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Project Title: **FURTHER DEVELOPMENT OF A COPPER OXIDE
DESULFURIZATION AND NO_x REMOVAL SYSTEM**

ICCI Project Number: 96-1/2.1A-5
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ABSTRACT

This work supports continued development of the Copper Oxide process for controlling emissions of sulfur dioxide and nitrogen oxides from coal combustion. This advanced process utilizes a moving bed of regenerable sorbent to capture sulfur oxides from hot flue gas and recover the collected sulfur as a saleable by-product such as fertilizer, elemental sulfur, or sulfuric acid instead of producing large quantities of solid waste requiring disposal. At the same time, the sorbent catalytically reduces nitrogen oxides. Previous pilot studies have confirmed the process is capable of high removal efficiencies for both pollutants while firing high-sulfur Illinois coal; and previous economic studies have shown the process is an attractive alternative to conventional flue gas desulfurization technologies.

The current project builds on the successful pilot testing performed to date to advance the technical and economic basis for furthering commercialization of the process. This project includes:

- Review of potential for copper-catalyzed dioxin formation.
- Characterization of SO₃ removal efficiencies for and determination of resulting acid dew points in the desulfurized flue gas.
- Evaluation of byproduct recovery options for conversion of recovered SO₂ to sulfuric acid, elemental sulfur, or ammonium sulfate byproducts for sale.

In general, this work addresses technical issues peripheral to the main process which has been the focus of development efforts to date. These issues are important to eventual commercial acceptance of the process, and concurrent work in these areas in parallel with ongoing process development and scale-up through the U.S. Department of Energy LEBS program will hasten commercialization of the technology.

EXECUTIVE SUMMARY

The Copper Oxide process promises to be an economical and attractive flue gas desulfurization process for Illinois coals with medium to high sulfur content. The process uses a regenerable sorbent in a moving bed to simultaneously capture sulfur dioxide and catalytically reduce nitrogen oxides in flue gas. Regeneration of the sorbent then releases the sulfur dioxide in a concentrated stream for recovery. The sulfur dioxide is recovered as a byproduct such as fertilizer, elemental sulfur, or sulfuric acid for sale rather than generating large quantities of waste products as with some other FGD options.

The U.S. Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) has performed pilot scale parametric testing of the process which showed sulfur dioxide removals greater than 93% when firing a 2.6% sulfur Illinois coal. Over 90% NO_x removal was also realized. These results validated the process model and provided a basis for continued process development.

These results were confirmed by a pilot testing program at the Illinois Coal Development Park (ICDP) test facilities. In this program, a medium-scale Copper Oxide pilot plant was constructed and operated and which achieved SO₂ removals of 98% and NO_x removals approaching 100% with no ammonia slip. This pilot plant is an order of magnitude larger than the pilot plant at PETC and is one-tenth the size anticipated for commercial adsorber modules. Economic analysis indicated the process is competitive with other FGD technologies, particularly when NO_x removal is required.

The purpose of this study is to continue the development of the Copper Oxide process for controlling SO₂ and NO_x emissions from coal combustion. This work is focused on three areas important for commercial acceptance:

- Potential catalytic formation of dioxin in the process
- Removal efficiency of the trace amounts of SO₃ in the flue gas
- Options for production of salable byproducts from recovered SO₂

Assessment of the Potential for Dioxin Formation

Low temperature formation of dioxins in municipal waste combustion facilities has been found to be promoted by copper-catalyzed reactions, so the use of copper in the Copper Oxide flue gas cleanup process has been brought into question. The Copper Oxide process relies on contacting flue gas with a copper and copper oxide based sorbent to capture SO₂ from the gas. This has raised suspicions that concurrent reactions similar to those in municipal waste combustors might promote dioxin formation as an unintended side reaction in the Copper Oxide process.

Published literature suggests that use of copper sorbents for desulfurization in the Copper Oxide process are not likely to cause increased polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) formation in treated flue gas. High amounts of SO₂ in Copper Oxide process applications appear to provide protection against copper-catalyzed

PCDD and PCDF reactions. In addition, the γ -alumina supported copper oxide sorbent has been found to capture HCl instead of promoting Cl_2 formation, again protecting against PCDD and PCDF formation. Confirmation of these indications by direct measurement at the planned scale-up to a single commercial module test facility treating a slipstream of flue gas from coal-firing at a commercial site should be carried out.

Characterization of SO_3 Removal Performance

The Copper Oxide process was found to provide high removals of SO_3 and reduce levels in treated flue gas to below 2 ppm. For flue gas from typical boilers combusting high-sulfur coals, this would reduce acid dew points by about 50° F. The additional heat recovery made available would improve boiler thermal efficiencies by 1.4 percentage points, with cost savings of about 15 to 20 cents per MWh. Alternatively, lower acid dew points would minimize corrosion from acid condensation in downstream ductwork. This collateral advantage provides additional commercial justification for use of the Copper Oxide process to treat flue gases from combustion of Illinois coals.

Evaluation of Byproduct Options

In order to be an economically viable flue gas cleanup process, the Copper Oxide technology must include byproduct production technology to convert SO_2 removed from the flue gas to a saleable byproduct. There are three primary byproduct options: sulfuric acid, elemental sulfur, and ammonium sulfate fertilizer.

Sulfuric acid and elemental sulfur can be produced by applying existing commercially available technology. Sulfuric acid will be an attractive option for large facilities only, because the chemical plant involved is capital intensive. Elemental sulfur can be economically produced at a wider range of plant sizes, but the market price has been depressed by high levels of byproduct production in natural gas fields for a decade and the economics of this byproduct are strongly influenced by proximity to customers.

Ammonium sulfate is an attractive third alternative, particularly with the high value of this material when manufactured in the most desirable grade. It will be especially appealing to smaller installations which cannot afford a sulfuric acid plant or which are not situated to compete in the elemental sulfur market. While ammonium sulfate has been produced both as a byproduct as well as from virgin raw materials for a century, a complete process utilizing the SO_2 -rich offgas as a feedstock is not commercially available. Therefore, continued development of a process for producing ammonium sulfate fertilizer based on processing to produce concentrated ammonium sulfate solution in combination with commercially available crystallization technology is needed to enhance commercialization prospects.

OBJECTIVES

The purpose of this study is to continue the development of the Copper Oxide process for controlling SO₂ and NO_x emissions from coal combustion. This work is focused on three areas:

- Potential catalytic formation of dioxin in the process
- Removal efficiency of the trace amounts of SO₃ in the flue gas
- Options for production of salable byproducts from recovered SO₂

Specific objectives of the work are as follows.

Dioxin Formation:

Because copper has been shown to catalyze the formation of dioxins in flue gas from municipal waste combustion facilities, there may be concerns over the likelihood of similar catalytic reactions occurring in the copper oxide sorbent bed. An objective of this study was to review published information on copper-catalyzed dioxin formation to assess the potential for such side reactions during flue gas cleanup and to determine whether operating conditions in the sorbent bed might lead to dioxin formation.

