for 18 to 60 percent of the by-product material from the clean coal combustion processes except for the NOXS0 and Columbia Gas (Parsons) processes, which do not use calcium, and the chelated lime process, where most of the calcium is converted to gypsum. For making a quick estimate, it was assumed that the processes yielding agriculturally useful calcium compounds are equivalent to 30 percent lime. These same processes yield 24 to 41 percent residue based on the weight of coal burned; it was assumed that 30 percent of the coal results in residue or by-product.

An 800-MW generating standard coal-burning unit would use about 1,400,000 tons of coal per year and potentially yield on the order of 130,000 tons of calcium compounds. In 1987 Ohio power plants burned a total of 47,000,000 tons of coal, which would have yielded about 4,200,000 tons of calcium oxide equivalent suitable for agricultural use, or about twice the existing market needs. Since not all plants will use the processes that have free lime or limestone, this is a good fit with the market.

Of the processes under consideration, the ones that would have a high enough liming value to make use worthwhile are as follow:

<u>Process</u>	<u>CaO equivalents in residue</u>
• PFBC	32 percent
• LIMB	32 percent
• HALT	35 percent
• Coolside	34 percent
• TRW Slagging Combustor	45 percent

4.4.5 Construction - Road Base

Many construction and building materials applications for clean coal combustion by-product have been considered and some laboratory work has been done on by-product use in road construction materials, structural fill, soil stabilization, asphalt admixture, and roofing materials (Dahlin, 1987). In Europe there is some experience using fluid bed by-product in roofing paper, asphalt, tiles, and in the cement and mining industries (Felwor, 1988). Of these, aggregate for road building and material for soil stabilization appear to be the largest potential markets. Although the smaller markets were not investigated, they are still promising as research opportunities. They could be profitable even though they do not constitute large uses.

Several studies have been conducted on the reuse of ash materials. A study by Dahlin (Dahlin, 1986) examined the critical characteristics associated with the disposal of LIMB by-product and the management of the ash/sorbent waste products from this process. Regarding beneficial use options, the study concluded that LIMB ash could be reused by mixing with water and pelletizing to make a product suitable for use as an aggregate in

asphaltic wearing courses. LIMB by-product can also be used for scrubber sludge stabilization, as a scrubber feed material, and for the production of synthetic aggregate.

Clean coal combustion by-product probably cannot be used as aggregate for concrete or bituminous surfacing because it lacks the ASTM C535 accepted standard for abrasion resistance and the compressive strength required. However, it may be a potential substitute for aggregate in various other construction applications, including stabilization of roads and soils and for use as graded road base or subbase. Likewise, the material probably is not suitable for use for surfacing unpaved roads for the same reasons. For example, the by-product from the PFBC has a compressive strength of 30 MPa, corresponding to low strength concrete (Anonymous, 1986). Pellets from LIMB by-product material has compressive strengths of 12.9-17.3 MPa (Dahlin, 1986). The use of the material for road construction, soil stabilization, asphalt admixture and roofing is currently being investigated (Dahlin, 1987). The stabilization applications will be considered separately from road construction because different materials are being used in the two applications at present.

4.4.5.1 Demand

Data for the U.S. and for Ohio are shown in Table 4-8. The total for all these applications of both crushed stone, primarily limestone, and sand and gravel is greater than 25,000,000 tons for Ohio (Tepordei, 1988; 1987). Aggregate for road base or unpaved surfacing is described as mixed coarse and fine crushed stone and sand and gravel. Of this category, 46 percent is used for surfacing unpaved roads, a use not suited to clean coal combustion by-product. In the data for sand and gravel, use on unpaved roads is not separated from road base use. To adjust for this, it was assumed that the same distribution applied as with crushed stone. Omitting 46 percent of the amount of sand and gravel gives an estimate that road base requirements would total 11,100,000 tons (i.e., the equivalent of 8,200,000 tons of crushed stone and 2,900,000 tons of sand and gravel).

