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Glass Science Tutorial: Lecture #4, Commercial Glass Melting and Associated Air Emission Issues

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Prepared for the U.S. Department of Energy
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MASTER

**Westinghouse
Hanford Company**

Richland, Washington

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January 24 - 25, 1994

Commercial Glass Melting and Associated Air Emission Issues

I - Commercial Glass Industry

Introduction (60 - Slides)

Commercial Glass Industry Segments & Melting Requirements

Container

Flat

Fiber Glass

Specialty / Press & Blown

Glass Compositions & Raw Materials

Commercial Oxide Families

Production / Economic Issues

Furnace Types

Segment Melting Requirements

Regenerative, Direct Fired, All-Electric, Advanced (SEG-MELT, Sorg, Lo-NOx, AGM, P-10)

II - Furnace Design / Construction Practices

Commercial Operation Objectives

Output, Quality, Continuity, Maintenance

Complete Furnace Rebuild (171 - Slides)

Melt Basin Functions

Superstructure / Crown

Exhaust Systems

Refractory Selection / Practices

Construction

Binding Steel, Insulation, Cooling

Heat Up / Cool Down Issues

III - Melting Furnace Operation

Fuel / Temperature Distribution

Melting Process (2 Dimensional)

Convection (Liquid / Gas Phases)

Electric Boosting / Bubblers

All Electric Blanket (20 -Slides)

(Cold Top / Glow Top / Mixed Melter)

Raw Material Choices / Issues

Furnace Operation Issues

Issues Relative to Air Emissions

IV - Energy Input Methods / Controls

Melting Control (32 - Slides)

Energy Sources / Considerations

Natural Gas, Electric, Oils, Coal / Coke

Air / Oxygen

Temperature Monitoring / Control Instrumentation

Charging / Level Control

Waste Heat Recovery / Agglomeration

Instrumentation, Combustion , Boost (55 - Slides)

Batch / Raw Material Preheating

P-10

January 25, 1995

V - Air Legislation / Regulations

Glass Industry Environmental Concerns

Air, Water, Solid, Employee Issues

Furnace Emissions

CAAA (12 - Slides)

NO_x Oxy-Fuel

SCAQMD NO_x Regulation Evolution - RECLAIM

VI - Soda Lime / Emission Mechanisms

Particulate

SO_x - Fuel, Batch Material Origin

NO_x - Thermal

Combustion Issues

EPA - ACT Reduction Technologies

Volatile / Condensable Studies

Sulfates, Borates

Equilibrium Studies / Future Issues

VII - Post Furnace Emission Controls

Capture Control (Costs , Efficiency, Operation / Maintenance)

Particulate

Bag House, E.P., Scrubber

SO_x

Wet / Semi-Dry / Dry Scrubber

Mass Balance / Batch Redox

NO_x

Combustion Options (Flue Gas Recirculation, Staged Combustion)

SCR / SNCR (NH₃ / Urea)

Gas Reburn

Batch Options

CO / VOC's

Available (Contacting) O₂ > 1200 °F

Recycling Issues

Particle Size (Handling / Storage / Mixing)

Chemical Consistency

Agglomeration

(Briquetting / Pelletizers / Pin Mixers)

Contamination

Condensates / Slags / Captured Particulates

VIII - Un-Addressed Subjects, Misc. Questions & Discussion

LLW Specifics / Concerns

General Questions & Review

January 24 - 25 1995
Westinghouse Hanford Corporation Presentation
Support Documents

Picture of Glassware

An Over View of the Glass Industry and its Natural Gas Use
C. Philip Ross

AP-42 Glass Manufacturing

Commercial Glass Compositions

Typical hollow ware glass furnaces

Glass Melting/Formation

* "FMC Treatment of Segregation Data"

Bill Brunig (FMC Corp.)