SO₃ Removal:

The Copper Oxide process is primarily intended for removal of SO₂ and NO_x in flue gas from coal combustion, but it also offers the potential for removal of trace amounts of SO₃ also present in the flue gas. This added benefit would contribute to successful commercialization of the technology. Another objective of this study was to measure the extent of SO₃ removal achieved concurrently with SO₂ removal in the process and to quantify the impact on enhancing heat recovery from flue gas.

Byproduct Recovery:

To be an economically viable flue gas cleanup process, the Copper Oxide process must provide for recovery of SO₂ as a saleable byproduct instead of disposal as solid waste. Three byproduct options - sulfuric acid, elemental sulfur, and ammonium sulfate - have been identified as promising uses for the SO₂. Another objective of this study was to evaluate technologies for production and marketing of these byproducts.

INTRODUCTION AND BACKGROUND

The Copper Oxide process promises to be an economical and attractive flue gas desulfurization process for Illinois coals with medium to high sulfur content. The process uses a dry, regenerable sorbent in a moving bed to simultaneously capture sulfur dioxide and catalytically reduce nitrogen oxides in flue gas. Regeneration of the sorbent then releases

the sulfur dioxide in a concentrated stream for recovery. The sulfur dioxide is recovered as a byproduct such as fertilizer, elemental sulfur, or sulfuric acid for sale rather than generating large quantities of waste products as with some other FGD options.

Background

This process treats flue gas from the economizer by passing it through a moving bed of sorbent beads in a cross-flow adsorber. Spherical beads of an alumina substrate impregnated with copper oxide move downward as narrow beds contained within vertical screens which allow gas to flow horizontally through the bed. Sorbent flow is continuous, with fresh sorbent added at the top of the adsorber and spent sorbent removed at the bottom. Treated gas exiting the adsorber is sent to the air heater.

The primary function of the sorbent is to remove SO_2 from the hot flue gas. This occurs most efficiently at higher temperatures, so the flue gas is treated at the economizer exit temperature. The sorbent beads are also an effective catalyst for removing NO_x . By injecting ammonia upstream of the adsorber, NO_x is reduced to nitrogen and water vapor by selective catalytic reduction (SCR) reactions. Simultaneous NO_x reduction is not necessary for the desulfurization process, however, and the adsorber can be operated for SO_2 adsorption alone if NO_x reduction is not needed. Additionally, the moving bed acts as a filter and removes much of the flyash from the inlet flue gas stream. This reduces ash loadings in the air heater and the particulate removal device, improving performances of these systems.

Spent sorbent is removed from the bottom of the adsorber, screened to separate captured flyash, and then conveyed to a separate vessel for regeneration. In the regeneration system, the spent sorbent is contacted with a countercurrent flow of a reducing gas to desorb SO_2 which was removed from the flue gas. The sorbent flows downward as a moving bed in the regeneration vessel and the reducing gas flows upward through the descending bed. Regenerated sorbent is returned to the moving bed adsorber for reuse.

Natural gas (methane) can be used directly as the reducing gas. Because reactions with methane are endothermic, regeneration with methane requires preheating of the sorbent in a separate gas fired heater prior to regeneration. The preheating step can be avoided by using a mixture of hydrogen and carbon monoxide instead of methane. Reactions with this gas mixture provide sufficient heat for sorbent regeneration without preheating. This gas is also more reactive than methane, enabling a smaller regenerator size as well, but a gas-fired reformer is needed to produce the reducing gas from a mixture of natural gas and steam.

Regeneration recovers the SO_2 in a concentrated acid gas stream which is processed further in a sulfur recovery unit to produce a by-product for sale. SO_2 in the acid gas can be oxidized and absorbed in water in a contact sulfuric acid plant to produce commercial-grade sulfuric acid. Alternatively, the SO_2 can be reduced to elemental sulfur in a Claus plant.

A third alternative is to react the SO₂ with ammonia to produce ammonium sulfate fertilizer. Selection of the optimum byproduct would depend on site-specific economics.

Status of Process Development

Process development thus far has focused on the testing needed to establish primary process parameters for application of copper oxide FGD chemistry to a system utilizing a cross-flow moving bed adsorber and counterflow moving bed regenerator. This design minimizes pressure drops and sorbent attrition rates which had hampered process economics in development of earlier fluidized bed designs.

The U.S. Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) has recently tested the process in a pilot system which modeled the complete adsorption and regeneration process. A series of tests established performances for varying flue gas flow rates, sulfur concentrations, adsorber operating temperatures, and sorbent flow rates. Tests also examined sorbent regeneration parameters including regeneration temperatures, sorbent residence times, and regeneration gas flow rates. Regeneration was generally done with methane, although some tests were performed using hydrogen as the reducing gas. This work has been supplemented by bench-scale studies with a packed bed tube furnace which have resulted in improved understanding of process mechanisms and kinetics.

The PETC work was supported in part with funds from ICCI. The results of PETC testing are reported in the final technical report for ICCI project number 94-1/2.1A-11 entitled "Moving Bed Copper Oxide Desulfurization and NO_x Removal Process Development".

Results from the PETC pilot system tests and tube furnace studies validated the process model and provided a basis for continued process development. Test results demonstrated high sulfur dioxide removals, well over 90%, can be achieved when firing a 2.6% sulfur Illinois coal. Over 90% NO_x removals were also realized in the tests. Moderate flyash removals, on the order of 70%, were seen in the pilot tests. Economic studies have indicated the process is competitive with other FGD technologies, particularly when NO_x removal is required.

Development of the Copper Oxide process continued in a pilot program at the Illinois Coal Development Park in Carterville, Illinois. A larger scale pilot Copper Oxide pilot plant, equivalent to one-half megawatt in size, was constructed to treat flue gases generated in the test facility and further test process removals of SO₂ and NO_x. This pilot plant is an order of magnitude larger than the pilot plant at PETC and is one-tenth the size anticipated for commercial adsorber modules.

The work at the ICDP is partially funded by DOE through the Combustion 2000 program to develop a low emission boiler system.

EXPERIMENTAL PROCEDURES

This project consists of three separate investigations:

1. Assessment of the potential for dioxin formation
2. Characterization of SO₃ removal performance
3. Evaluation of byproduct options

In general, the work addresses technical issues peripheral to development of the main process which has been the focus of development efforts to date. These issues are necessary steps toward eventual commercial acceptance of the process, and concurrent work in these areas in parallel with ongoing process development will hasten commercialization of the technology.

Assessment of the Potential for Dioxin Formation

Low temperature formation of dioxins in municipal waste combustion facilities has been found to be promoted by copper-catalyzed reactions, so the use of copper in the Copper Oxide flue gas cleanup process has been brought into question. The Copper Oxide process relies on contacting flue gas with a copper and copper oxide based sorbent to capture SO₂ from the gas. This has raised suspicions that concurrent reactions similar to those in municipal waste combustors might promote dioxin formation as an unintended side reaction in the Copper Oxide process.