In addition to use as road base, sizable amounts of crushed stone and gravel are used for fill. The amount of crushed stone actually used is uncertain because in the Bureau of Mines' data the category is described as

TABLE 4-8. CONSTRUCTION USES OF LIME OR CRUSHED STONE OR SAND AND GRAVEL SOLD OR USED IN THE UNITED STATES AND OHIO, MILLION SHORT TONS, OR ANNUAL

Application	Lime, 1987		All Crushed Stone, 1987		Sand and Gravel, 1986	
	U.S.	Ohio	U.S.	Ohio(a)	U.S.	Ohio
Road stabilization	0.4	NA	-	-	-	-
Soil stabilization	0.4	NA	-	-	-	-
Graded roadbase or subbase	-	-	281.6(b)	8.2(b)		
Unpaved road surfacing	-	-	44.1(b)	7.0(b)	130.5	5.1
Fill	-	-	30.7(b,c)	0.9(b,c)	66.1	3.9
ALL USES	15.76	1.53	1,200.1	51.6	883.0	36.8

(a) Ohio total includes limestone, dolomite, and sandstone.

(b) Data adjusted for substantial amounts (32% to 50%) of crushed stone listed as "other unspecified uses," based on the assumption that these unspecified uses are distributed among all applications in proportion to their share of the total.

(c) Amount shown is one-third of total crushed stone used for crusher run, fill, and waste.

Sources:

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Tepordei, V. V., "Sand and Gravel," 1986 Minerals Yearbook, U.S. Bureau of Mines, Washington, D.C., 1987.

"crusher run or fill or waste." Crushed stone was taken as one-third of the amount for this category. Fill requirements are estimated as approximately 4,800,00 tons, giving an overall total of 15,900,000 tons for all road building use in Ohio that could be satisfied by clean coal combustion by-products.

4.4.5.2 Supply

As indicated in Section 4.4.4.2, Ohio has abundant reserves of limestone. Ohio was 11th in production of crushed stone in 1986 with 4 percent of the U.S. production. Gravel for construction is likewise abundant. Because of the high relative cost of truck transportation, contractors usually use material quarried near the construction site. Therefore, some stone from adjacent states could be used near the borders of Ohio. Some quarry operators may consider the usage of by-product in highway construction as threat to their sales. On the other hand, they are profiting from increased sales of limestone to scrubber plants or lime kilns and, without the by-product use, calcium-based processes might lose out to noncalcium processes.

4.4.5.3 Pricing

In Ohio, the Bureau of Mines estimates the value in 1987 of coarse and fine aggregate for graded road base or subbase to be \$3.53 per ton (Ewell, 1989). Transportation costs limit shipping to approximately 50 miles.

In Texas, Gulf State Materials is involved in the beneficial use of calcium sulfate-based materials marketed under the name of Calcium Sulfate Flexible Base (also called Scrubber Base). The material is a coproduct of Du Pont's hydrogen fluoride production. This material has not been qualified for use on state highways, but is being used for parking lots, driveways, and haul roads. Calcium Sulfate Flexible Base is sold to contractors and private individuals for half the price of crushed limestone. It sells for about \$6 per ton in competition with crushed limestone at \$12 to \$13 per ton and by-product gypsum from an oil refinery at \$7 to \$8 per ton. Significantly, regulatory support, the need for which is discussed in Chapter 5.4, increased

sales through a 1987 State of Texas reclassification of calcium sulfate from a "by-product" to a "coproduct." The reclassification was granted after Du Pont was able to show that calcium sulfate is environmentally safe and commercially useful (Butterworth, 1989; Anonymous, 1989c).

4.4.5.4 Outlook

Standards for aggregate and subbase are published by the state of Ohio (ODOT, 1987). It is assumed that "synthetic gravel" from clean coal combustion by-product will meet the sodium sulfate cycling test and can have the appropriate size distribution. However, the Los Angeles Abrasion Test (also referred to previously as ASTM C535), which measures fines produced when the material is tumbled with steel balls, will disqualify the material from any use except subbase. (Evaluation of each material in all road construction applications is a research need.) Assuming clean coal combustion by-product can be used for road base applications with little or no processing, all of the by-product could be consumed in the local market. A standard 800-MW generating unit as previously described would make available 420,000 tons of by-product from processes that include fly ash in the by-product. The state as a whole burns 47,000,000 tons of coal, potentially yielding an estimated 14,000,000 tons of such by-product, roughly sufficient to meet this entire demand.

A large fill area (40-ft wide, 1,490-ft long, and with an average depth of 50 in.) for a portion of a Pennsylvania interstate highway was reported to be using a mixture of fly ash and up to 10 percent of a scrubber sludge material called Poz-O-Tec (Anonymous, 1988b). The latter consisted of a mixture of lime, fly ash, and FGD sludge. However, on a direct inquiry to the Pennsylvania State Department of Transportation (PennDOT), it was learned that the scrubber material had not, in fact, been used. Instead a fly ash from a nearby power plant was applied. It is believed that neither material cost essentially more than the hauling price, which was not separately costed by the contractor.