Review of three-dimensional mathematical modeling of Glass melting
R. Viskanta (Purdue University)

Stack Opacity Meter Diagram

Particulate Reduction From Various Type of Glass Furnaces
Donald J. Keifer (United McGill Corp.)

Control of Emissions from a Container Glass Furnace
A.J. Teller and J.Y. Hsieh
Walter Van Saun Latchford Glass

Strategies for Complying with PM-10 and related air quality requirements
William Gregg (MikroPul Environmental) Systems

Using cartridge filters for fluid bed processes
Tim Smith (Vector Corp.)

Meeting tougher pollution requirements:
Electrostatic precipitators for combustion and drying processes
Kevin Kaff (M-E-C Company)

Methods of treating gaseous emissions from glass furnaces
G KlampLurgi (GmbH)

NOx Control For Glass-Melting Tanks
Donald K. Fleming (Institute of Gas Technology)
F. Richard Kurzynske (Gas Research Institute)

Denox Installation Success For Swiss Container Plant

Measurable Success For LoNO_x Melter Six Years On

Richard Sims (Sorg Engineering)

Application of Gas Reburning Technology to Glass Furnaces for NO_x Emissions Control

D.F. Moyeda, R. Koppang (EER Corp.)

Oxy Fuel Glass Furnaces & Air Pollution Control Systems

NO_xOUT Process Description - NALCO Fuel Tech

NO_x Reductions Using UREA

C. Philip Ross

Oxy-Fuel Combustion Calculations Spread Sheet

Part 1: Emissions Concerns for Glass Manufacturing

Linda E. Jones (NYS Col. of Ceramics Alfred Univ.)

Microstructures of Silica and Magnesia Refractories and the Corrosion in Glass Tank Furnaces

Akira Yamaguchi (Yaikabutsu Overseas)

United States Patent

Bryant (United McGill)

Reactive vaporization of sodium tetraborate with water vapour

M. H.V. Fernandes (Univ. of Aveiro, Aveiro Portugal)

M. Cable (University of Sheffield, Sheffield, UK)

Particulate emission control and raw material preheating

Peter Larsson (Edmeston AB)

Recycling Electrostatic Precipitator Dust

D. Boothe & Co.

Understanding and applying compaction - granulation

Christian Fayard

EPA Handbook Control Technologies for Hazardous Air Pollutants

The Reactor Filter System: Air Toxics Control For Soil Thermal Treatment Processes

N.C. Widmer and J.A.Cole (E. E. R. Corp.)

Flow of Particulates

Calculations Involving Ideal Gas Law

"FMC Treatment of Segregation Data" - [Brunig 2/2/78]

Example DATA

<u>X</u>	<u>X_D</u>
25	28
26	
24	
20	19
18	
17	
16	18
15	
18	
16	15
19	
18	
20	21
21	
22	
21	21
24	
26	
25	23
27	

N = 27

S_{total} = 3.790

X_A = 20.85

ANOVA Table

Source	degree of Freedom dF	Sum of Squares	Mean Square	Confidence Factor
Trend	N - 1 - D	(n - 1) * S ²	MS _T	(F)
Duplication	D	$\frac{1}{2} \times \Sigma (X - X_D)^2$	MS _D	
Total	N - 1	Trend + Dupl.		

Source	degree of Freedom dF	Sum of Squares	Mean Square	Confidence Factor
Trend	19	363.4	19.12	13.37
Duplication	7	10	1.43	
Total	26	373.4		

Sum of Squares

$$SS_{\text{trend}} = (N-1) \times S^2 = (26) (3.790)^2 = 363.4$$

$$SS_{\text{dupl.}} = \frac{1}{2} \Sigma (X - X_D)^2 = 10$$

$$SS_{\text{total}} = SS_{\text{total}} - SS_{\text{total}} = 373.4 - 10 = 363.4$$

Mean Square

$$MS_X = SS_X \div dF_X = \frac{363.4}{19} = 19.12$$

Confidence Factor

$$F_{\frac{19}{7}} = MS_{\text{trend}} \div MS_{\text{dupl.}} = \frac{19.12}{1.43} = 13.37$$

N = total number of samples taken

D = number of duplicate samples

S = Standard Deviation of all (N) sample meas.