Investigations of municipal waste combustor dioxin formation have revealed that dioxins and closely related compounds, particularly polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF), are formed downstream of the combustion zone by heterogenous reaction of carbon compounds and inorganic chlorine reactants on flyash particles. In these reactions, molecular chlorine, Cl₂ is the reactive species for organic chlorination. It is formed from HCl originating from fuel chlorides via the Deacon reaction in which HCl in the gas is oxidized to Cl₂ by excess oxygen. This reaction is catalyzed by copper and copper oxide species present in the flyash particles.

Although formation of PCDD and PCDF is not appreciable in coal fired combustion facilities, flue gases from these facilities do contain sources of carbon, HCl, and excess oxygen. The addition of the Copper Oxide process to such facilities would place large quantities of copper compounds in contact with the hot flue gas.

The likelihood of this catalyzing PCDD and PCDF reactions was investigated by a technical review of the literature for studies of dioxin formation at waste combustion facilities and strategies for minimizing dioxin formation. This review involved identifying background chemistry, precursors, and conditions which facilitate PCDD and PCDF formation. Conditions in the Copper Oxide system were then compared to key factors identified in the literature.

Characterization of SO₃ Removal Performance

A collateral advantage of the Copper Oxide process is that it desulfurizes hot flue gas ahead of the air heater. Removal of sulfur compounds, particularly SO₃, lowers the acid dew point and allows additional heat recovery from the flue gas for enhanced power plant efficiency without creating corrosive conditions. The magnitude of SO₃ removal in the Copper Oxide process had not been quantified, and characterization is needed for projecting the additional heat recovery benefits attainable with the process.

This was done by sampling flue gas entering and exiting the adsorber in the pilot system at the Pittsburgh Energy Technology Center and measuring the levels of SO₃. A gas sampling and analysis procedure permitting the desired differentiation and sensitivity for SO₃ was used, and test runs were performed with both gas-fired and coal-fired system operation for characterizing SO₃ removal performance. In these tests, flue gas was spiked with SO₃ to levels typical of power plant operation.

Evaluation of Byproduct Options

The Copper Oxide FGD process, like other regenerable FGD processes, produces a concentrated stream of SO₂ which must be recovered in downstream facilities. Conversion of the SO₂ into a saleable byproduct instead of a solid waste is a key advantage of the process. Potential byproducts include:

- Sulfuric Acid
- Sulfur
- Ammonium Sulfate

Commercialization of the Copper Oxide process will require integration with byproduct production technology. An engineering evaluation was performed to examine commercial production processes, to determine overall domestic markets for the byproducts, and to evaluate application of these byproduct production processes to coal-fired power plants. This study is also applicable to other regenerable FGD systems that produce a concentrated SO₂ stream as well.

This study evaluated use of a contact acid plant for production of sulfuric acid, a Claus plant for production of elemental sulfur, and an ammonia neutralization plant for production of ammonium sulfate.

RESULTS AND DISCUSSION

Assessment of the Potential for Dioxin Formation

A literature search was performed to obtain published data on the chemistry of dioxin formation in flue gases. A number of relevant references were found and are listed in the References section.

This information suggests conditions in the Copper Oxide process may not be especially favorable for formation of dioxins or related compounds, in particular polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF). The effective temperature range for copper oxide-catalyzed formation of PCDD and PCDF is reported to be 250 to 400°C, with a maximum formation rate occurring at 300°C. The design operating temperature of the copper oxide sorbent bed is preferably 750° F (400° C) for best desulfurization performance, and temperatures will typically be above 650° F (350° C) due to rapidly declining performances at lower temperatures. This is at the upper extreme of the effective PCDD and PCDF formation range. Further, reaction times are limited by the relatively short flue gas residence time of less than 2 seconds in the copper oxide bed.

More importantly, the presence of SO₂ was reported to significantly inhibit PCDD and PCDF formation. Little PCDD and PCDF is found in emissions from coal-fired utility power plants, while substantial PCDD and PCDF formation has been observed at municipal waste combustors. Co-firing coal with refuse has resulted in insignificant amounts of PCDD and PCDF which would otherwise be expected to form. A key factor has been shown to be the sulfur/chloride ratio. Municipal waste combustors typically have S/Cl ratios of about 0.2, which is an order of magnitude less than ratios for coal combustion. This is also supported by reports that low PCDD and PCDF emissions from coal combustion are not a result of a smaller amount of copper in coal as compared to municipal waste, indicating that copper is not a limiting factor in the observed differences.

SO₂ was shown to reduce Cl₂ to HCl in a homogeneous gas-phase reaction within the PCDD and PCDF formation temperature window. This converts Cl₂ which may have been produced via a copper-catalyzed Deacon reaction back to the inactive HCl species. SO₂ also reacts with the copper Deacon catalyst, sulfating it to CuSO₄. This step effectively deactivates the catalyst for initial production of Cl₂. As a result, SO₂ causes a depletion of the Cl₂ reactant necessary for organic chlorination reactions and suppresses PCDD and PCDF formation.

These reports suggest that use of copper sorbents for desulfurization in the Copper Oxide process are not likely to cause increased PCDD and PCDF formation in treated flue gas. High amounts of SO₂ in Copper Oxide process applications appear to provide protection against copper-catalyzed PCDD and PCDF reactions. In addition, the γ -alumina supported copper oxide sorbent has been found to capture HCl instead of promoting Cl₂ formation, again protecting against PCDD and PCDF formation.

Confirmation of these indications by direct measurement was planned, but testing could not be carried out at either the ICDP or the PETC pilot facility. Sustained steady state operation of the pilot plant while firing high-sulfur, high-chloride coals is needed to provide

representative conditions for qualitative flue gas monitoring of PCDD and PCDF. It was concluded that more representative and more reliable testing would better be accomplished at the planned scale-up test facility treating a slipstream of flue gas from coal-firing at a commercial site.

Characterization of SO₃ Removal Performance

Several test runs to measure SO₃ removals were completed at the PETC pilot plant. In testing with flue gas from natural gas firing, inlet SO₃ levels of 46 ppm were reduced to outlet levels of 1.8 ppm, a reduction of 96% across the Copper Oxide adsorber. Testing with coal firing resulted in SO₃ reductions of 73%, with inlet levels of 6 ppm and outlet levels of 1.6 ppm. The lower percentage removals were attributed to the lower inlet level, as comparable outlet concentrations were observed in both tests.

These SO₃ removals lowered the acid dew point to about 250° F, a reduction of approximately 50 degrees F from the typical flue gas 300° F acid dew point. This reduction allows additional heat recovery from the flue gas and an attendant improvement of 1.4 percentage points in boiler efficiency. In new installations, the smaller flue gas volumes at the lower temperature would enable downstream equipment to be 8 to 10% smaller. The lower gas volumes also reduce auxiliary power requirements by 1.3 percentage points.