4.4.6 Construction - Stabilization

Lime is used to improve clay soils to produce better bases and subbases for roads, parking lots, building foundations, airports and dams composed of earth. The Bureau of Mines divides these in two categories -- road and soil stabilization -- and reported U.S. consumption as 400,000 tons for each category in 1987. Ohio consumption is not separately identified. If it can be assumed that Ohio's 9.7 percent share of total lime (both quick and hydrated) consumption is applicable to the fraction used for stabilization, then an estimated 77,000 tons of lime would be used in stabilization. Alternatively, one can use the fact that Ohio has 113,000 miles of public road and street mileage compared with 3,880,000 miles for the U.S. as a whole, or 2.9 percent. If 400,000 tons of lime are used for road and soil stabilization, then 12,000 tons should be consumed for that purpose in Ohio. Similar data on Ohio nonroad construction areas are not available. However, nonroad construction would be expected to be a higher proportion in Ohio, as an urban state.

In any case, soil stabilization use of lime in Ohio is estimated to be between 30,000 and 77,000 tons. If one estimates 30 percent of the by-product to be active in stabilization, namely the calcium oxide or calcium hydroxide from the LIMB, HALT, or Coolside, then there is about 170,000 tons of stabilization-equivalent of the product available from one 800-MW generating unit. The TRW Slagging Combustor would produce about 220,000 tons of stabilization-equivalent. These amounts far exceed the state's estimated consumption and, therefore, this application was not considered further.

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5.0 TASK 5: BASELINE OF KNOWLEDGE CONCERNING STATE AND FEDERAL REGULATORY REQUIREMENTS FOR BY-PRODUCT DISPOSAL OR REUSE

5.1 SUMMARY

Federal and State environmental statutory requirements related to Ohio's initiative to develop and install clean coal combustion technologies, along with the status of existing and future regulations to deal with by-products, are discussed in this section. The different technologies do not have separate environmental regulations associated with the management and/or disposal of their combustion by-products; moreover, most of the environmental issues are the same for conventional combustion by-products.

Results of tests to characterize by-products from clean coal combustion processes have largely shown the by-products to be nonhazardous, as defined by the Resource Conservation and Recovery Act (RCRA). The recognition that large volumes of these low toxicity by-products will be produced from construction of commercial plants has triggered the necessity for (1) short-term disposal/storage options to be in place that will comply with State water quality criteria, and (2) acceleration of research on commercial outlets for the technically and economically feasible reuse of by-products in the long term. Regulatory concern, particularly at the State level, is focused on the long-term potential for release of toxic constituents from the by-product, and the rates at which leaching may occur in disposed or reused by-products.

The OEPA considers clean coal combustion by-products to be solid waste, but to date has granted exemptions to solid waste disposal requirements on a case-by-case basis. However, in the continued absence of a more substantial data base on by-product environmental impact from which to make scientifically based decisions, public pressure and regulatory policy will continue to support a conservative, high level of disposal protection, leading to a continued rise in disposal cost. By resolving the environmental impact of by-product disposal and developing an associated clear set of clean coal facility permitting guidelines, the state could facilitate decision making regarding large-scale commercial construction of new or modified Ohio coal-fired generating plants. These actions can take into consideration the surrounding states of Pennsylvania, Kentucky, and West

Virginia which have established differing positions on the regulation of these by-products. The ease of facility permitting within these states and Ohio can be a factor in future siting decisions by industry for commercial-scale construction projects. Current studies under the sponsorship of the federal Department of Energy may help toward resolving the environmental impacts under question.

Beneficial use of clean coal combustion by-products is essential as a more viable long-term option to land disposal, but environmental legislation is needed to provide a vehicle for increased market support of reuse options for the by-products.

5.2 INTRODUCTION

The purpose of this task is to review the effect of current and potential environmental regulations on the application of Ohio clean coal combustion by-product disposal or reuse and to provide a baseline of knowledge distilled from the various and numerous perspectives found within government and industry. Current Federal and State environmental statutory requirements germane to Ohio's initiative to develop and install clean coal technologies for the expanded use of Ohio coal are presented, and the state's regulatory compliance policy related to disposal activities is discussed. It is not the intent of this task to restate or explain the actual regulations which are publicly available and widely interpreted, but rather put into context the effects of regulations on the application of Ohio clean coal technology in the future.