X_A = average of all (N) sample measurements

X = sample measured value (+ 40 Mesh)

X_D = value of duplicate measurements (freq. = 3)

SS_T = Sum of Squares = (N-1) × S²

SS_D = $\frac{1}{2} \times \Sigma (X - X_D)^2$

dF_T = Degree of Freedom Trend = N-1-D

dF = Degree of Freedom Total = N-1

MS = Mean Square = SS ÷ dF

F = MS_T ÷ MS_D = F ratio (Confidence Factor)

Corrected S_{trend}

$$= \left((MS_{\text{trend}} - MS_{\text{dupl.}}) \div \left(1 + \frac{1}{\text{freq}} \right) \right)^{\frac{1}{2}}$$

$$= 3.64$$

Coefficient of Variation

$$= \frac{3.64}{20.85} \times 100 = 17.4 \%$$

Attached is the "FMC Treatment of Segregation Data" procedure, refined by Bill Brunig.

The glass industry has traditionally utilized procedures developed by Bill Manring of FMC to quantify raw material and mixed batch segregation .

Standard Deviations for specific particle size distributions are a key element of FMC's method of analyzing the relative segregation issues.

Very generally, Standard Deviation values are categorized with the following qualitative descriptions:

Std. Dev.	< .8	"Good"
	1 - 1.5	"Marginal"
	1.5 - 2.0	"Poor"
	> 2.0	"Serious"

The "F" confidence factor is a ratio of the Mean Square trend variation vs Mean Square duplication variation.

A high F factor indicated that the trend is confidently distinguishable from the duplicate samples.

A low "F" factor (typically less than 5) can indicate that there is a high degree of short term variation, or that the samples were not taken in a consistent manner.

This indicates a high degree of segregation at the sampling point and it is masking any long term (or trend) segregation measurements.

The corrected trend Standard Deviation (S_{trend}) is a number representing long term variation.

The Coefficient of Variation (C_v) is a comparative measure of the system's segregation between measurement period.

For "F" factors less than 1.0, no trend vs duplication Standard Deviation or Coefficient of Variations can be generated.

Glass Melting / Formation

Commercial Soda Lime Glass

68 - 73 % SiO_2 Base (from Silica Sand)
11 - 15 % Na_2O / K_2O (Flux for Eutectic Melting)
9 - 12 % CaO / MgO (Stabilizer for Durability & Forming Properties)

Glass Formation Process

1st Step - Solid Heating (Ambient to ~ 1110 °F)

Physical Water Removal 212 °F
Rapid Surface Heating with Exposure to Furnace Melter
Slow Heating Within Batch Piles

2nd Step - Solid / Liquid Eutectics (to ~ 1425 °F)

Solid State Reactions (Na_2CO_3 & CaCO_3 + SiO_2 @ 1425 °F)
 $\text{Sodium Disilicate} + \text{SiO}_2 + \text{Na}_2\text{O} \rightarrow \text{Meta Silicates}$
Consistent Atmosphere & Temperatures

3rd Step - Permanent Liquid Phases (above ~ 1560 °F)

Soda Ash Melting Point 1560 °F
Rapid & Violent CO_2 Evolution
Sulfates Promote Reduced Surface Tension "Wetting" of Sand Grains
Cascade Flow off Batch Pile Surface

4th Step - Final Grain Solution (1850 - 2000 °F)

Coarse Grain Solution (Sand, Feldspathic, Chromite)
Mutual Solution of Liquid Phases
"Batch Free Time"
Batch Pattern / Scum Line (Return Flow)

5th Step - Refining

Gases - N_2 , O_2 , CO_2 , SO_2 / SO_3
Time / Temperature
Chemical Refining
Thermal Refining

Annual Meeting
Industrial Gas Technology Commercialization Center
Washington, D. C.
June 22, 1993

An Over View of the Glass Industry and its Natural Gas Use

As a new member of the Center's Technical Specialists Network, I appreciate the opportunity to discuss with you a few aspects about the Glass Industry, particularly its energy use practices by industry segment and some timely issues it is facing.