These results show that utilization of the Copper Oxide process for flue gas cleanup enables added economic benefits of improved plant thermal efficiencies. At a fuel value of \$1.00 per MBtu, the increased efficiencies translate to cost savings of 15 to 20 cents per MWh. Further, for new facilities, capital savings could be realized in downstream flue gas equipment.

Evaluation of Byproduct Options

Offgas from regeneration of the sulfated copper oxide sorbent with methane exits the process at approximately 850 to 900° F and essentially atmospheric pressure and has the following stoichiometric composition:

38% SO₂
42% H₂O
21% CO₂

The offgas could also contain trace amounts of flyash particulates carried over with the spent sorbent or unreacted methane from incomplete regeneration.

SO₂ in this stream can be converted to sulfuric acid, elemental sulfur, or ammonium sulfate for sale in the commercial marketplace. Production of other specialty byproducts is also possible, but would have limited applicability due to small or unique markets. Examples

would include production of purified SO_2 gas or production of steep acid (sulfurous acid) produced and used internally at corn processing plants.

Sulfuric acid can be produced using commercially available technology as shown in Figure 1. The production process first oxidizes SO_2 to SO_3 in a four-pass catalytic converter. Gas is cooled between passes to improve conversions of SO_2 . SO_3 produced in the converter is contacted with concentrated acid where it is absorbed and reacted with water and form sulfuric acid. This resulting concentrated acid is then diluted with water to produce the commercial strength 66° Be sulfuric acid.

Pretreatment of offgas from the Copper Oxide process would be required to provide the clean, dry feedgas required by the contact acid process. In the pretreatment step, excess moisture that would dilute the acid is condensed and dust that would foul the catalyst is removed. Pretreatment also cools the feed gas so that catalytic conversion reactions are not inhibited. This process would be similar to pretreatment normally provided for metallurgical contact acid plant applications which produce acid from ore roaster offgas.

A 500 MW boiler firing 3% sulfur Illinois coal would generate about 23,000 lb/hr SO_2 in the flue gas. If all the SO_2 were removed in the desulfurization process, byproduct acid production would require a 420 ton per day acid plant and annual acid production at a 65% capacity factor would be 100,000 tons per year. This production capacity is small for commercial contact acid plants, which tend to be over 1,000 ton per day to realize economies of scale. Since acid plants are capital-intensive, economic production of sulfuric acid would tend to be favored only by larger Copper Oxide installations.

The market for byproduct sulfuric acid is large, as shown in Figure 2. Annual domestic acid production approaches 50 million tons. Most of this production, however, is by captive acid plants in the fertilizer industry producing acid for internal consumption. Shipments to external customers is approximately 13 million tons per year. As shown in Figure 3, the value of sulfuric acid in the domestic market is about \$50 per ton H_2SO_4 . This value is equivalent to \$77 per ton of SO_2 removed. Annual production from the example 500-MW facility would account for about 0.2% of the total domestic market or about 0.8% of the interplant shipments; and it would generate an annual revenue of \$5,000,000.

Elemental sulfur can be produced from the recovered SO_2 in offgas from the Copper Oxide process using a commercially-available Claus plant as shown in Figure 4. The Claus reaction requires a 2:1 mixture of H_2S and SO_2 , so some of the SO_2 in the offgas must first be hydrogenated to form the necessary H_2S . Methane would be utilized as the reducing gas and hydrogen source. Sulfur vapor formed in the hydrogenation and initial thermal reaction step is condensed, and the remaining gas is sequentially reacted in a multi-stage reactor with interstage sulfur condensation. Sulfur is collected and stored in molten form.

Pretreatment of offgas is also required for sulfur production. Excess moisture must be removed from offgas to minimize the volumes of gas handled in Claus process reactors and

sulfur condensers. This minimizes process equipment size and optimizes plant capital costs. In addition, water is a product of Claus reactions so moisture removal enhances conversions.

For a 500 MW boiler firing 3% sulfur Illinois coal and capturing about 23,000 lb/hr SO₂ from the flue gas, a 140 ton per day Claus plant would be needed. Annual elemental sulfur production at a 65% capacity factor would be 33,000 short tons per year. This production capacity is large for commercial Claus plants, but within the size range of existing commercial units. Most Claus plants are under 50 tons per day, but multi-train installations with capacities of 1,000 tons per day can be found in natural gas sweetening applications in Canada.

The market for byproduct elemental sulfur is also large, as shown in Figure 5. Annual domestic sulfur consumption totals about 13 million short tons, most of which is used for production of sulfuric acid in sulfur-burning contact acid plants. Sulfur had historically been mined at Frasch plants in Louisiana to yield virgin sulfur, but this production has been steadily displaced by recovery of sulfur from sour petroleum and natural gas. Today, virgin production accounts for little more than one-fourth total annual consumption.

As shown in Figure 6, sulfur prices have fallen from peak levels of nearly \$100 per ton and are now at about \$30 to \$50 per ton as a result of importation of large quantities of recovered sulfur from Alberta, Canada. This pricing spread reflects a premium for molten sulfur shipped to regional markets compared to lower values for recovered sulfur shipped long distances in solid form.

Annual production from the example 500-MW facility would account for about 0.3% of the total domestic sulfur market. Much of this market is already served by byproduct recovery sources and might be difficult to economically displace. However, a 500-MW facility would still represent only about 1% of virgin Frasch sulfur production. Using a median sulfur value of \$40 per short ton, equivalent to \$20 per ton of SO₂ removed, byproduct production of elemental sulfur would generate an annual revenue of \$1,300,000.

Recovered SO₂ in Copper Oxide offgas can be converted to ammonium sulfate fertilizer as shown in Figure 7. The first step in the process is production of an ammonium sulfate solution by absorption of the SO₂ in water, reaction with ammonia, and oxidation to sulfate. This technology is related to currently available processes, but application to the concentrated SO₂ offgas stream is still under development. The resulting concentrated ammonium sulfate solution is then crystallized in commercially available crystallizer systems to yield a preferred large-granular size dry product.

A 500 MW boiler firing 3% sulfur Illinois coal would produce 570 tons per day of dry ammonium sulfate with an annual production of 135,000 tons per year at a 65% capacity factor. This capacity would be extremely large for ammonium sulfate production facilities, exceeding the capacities of the largest ammonium sulfate crystallizers. The process scale for ammonium sulfate production is more suited for smaller Copper Oxide installations.

The market for byproduct ammonium sulfate, shown in Figure 7, is about 2.7 million tons per year. This market is comparatively small compared to the ammonium sulfate production possible at larger coal-fired power plants. For example, the potential production from a 500 MW plant firing 3% sulfur coal would equal 5% of this total domestic market. This also makes ammonium sulfate byproduct production more suited to smaller installations.