Included throughout this section is a discussion of (a) regulatory policy in border states that could influence the ability of Ohio to attract construction of commercial clean coal technology facilities, and (b) future regulatory developments that are needed to provide greater incentives for disposal, reuse, and recycling of by-products by Ohio generators.

The individual clean coal combustion processes supported by OCDO and covered by this report are (1) advanced wet FGD, (2) advanced dry FGD, (3) FBC, and (4) LIMB. As reported in Chapter One, the general composition of by-products from these processes are similar. There are no separate environmental regulations for management and/or disposal of their combustion by-products; nor are there differing compliance strategies aimed at the different technologies. The main issue at the Federal and State level concerning disposal of clean coal combustion by-products is the same as the one for conventional combustion by-products, i.e., whether to designate the by-products as either hazardous or nonhazardous and the corresponding management/disposal practices based on this categorization.

5.2.1 Clean Coal Technologies

5.2.1.1 Advanced Wet Flue Gas Desulfurization

The solid by-products produced by burning coal with wet desulfurization systems include "scrubber sludge" and fly ash; the fly ash is collected separately from the sludge but is often added to the scrubber sludge for disposal purposes. As described in Chapter One on by-product characteristics, sludge composition varies as a function of the properties of the flue gas and the FGD design and operation. Environmental issues for the codisposal of the two by-products center around the migration potential of sulfates and trace elements, particularly heavy metals. Unlike the calcium-sulfur compounds, which are a direct result of the desulfurization process, trace elements originate primarily from the fly ash.

5.2.1.2 Advanced Dry Flue Gas Desulfurization

Most sodium- or calcium-based clean coal combustion by-products associated with these technologies will yield a somewhat alkaline leachate upon contact with ground water. Although none of the OCDO sponsored clean coal demonstrations use sodium-based injection systems, any future consideration of these systems would have to take into consideration the two orders of magnitude greater solubility of sodium injection by-products in water viz a viz calcium compounds. State water quality criteria could potentially be exceeded due to higher concentrations of TDS and sulfates associated with the more soluble sodium compounds (Dawson et al., 1987).

5.2.1.3 Fluidized Bed Combustion

FBC, involving the burning of coal in a fluidized bed of hot air and calcium-based sorbent, produces two basic solid by-products that are subject to land disposal regulation: fly ash and spent bed material. As

discussed in Chapter 1, the concentrations of FBC by-product leachate tested in numerous independent studies indicate the leachate falls within the national drinking water standards and is of better quality than conventional fly and bed ash leachate.

5.2.1.4 Limestone Injection Multistage Burner

As with other dry FGD systems, LIMB by-products, consisting of fly ash, unreacted sorbent, and calcium-sulfur reaction products, are more alkaline than conventional ash. Surface runoff that comes in contact with the leachate or by-product has the potential to exceed the state water quality pH standard of 6.5 to 9.0.

5.2.2 Waste Management Programs

The clean coal technologies identified above have generated national interest in terms of engineering more effective utilization of our high-sulfur coal resources and developing environmentally acceptable approaches to handling the by-products. Conventional best control technologies involving wet FGD systems produce a wet sludge that is a major economical and environmental drawback to their use. The federal Department of Energy (DOE) encourages the development of advanced dry FGD systems which can be more economical and produce a more easily managed dry by-product in less volume than wet systems (Harness, 1989).

DOE's Waste Management Program is concerned with ensuring that by-products produced in advanced coal combustion processes do not become an impediment to the application of these technologies. Recent emphasis of the program has been directed on characterizing the by-products from clean coal technology processes. Results of tests to date have largely put to rest the earlier concerns that such by-products might generally be found to be hazardous (Rubin, 1985). While these by-products have been shown to be nonhazardous under the definition provided by RCRA, the most important questions receiving study by the Waste Management Program center around the

degree of environmental impacts they represent (Harness, 1989). The three principal questions being addressed are as follow:

- What, if any, are the potential hazardous materials contained in and released from the by-product?
- How are such materials released from the by-products?
- At what rates are the potentially hazardous materials released?

States that regulate, or are planning to regulate, coal combustion by-products separately from solid waste, or as a subset of solid waste, have addressed these basic issues in either performance-based or design operating standards for land disposal facilities.