The U.S. glass industry represents a major source of natural gas demand -- approximately 190 billion cubic feet per year, of which about 160 bcf are used for melting and the balance is used for downstream operations. At the present time, natural gas is the principal energy source for melting glass and for downstream operations. The industry prefers gas over oil - because of its cleanliness and ease of control, and over electric energy - because of its lower cost.

Gas is the preferred fuel because:

- a) its cleanliness of combustion minimizes environmental problems,
- b) it does not add deleterious elements of the glass forming constituents of the batch, and
- c) heat released rates can be easily and rapidly controlled to maintain stable conditions in the furnace.

Gas will always be selected for use at prices up to or exceeding those for other fuels on a delivered Btu basis.

Approximately 22 million tons of glass are melted each year in the United States, of which more than 60 percent is used for containers. The industry's typical annual production consists of :

	<u>Production</u>	<u>Value</u>	<u>190 × 10¹² BTU's</u>
Containers	13.5 Million Tons	\$ 4.7 Billion	42 %
Flat	3.9 " "	\$ 2.7 "	22 %
Fiber	2.0 " "	\$ 2.3 "	18 %
Pressed and Blown.	3.1 " "	\$ 1.7 "	18 %

The raw materials used by the glass industry are abundant from domestic sources and relatively inexpensive. With some exceptions, the raw material constituents and the melting process into molten glass are similar between these four segments. Downstream fabrication operations are quite different.

Plant locations are based on a historical rationale. In the case of Flat glass (a product that can better absorb long-distance transportation costs), the plants have located principally near sources of energy. For Containers, (a product that cannot absorb much transportation cost), the plants are mainly located near the product markets, in areas of considerable population density. Some container plants were built 50 years ago in the Pennsylvania / West Virginia area because of availability of coal (from which producer gas was derived). Fiberglass manufacturing locations are largely established by the end markets for insulation products. Location is less of a factor for textile Fiberglass than Insulation products.

The fabrication processes are specific for each product line. Containers are fabricated in the so-called "I.S." machines which usually have a 75- to 100- TPD capacity. Flat glass is produced almost exclusively by the "float" process. Fiber, which is subdivided into production of "textile" (continuous filament) and "insulation" (also called "wool") is produced by one of several processes, each of which uses a different amount of energy.

A variety of processes are used to fabricate pressed and blown products such as kitchenware, tableware, TV tubes, lighting envelopes, tubing, and optical items.

Many products are treated after fabrication by tempering, annealing, labeling, coating, and / or decorating. Tempering of flat glass is very energy intensive; for the annealing of flat glass or containers, energy intensity depends on the efficiency of the annealing lehrs.

All segments of the glass industry are burdened by significant capital investments. Today's "typical" glass plant represents the following investment costs:

		<u>Estimated Facility Cost</u>	<u>"Std" Selling Value</u>
250 Ton / Day	Container	\$ 55 Million	\$ 475 / Ton
400 Ton / Day	Float Glass	\$ 80 "	\$ 290 / Ton
80 Ton / Day	Fiber Glass	\$ 45 "	\$ 750 / Ton
150 Ton / Day	Tableware	\$ 25 "	\$ 1,500 / Ton

The industry has been affected by major restructuring especially in its *Container* segment, where only four companies account for over 80 percent of the production capacity. This is somewhat consistent with the merger trend that has affected other U.S. industries and partially reflected the need of the industry to decrease capacity and increase efficiency in order to remain competitive in view of the aggressive inroads of other materials.