As shown in Figure 9, ammonium sulfate is a high-value byproduct with prices at about \$85 per ton. This value reflects a weighted average of standard commercial grade and the preferred, higher-valued large-granular grade. These two grades differ only in physical size. A value of \$90 per ton of ammonium sulfate is equivalent to \$186 per ton of SO₂ removed. At these average prices, a smaller 100 MW plant using 3% sulfur coal and producing ammonium sulfate byproduct would generate revenues of \$2,400,000 from byproduct sales.

The smaller size of ammonium sulfate byproduct facilities coupled with the high byproduct value, particularly in premium grades, make ammonium sulfate appealing to smaller Copper Oxide applications which could not justify capital-intensive byproduct facilities such as sulfuric acid systems. Continued commercialization of this technology is therefore needed.

CONCLUSIONS AND RECOMMENDATIONS

Assessment of the Potential for Dioxin Formation

Published literature suggests that use of copper sorbents for desulfurization in the Copper Oxide process are not likely to cause increased PCDD and PCDF formation in treated flue gas. High amounts of SO₂ in Copper Oxide process applications appear to provide protection against copper-catalyzed PCDD and PCDF reactions. In addition, the γ -alumina supported copper oxide sorbent has been found to capture HCl instead of promoting Cl₂ formation, again protecting against PCDD and PCDF formation. Confirmation of these indications by direct measurement at the planned scale-up test facility treating a slipstream of flue gas from coal-firing at a commercial site should be carried out.

Characterization of SO₃ Removal Performance

The Copper Oxide process was found to provide high removals of SO₃ and reduce levels in treated flue gas to below 2 ppm. For flue gas from typical boilers combusting high-sulfur coals, this would reduce acid dew points by about 50° F. The additional heat recovery made available would improve thermal efficiencies by 1.4 percentage points, with cost savings of about 15 to 20 cents per MWh. Alternatively, lower acid dew points would minimize corrosion from acid condensation in downstream ductwork.

Evaluation of Byproduct Options

In order to be an economically viable flue gas cleanup process, the Copper Oxide technology must include byproduct production technology to convert SO₂ removed from the flue gas to

a saleable byproduct. There are three primary byproduct options: sulfuric acid, elemental sulfur, and ammonium sulfate fertilizer.

Sulfuric acid and elemental sulfur can be produced by applying existing commercially available technology. Sulfuric acid will be an attractive option for large facilities only, because the chemical plant involved is capital intensive. Elemental sulfur can be economically produced at a wider range of plant sizes, but the market price has been depressed by high levels of byproduct production in natural gas fields for a decade and the economics of this byproduct are strongly influenced by proximity to customers.

Ammonium sulfate is an attractive third alternative, particularly with the high value of this material when manufactured in the most desirable grade. It will be especially appealing to smaller installations which cannot afford a sulfuric acid plant or which are not situated to compete in the elemental sulfur market. While ammonium sulfate has been produced both as a byproduct as well as from virgin raw materials for a century, a complete process utilizing the SO₂-rich offgas as a feedstock is not commercially available. Therefore, continued development of a process for producing ammonium sulfate fertilizer based on processing to produce concentrated ammonium sulfate solution in combination with commercially available crystallization technology is needed to enhance commercialization prospects.