A broader regulatory concern associated with coal utilization technologies is the uncertainty regarding cross-media environmental impact; i.e., questions regarding whether coal combustion solid waste/by-product is a "sink" for any undesirable materials, that in the course of their reuse, recycling, or transfer result in an environmental problem being moved from one medium (air, water, or land) to another (Rubin, 1985). The current DOE studies may provide some data for eventually resolving this question.

The backfilling of surface coal mines with combustion by-products of the coal derived from such mines is seen by some states as a measure to minimize the number of disposal locations involved in the coal-energy-waste cycle. States such as Pennsylvania have promulgated regulations to provide for environmentally acceptable disposal of coal combustion by-products at permitted mines. Similar provisions enacted in Ohio, perhaps initially through experimental permits, is an option that should be evaluated further.

5.3 ENVIRONMENTAL REGULATIONS

5.3.1 Background for the Current Regulatory Environment

A variety of methods exist for managing and disposing of coal combustion by-products, and nearly 70 percent of all generating units in the U.S. provide for on-site management. Surface impoundments and landfills are the two waste management methods most commonly used by electric utilities, and these two methods are also the ones used by Ohio utilities for management of clean coal combustion by-products. Nationwide, 80 percent of coal combustion by-product is treated, stored, and/or disposed by means of land management, with the remaining 20 percent recycled or recovered (EPA, 1988).

EPA, expecting that most coal combustion by-products will continue to be disposed of on land, has promulgated Federal regulations for the management of solid wastes; these regulations incorporate the guidelines and requirements for land disposal of different categories of wastes, of which utility coal combustion by-products are included. OEPA generally considers clean coal combustion by-products to be solid waste, but exemptions have been granted on a case-by-case basis. Currently the status of waste classification in Ohio is more policy driven than rule driven, and future policy decisions on disposal of clean coal combustion by-products need to steer the regulatory process in a direction that will ensure successful implementation beyond the demonstration stage in Ohio.

5.3.1.1 Federal Regulations

Congress dealt with the expanding problem of solid waste management in legislation passed in the Solid Waste Disposal Act of 1965 and the Resource Recovery Act of 1970, but the first comprehensive statute dealing with these problems specifically was the Resource Conservation and Recovery Act of 1976. Amendments to these laws in 1980, 1984, and 1986 have added more detail for implementing a nationwide waste management program. To

achieve the goals of this program, EPA promulgated regulations for solid waste (nonhazardous) under Subtitle D of RCRA and for the handling and disposition of hazardous waste under Subtitle C. These regulations were codified in Volume 40, Parts 240 to 271 of the Code of Federal Regulations (40 CFR 240-271). Within these regulations, EPA established both technical standards for environmentally acceptable facilities and a program under which individual states may develop and implement their own programs; State programs may be more but not less stringent than the Federal criteria.

EPA specifically excluded high volume utility by-products from regulation as hazardous waste under Subtitle C of RCRA in 1980; and subsequently, findings from various studies continue to indicate that most coal combustion by-products do not exhibit any of the four hazardous characteristics defined in Subtitle C as toxicity, ignitability, reactivity, and corrosivity (EPA, 1988). EPA concluded that, while it has not done so, it prefers to regulate disposal of fly ash, bottom ash, boiler slag, and FGD by-products under Subtitle D, which requires mitigative measures such as liners, leachate collection systems, and ground-water monitoring systems to control leaching and migration of potentially hazardous constituents in order to reduce the likelihood of ground-water contamination. The ground-water protection criteria require that (a) leachate may not cause ground-water drinking supplies to exceed primary and secondary drinking water standards (40 CFR 142 & 143) beyond the waste boundary or a State-approved alternate limit; and (b) that the facility not adversely affect an existing or potential water supply source for domestic, agricultural, commercial, industrial, or other uses. Discharges to surface water may not adversely affect any existing or potential uses of that surface water.

Proposed revisions in 1988 to the RCRA solid waste regulations (40 CFR 257 & 258) establish this trend for land-based facilities by requiring ground-water monitoring, corrective action provisions, and location standards for new and existing solid waste disposal facilities. Ohio's regulations reflect this same philosophy and such measures as are necessary to reach an acceptable level of public assurance regarding safe drinking water supplies in areas of disposal in the State.