The *Flat* and *Fiber* segments have been similarly concentrated for many years and are more stable. The *Pressed and Blown* segment is more dispersed, consisting of a few large manufacturers, mainly producing machine made ware, and many small manufacturers that depend primarily on manual "hand working" operations.

Container Glass

Glass packaging has been the product of choice for centuries. The major use for glass in the container glass sector is in melting, with some consumption in annealing and finishing. This sector has encountered significant intermaterial competition and loss of market share; less efficient producers have shut down and production is concentrated in relatively newer, more efficient plants. Average fuel consumption for melting is about 4.5 to 6 mmBTU / ton.

Inert- Glass is more inert than almost every other alternative packaging. Glass does not permit oxygen and other gases to permeate into the product, so vitamins and other nutrients are better preserved. Foods packaged in glass have a longer shelf life than those packaged in most forms of plastic containers.

Transparent- The average consumer wants to examine the contents of the product before purchasing. Glass gives the truest indication of the amount of product one is purchasing.

Tamper Evident- Glass is an extremely desirable material to prevent product tampering, or make the tampering evident. It can hold the vacuum created when food is pasteurized.

Durability- Glass can be heated to higher temperatures than most plastic containers. Glass is structurally more durable than many plastics. It may be stacked without deformation or required internal pressure until used.

Recyclable- People are realizing that waste disposal is a serious long term problem for our nation. True recycling allows the base material to be made into the same category of product and is not a "Deferred Landfill" practice.

Cost- In the food industry, glass is still the least expensive packaging. Consumers uniformly appreciate a cost savings and can realize that increase in packaging costs must be passed on the consumer.

The number of units and the total weight of glass containers produced have decreased between 1986 and the present. By 1995, the total weight is expected to be about 10 million short per year or 10 percent below the 1985 level. During the same period, the recycling of glass containers will significantly increase. This will be due to:

- a) Government mandated recycling laws
- b) Promotional activities of the glass companies that see a cost advantage in using more "cullet"
- c) the increasing number of voluntary recycling centers and collection systems

In the nine states with "deposit" legislation, collection systems are well developed. California and New Jersey adopted a tax penalty in lieu of a deposit system. Recycling of glass containers reached 33 % this year (vs ~5 % for Plastic) and will continue to increase. A survey of New Jersey recycling rates for their "Curb Side" program showed glass at 65 %.

Future demand for glass containers will be affected by the outcome of the inter-material competition and by the actions of the glass industry in terms of new product development and cost reduction. This segment is severely affected by competition from plastics, metals (steel and aluminum), and cellulose based materials. Other factors are the demand for the contained products and the international trade of filled containers. International trade basically involves imported filled containers - such as beer, wine, and liquors.

Plastics will continue to make inroads but may be negatively affected by their disposal problems. Demand for contained products will change with consumer preference and because of demographic factors. For instance, demand for hard liquor has substantially decreased, and demand for wine coolers generated the need for over 1 billion glass bottles per year in 1987. Glass has also gained about 400 million units for non-carbonated juice bottles, more than half of which was at the expense of three-piece metal cans.

Flat Glass

The Flat Glass segment is important and is primarily supported by the demand of the Transportation and Construction industries. In 1992 about 3.9 million tons of flat glass, equivalent to about 4.6 billion square feet, were shipped from U.S. factories.

The "front end" of the flat glass industry is simple, because the fabrication step now consists almost universally of the float process. In the mid 1960's, the Flat glass industry converted from *Draw Sheet* and *Plate Grinding* fabrication to the *Float* process. The Pilkington "float" glass process involves floating molten glass onto a bed of molten tin, an inert atmosphere of nitrogen to prevent oxidation, as the glass cools and becomes rigid.