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Figure 1

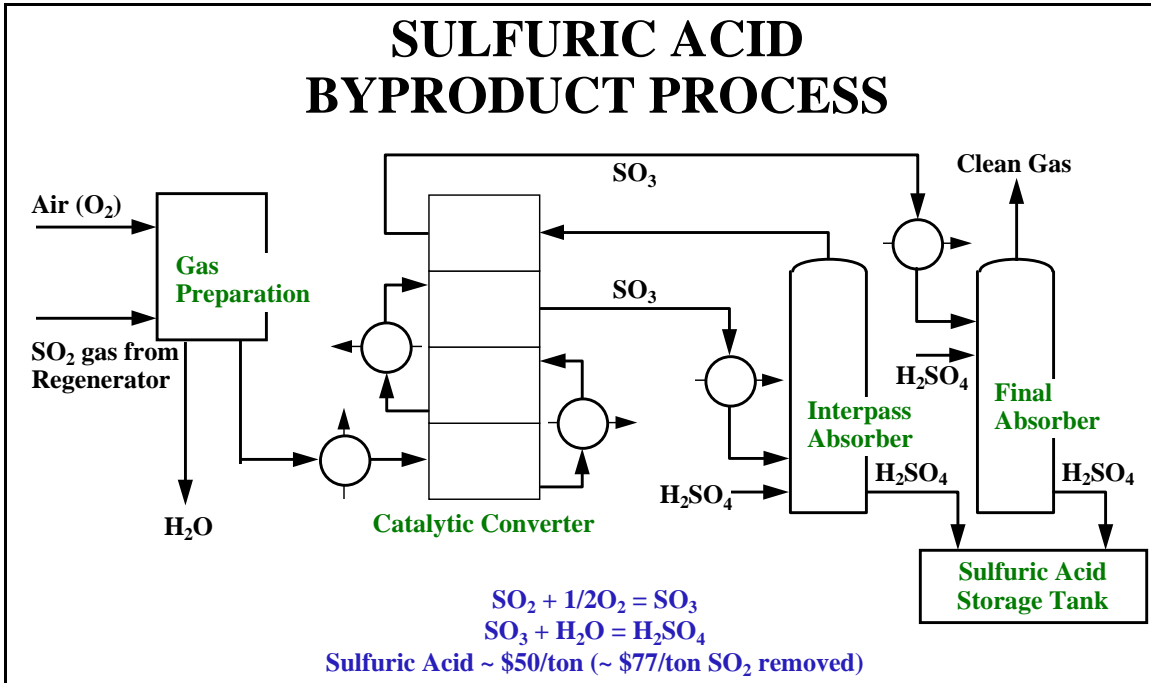


Figure 2

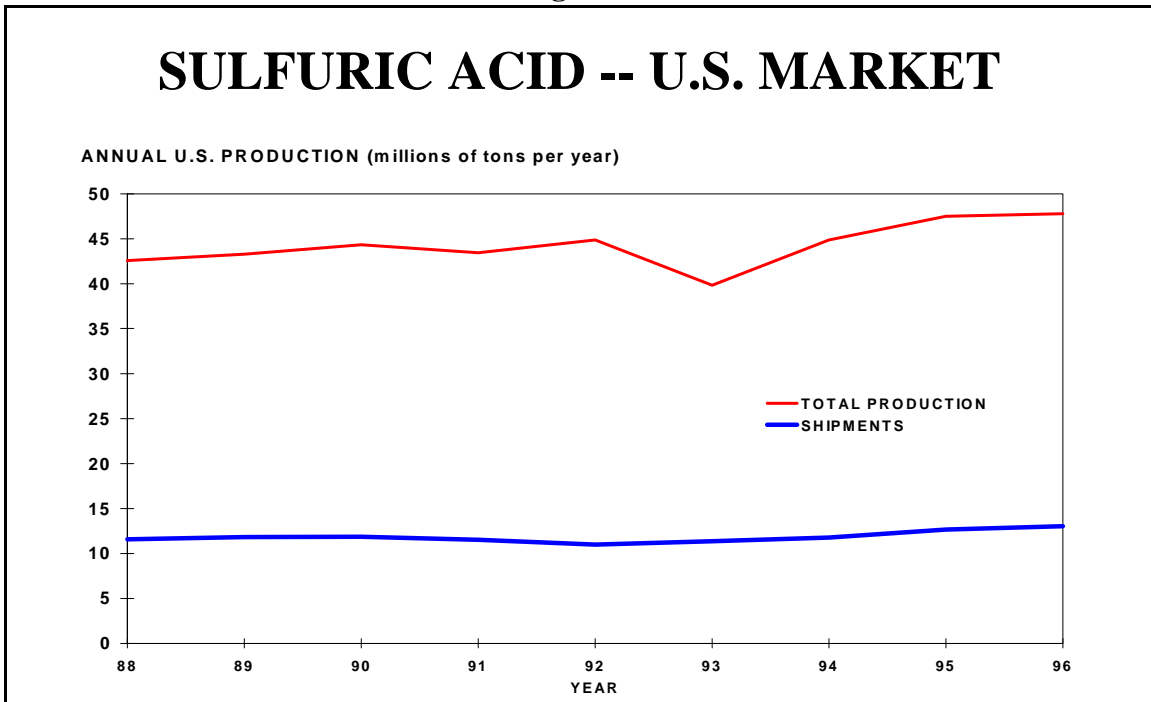


Figure 3

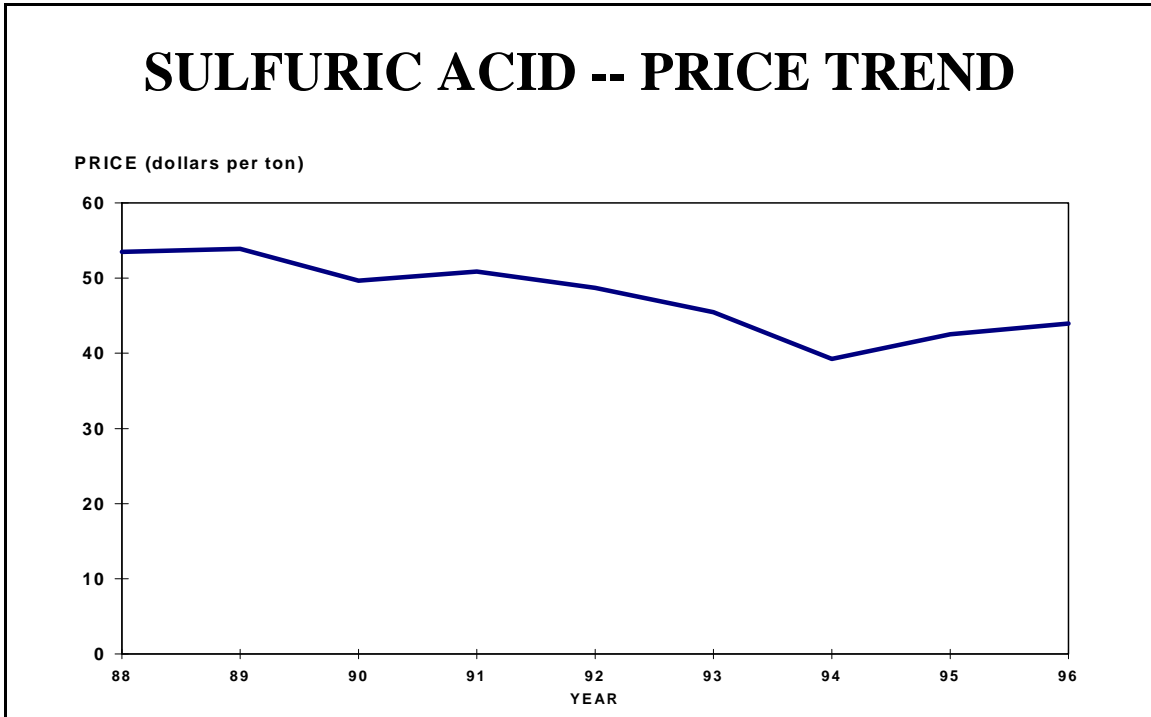