EPA has selected technical performance standards for the revised rules over uniform design and operating standards and methodology-based decision frameworks. High volume (ca. 56 million tons per year) utility by-product disposal requirements are being considered separately as part of EPA's rulemaking process. Clean coal combustion by-products are a subset of this general category and should be addressed in future rulemaking at the Federal level and then consistently passed down to the individual states for regulation.

5.3.1.2 State of Ohio Regulations

Clean coal combustion by-products are considered solid waste under the jurisdiction of the OEPA, Division of Solid and Hazardous Waste, with exemptions awarded, to date (June 1989), on a case-by-case basis. Nonhazardous solid waste is regulated primarily under Section 3734 and Chapters 27 and 37 of Section 3745 of the Ohio Revised Code with other pertinent sections referenced for air and water pollution control associated with land disposal of solid waste. Ohio's hazardous waste rules, Chapters 50 to 58, and 65 to 69 of Section 3745 of the Ohio Revised Code, exempt coal combustion by-products from regulation.

Ohio has a general exemption for nontoxic fly ash, which is not regulated as a solid waste; however, disposal of this by-product is subject to Ohio water pollution and air pollution regulations under the jurisdiction of the OEPA, Division of Water Pollution Control (Rotering, 1989). Utility fly ash is considered to be nontoxic and, therefore, is exempt from regulation as a hazardous or solid waste if its leachate does not exceed 30 times the levels specified in the Ohio Drinking Water Standards (Ohio Revised Code 3745-81-11(B)), shown on Table 5-1 (OEPA Policy 4.07, August 1988).

OEPA can waive certain disposal requirements provided the site hydrogeology and by-product leachate characteristics justify the decision. While conventional combustion technology fly ash and bottom ash were grandfathered as exempt waste under the solid waste rules, clean coal technology by-products were not recognized as the same by the OEPA and were

TABLE 5-1. OHIO WATER QUALITY STANDARDS FOR METALS

Parameter	[Ohio Revised Code 3745-81-11(R)] Ohio Drinking Water Standards mg/l	30 x Standard mg/l	Federal/State HW Criteria mg/l
Arsenic	0.05	1.5	5
Barium	1.00	30.0	100
Cadmium	0.01	0.3	1
Chromium	0.05	1.5	5
Lead	0.05	1.5	5
Mercury	0.002	0.06	0.2
Selenium	0.01	0.3	1

(OEPA, 1988)

grouped with municipal sanitary wastes as solid waste requiring disposal in a licensed landfill. The operator of a clean coal technology facility can petition for an exemption from this requirement. Such a variance has been issued in the past for two low-volume demonstration projects in the form of OEPA Director's findings and orders which include site-specific disposal requirements. On-site disposal at the Tidd Plant was granted by the OEPA Director upon approval of a ground-water monitoring plan for the site, whereas the LIMB project disposes of by-product at an approved off-site landfill.

House Bill (H.B.) 592 amended Ohio's solid waste law and calls for control of solid waste activities through a planning process initiated at the state level but administered at the county level (Ohio Revised Code 3734). A waste generated from the combustion of coal that is not combined with garbage, or a solid waste facility that disposes of waste generated exclusively by the owner of the solid waste facility (i.e., a utility's on-site disposal facility), is largely exempt from H.B. 592. New regulations for the design, operation and closure of solid waste landfills in Ohio will require liners, a leachate collection and removal system, and other design standards that will also apply to clean coal technology by-products by virtue of their present solid waste classification. The OEPA Division of Groundwater is also interested in seeing siting criteria established for all combustion by-products/wastes that currently do not fall within the category of solid waste. One option would be to consider siting criteria along the lines of hazardous waste facility siting criteria established by the Ohio Facilities Siting Board. Draft proposed criteria are being prepared in 1989 for the disposal of fly ash and clean coal technology by-products (Allen, 1989). The proposed criteria were not publicly available for consideration during the time of this report's preparation.

5.3.1.3 Surrounding States' Regulations

Surrounding coal-producing states such as Pennsylvania, Kentucky, and West Virginia have similar interests in developing and installing clean

coal technologies that provide for the expanded use of their states' coal resources. Because these states will compete with Ohio for large-scale commercial construction of new coal-fired generating plants, the nature of the state regulations to facilitate environmental permitting of these projects can be one of several factors that collectively steers an electric utility toward deciding to build in one neighboring state over another. These states' regulations for coal combustion by-products are summarized below for purposes of comparison (EPA, 1988).