Figure 4

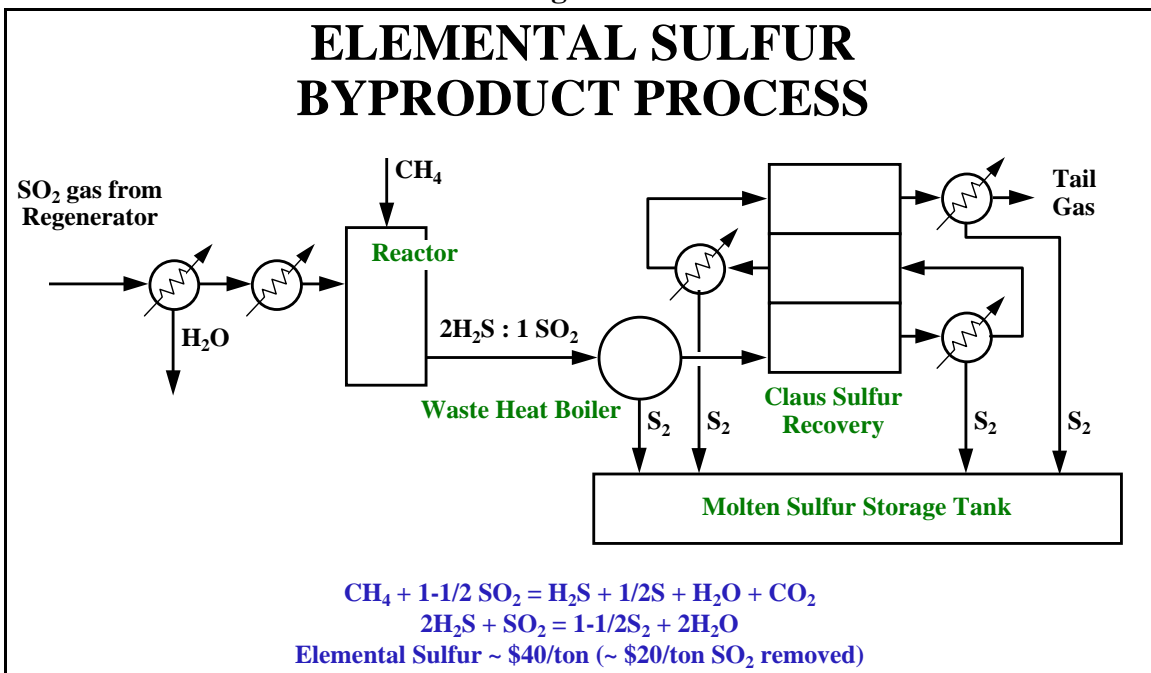


Figure 5

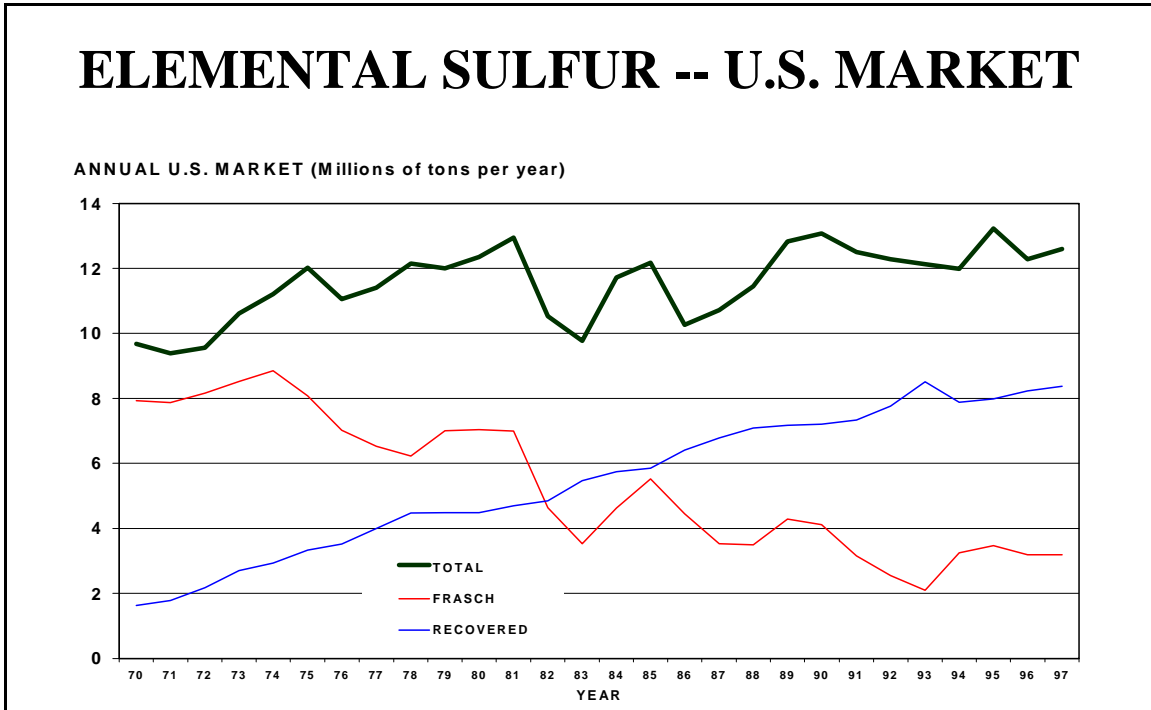


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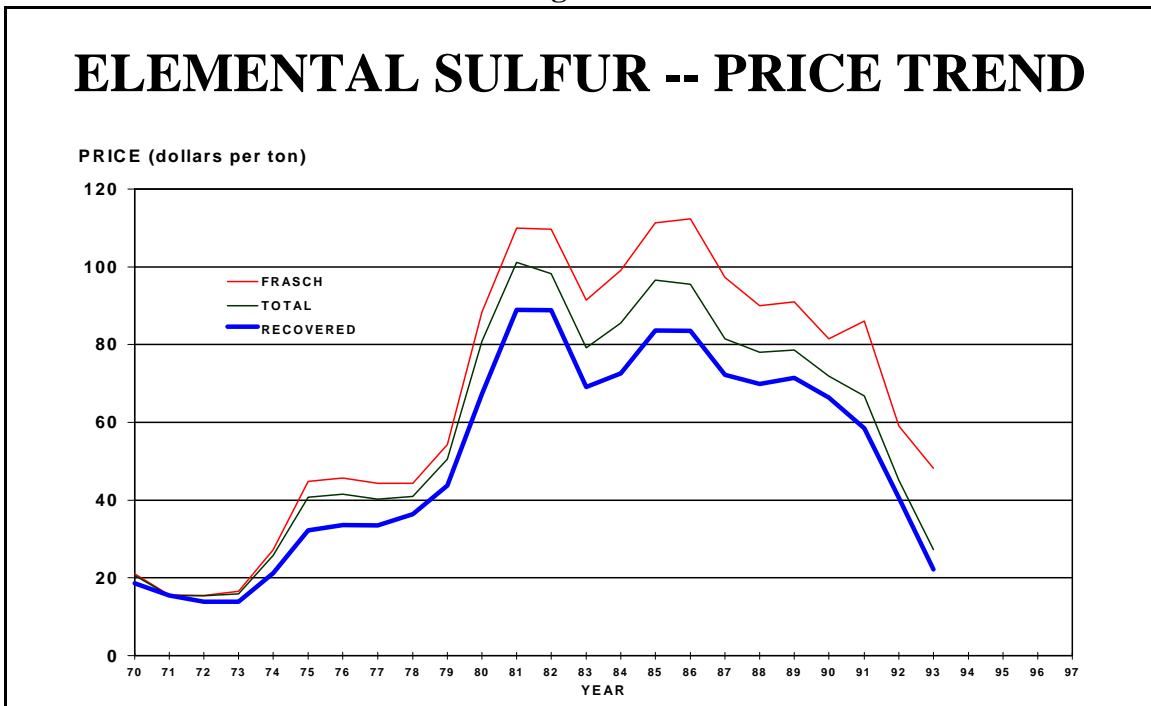