Pennsylvania. Pennsylvania has written regulations specifically for the disposal of coal combustion by-product. Clean coal technology by-product is classified as a residual waste with on-site and off-site disposal permitted. If an operator has an active coal mining permit, the ash material can be disposed at the mine. Siting criteria for disposal of clean coal technology by-product require ground-water monitoring and leachate collection. Fly ash ponds require State and NPDES permits. Design standards include ground-water monitoring and leachate control (Socash, 1989).

Kentucky. Coal combustion by-products are "special wastes" regulated under Kentucky's solid waste rules. Clean coal technology by-products are categorized as residual waste which carry no special design standards for land disposal (i.e., liner or leachate control system). Clean coal technology by-product can be backfilled at mine operations. Surface water and ground-water monitoring are required (Jett, 1989).

West Virginia. Coal combustion by-products are regulated by the State's solid waste regulations, which require a permit for disposal. The siting criteria are the same as for sanitary landfills. Sites must meet leachate, waste confinement, and aesthetic standards, with specific requirements for ground-water monitoring (Chaney, 1989). The West Virginia Department of Energy currently (June 1989) has jurisdiction over the disposal of coal ash waste on mine property from which the coal originated; however,

the West Virginia Department of Natural Resources may take responsibility for these wastes in the future. Returning wastes to the mine site is seen as a beneficial use because it acts to neutralize acid drainage produced from mining operations (Politan, 1989).

5.3.2 Effects of Environmental Regulations On Ohio Clean Coal Technologies

EPA expects that the major portion of coal combustion by-products will continue to be disposed of on land, and that the potential for significantly increasing the amount of by-product utilization has an upward limit. A number of the processes supported by the Ohio Clean Coal Technology Program are expected to produce more solid waste on a per-ton-of-coal-burned basis than conventional wet-lime scrubbing. Therefore, trends for stricter environmental standards at land-based disposal facilities will affect increased volumes of by-product as advanced clean coal processes are chosen over conventional systems for construction.

Upward pressure is needed nationwide for enactment of state legislation that will facilitate the beneficial use of coal ash and raise the percentage of coal ash utilization. With each pound of sulfur dioxide removed by clean coal technology processes producing from 3 to 6 pounds of by-product, methods and regulations to provide for and facilitate the reuse of these by-products are critical to the commercial development of clean coal technology processes.

Long-term leaching and migration of coal combustion by-products and reused coal combustion by-products are the primary concern of State environmental compliance agencies nationwide. Such technical concerns are being addressed by the OEPA staff writing new performance standards and ground-water protection criteria. These are anticipated in the latter part of 1989.

5.4 FUTURE ENCOURAGEMENT OF BY-PRODUCT REUSE

With appropriate regulatory support, beneficial use of high volume, low toxic, clean coal technology by-products needs to become a more viable option to the traditional disposal of ash materials by landfilling. This is especially true since landfills are becoming more cost-prohibitive due to increased regulatory requirements imposed on them. For example, the cost of disposal of advanced combustion by-products is expected to reach the range of \$15 to \$20 per ton on a levelized basis in the next decade (EPA, 1987; EPA, 1988; Golden, 1988). As discussed in Chapter 4, the current market value for by-products containing flyash and calcium salts is low, and the markets are not well developed. Gypsum and sulfur have higher value but the market is limited with respect to economical shipping distances. There is currently little economic incentive to stimulate their utilization in the marketplace, but several factors can be optimized to play a key role in changing this situation, including the role of regulatory stimulation.

Figure 5-1 is a graphical representation of how these important factors--technology, economics, and regulatory requirements--are interrelated and share in this issue. This pyramid represents an evolution of society's experience with management of solid waste, and directly relates to the recognized problems associated with long-term handling of clean coal technology combustion by-products. The base of the pyramid represents conditions characteristic of past decades where high volume land disposal occurred due to low regulatory pressures and low disposal costs; technology for reuse/recycling was not generally available nor attractive primarily due to the low cost of disposal.

The second tier of the pyramid, indicative of the late 1980s, reflects increased incentives for reuse/recycling due to growing public and regulatory pressures, associated higher costs for land disposal arising from stricter landfill design and pollution control requirements, and advances in technology that increased applications for beneficial uses. The highest tier is the goal for the next decade in which ultimate disposal volume is

FIGURE 5-1. INCENTIVES FOR BY-PRODUCT REUSE
(modified from: Power Engineering, 1987)

minimized and reuse is maximized because improved technology opens up new market opportunities and/or drives reuse costs down relative to rising disposal costs.

Throughout the entire process, the overall benefits to the environment and the economy rise in concert with increased utilization of the wastes. Although the beneficial use of clean coal combustion by-product material is not widely practiced, greater emphasis on providing means of reuse should be encouraged through environmental studies to determine the impact of reuse options and through policy analysis of existing regulations. Environmental legislation geared toward beneficial use of clean coal combustion technology by-products will provide a vehicle for increased market support of reuse options. Precedent for this action was discussed in Section 4.4.5.3, wherein the State of Texas promoted a reuse market for calcium sulfate-based materials when it reclassified a calcium sulfate waste from a by-product to a coproduct, based on data that it was environmentally safe.

5.4.1 States' Policies

State environmental protection agencies, aware of limited land disposal capacity and the increased regulatory requirements imposed on these landfills, need to develop alternative guidelines for the disposal or reuse of relatively innocuous by-product materials. Some states adjacent to Ohio encourage beneficial reuse of these materials, including clean coal technology by-products. The Pennsylvania State legislature recently enacted an interim policy to address requests for exemptions from the residual waste permit requirements based on beneficial use determinations by the Bureau of Waste Management of the Pennsylvania Department of Environmental Resources (1987). This policy includes the beneficial use of residual waste including coal ash and clean coal technology by-products. In part, the policy requires that the operator provide the following information to the Department:

1. Chemical and physical characteristics of the material along with the quantity, quality, and source of the material to be used

2. A description of the proposed method of application or use of the material
3. A demonstration of the intended use showing that it will not adversely affect the public health, safety, welfare, and the environment.

If the use is approved, the request may

1. Be limited to the material used as to type, source, and amount
2. Be limited to a term for approval
3. Require submission of an annual analysis or other appropriate information to ensure the quality of the material to be used beneficially remains consistent with that stated in the approval.

The State of West Virginia also encourages the beneficial reuse of fly ash at surface mine operations. Fly ash is routinely applied to soils near surface mine operations to promote vegetative growth, mixed with backfill, and combined in coal refuse piles (Politan, 1989).

OEPA has taken a conservative approach to the beneficial reuse of clean coal technology by-products. OEPA believes that by-products such as LIMB wastes are considered solid waste and do not normally qualify unless proven otherwise. Concerns include environmental degradation of reused fly ash when used for purposes such as road bed aggregate where breakdown products, potential runoff, and sulfate contamination are not fully understood. Data needs on environmental impacts of erodability, freezing/thawing, and leaching of metals and sulfate to ground waters are factors influencing the OEPA decision-making process. OEPA will continue to be conservative until these issues are resolved to its satisfaction. There is no plan to deregulate these by-products across the board.

Kentucky does not recommend the reuse of fly ash materials (Jett, 1989).

5.5 CONCLUSIONS

Several factors influence the choice of land disposal versus reuse including supply and demand, cost, technical feasibility, and social issues. Further laboratory and field studies are necessary to understand the environmental impact associated with the beneficial use of clean coal combustion by-products. That information, in turn, can be used in regulatory decision-making to address reuse proactively and facilitate viable options consistent with environmental and public concerns.

Recommended actions, in order of priority, that can be taken by State officials and organizations such as OCDO are listed below:

- Sponsor in-field research of coal combustion by-products generated from Ohio coals (a) to better understand and quantify the leach rate, fate and transport of sulfates, and trace metals; and (b) to demonstrate the level of protection necessary to build public acceptance of disposal at land-based facilities.
- Sponsor environmental studies to determine the impact of reuse options and encourage policy analysis of existing regulations that impede or do not facilitate adoption of such options.
- Develop a permit for placement of low toxicity by-products that includes location criteria and level of performance measures to meet existing water quality standards. Promote the environmentally acceptable placement of this material in such locations as road embankments, structural fills, mine backfill, and road bases.
- Accelerate research on commercial outlets for the technically and economically feasible reuse of the by-products in the long term.
- Enact legislation or effect regulatory change to facilitate options for greater incentives for reuse and recycling of coal combustion by-products.
- Sponsor a multistate symposium of representatives from midwestern coal-producing states and generators to address

common regional issues and to focus on individual differences in each State's approach to reuse/disposal problems.

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