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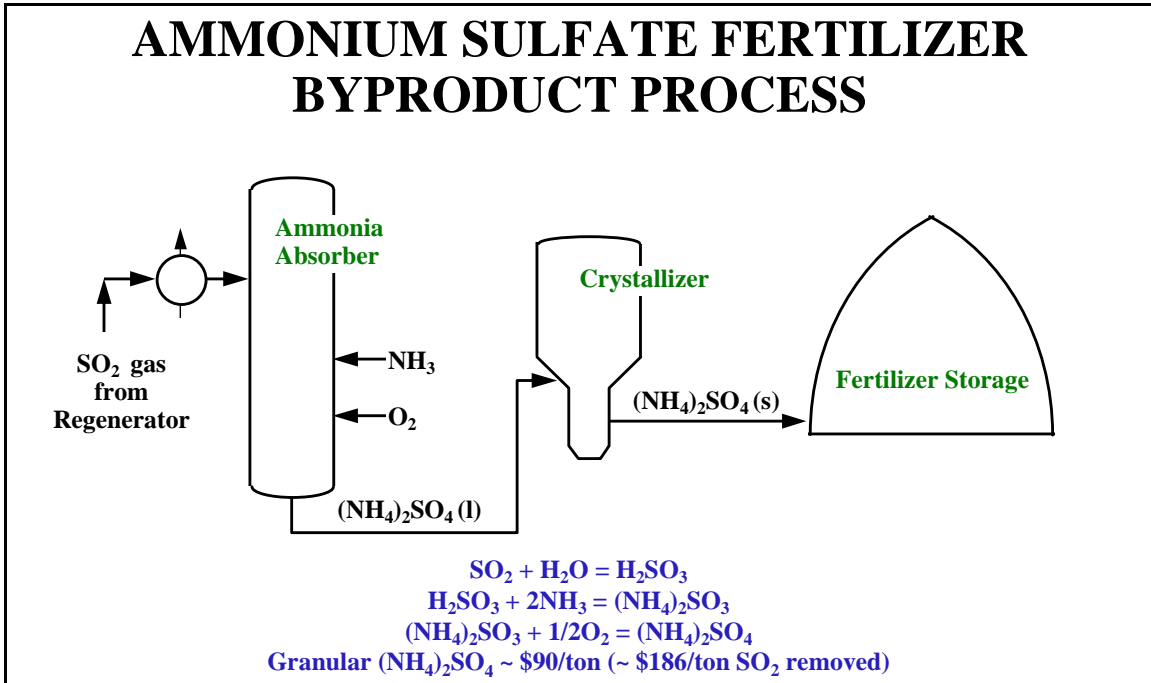


Figure 8

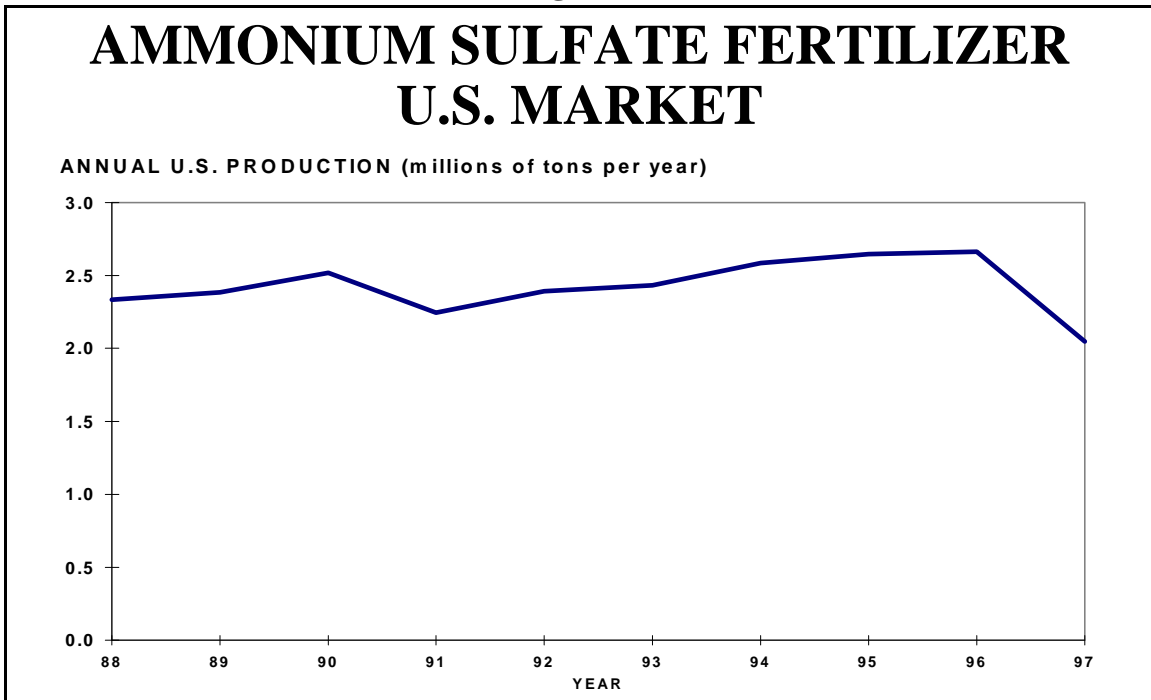
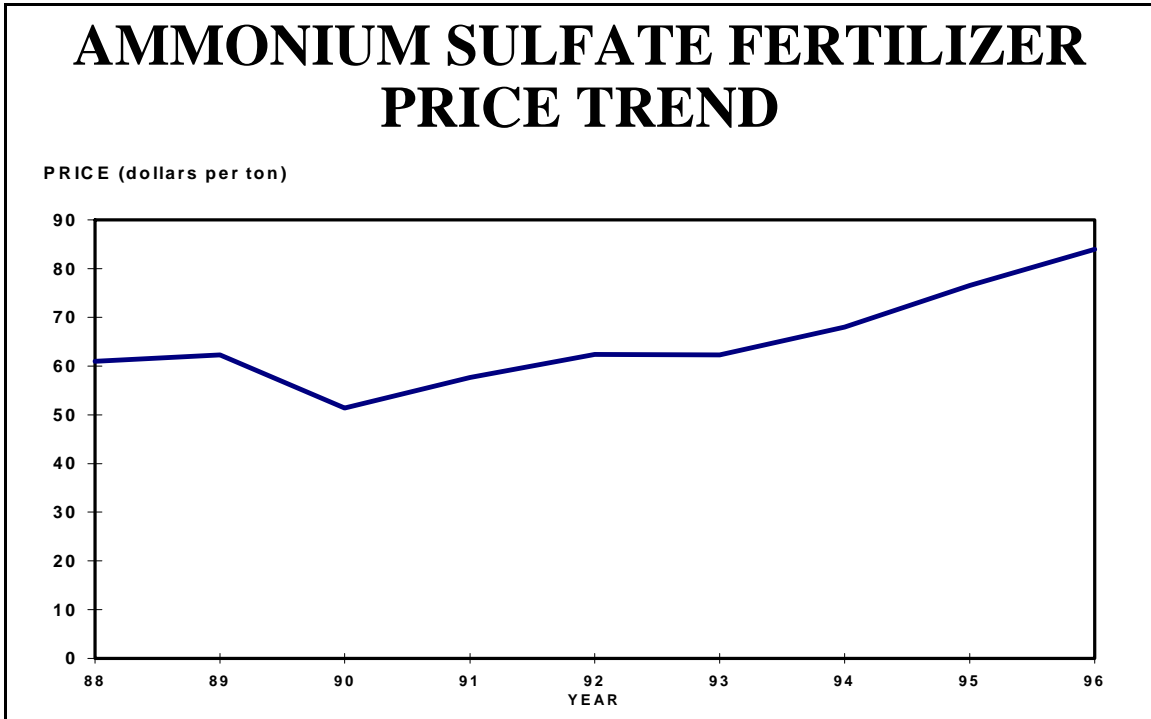


Figure 9



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