The major use for natural gas in the flat glass sector is in the melting furnaces. Furnaces are generally very large, ranging from 400 to 800 TPD, and the refiner is much larger than in other plants because of the need to eliminate "seeds" (gas bubbles) and other defects for maximum optical clarity. Some consumption is in the downstream laminating, autoclaving, annealing, and tempering steps.

The total unit energy consumption (natural gas, fuel oil, and electricity) for flat glass has declined substantially. In 1976 it required 23 million Btu to produce one ton of glass, in 1986 less than 13 million Btu is required. The use of advanced refractories for energy conservation and higher production rates have resulted in fuel consumption per ton for glass melted to decrease by more than 25 % in the last 15 years. At the same time, the average life of the melting furnace has increased significantly. Typical furnace fuel consumption is in the range of 8 to 10 MMBtu / ton melted, depending on the age and size of the furnace / regenerator system.

Certain companies purchase flat glass from the major producers and reprocess it, e.g., to make mirrors or laminated safety products. The industry appears to be moving toward more specialty line products which have substantial value added and enhanced profitably. These include coating (e.g., anti-reflecting), laminating (e.g. fabrication of safety glass for transportation equipment by embedding a sheet of plastic), tempering (to increase resistance to impact), frosting or texturing (for optical or decorative reasons), and the production of dual or triple glaze (to decrease heat loss). In the future, these may require short runs, and therefore the current massive equipment may not be optimal for production flexibility.

Flat glass is an international product, and therefore domestic production is affected significantly by international trade and, indirectly, by currency exchange rates. Inter-material competition derives from plastics. Major inroads of plastics are not foreseen unless new U.V.- and abrasion - resistant compositions can be developed.

Fiberglass

The fiberglass segment is subdivided into a) Wool Insulation - used primarily by the construction industry and b) Textile - used principally by the production of polymer based, continuous filament reinforced composites. It is further subdivided into "low technology" (e.g., furniture and boats) and "high technology" (e.g., electronics, automotive and aerospace components) areas. Neither product can support the cost of long-range transportation, and therefore international trade is negligible.

Most Textile production is from continuous, on-line melting furnaces primarily fueled by natural gas. The melting furnaces have a capacity of 150-200 TPD. Insulating Wool is more typically made in electric furnaces. Some remelting is performed in electric furnaces from marbles made in gas-fired furnaces. This less common process consumes 50 % more energy. Some of the gas consumed in fiberizing is used to produce steam, and some is used to supply heat directly to the fiberizing process.

The unit consumption of natural gas for melting has declined from about 28 mmBTU per ton of fiberglass produced in 1978 to about 12 mmBTU per ton in 1986 and is now in the 8 to 10 mmBTU range. Unlike in the container and flat glass segments, a large amount of energy is used in the fabrication step. Fiberizing can consume 6 to 10 mmBTU / ton.

Fiberization for fiberglass is usually by:

Rotary Wool Forming - Molten glass is delivered to a perforated rotating cylinder. The glass, propelled by the centrifugal force of the cylinder, is hit by a high velocity gas stream

Continuous forming. The molten glass is drawn from a multi-holed platinum bushing at speeds in excess of 5,000 feet per minute. Typical resulting fibers are 5 to 20 micrometers in diameter.

Inter-material competition to insulation fiberglass is essentially limited to mineral wool; for textile continuous filaments there are many alternatives (including polymers), particularly in high technology applications. There have been recent concerns about health hazard, mainly for very fine fiberglass. Recent studies have generally discounted these concerns.

Pressed and Blown Glass

The Pressed and Blown segment of the glass industry is a significant "catch all" for glassware not otherwise classified. A large fraction of this segment consists of owner managed, small, labor-intensive manufacturers. The pressed and blown segment generally depends on several post forming operations including annealing, tempering, and/or decorating. Many plants in this sector are small and relatively inefficient in energy use, so unit energy consumption for melting is 12 to 16 mmBTU / ton shipped. In these shops the melting furnaces have small capacity (on the order of 5 to 25 TPD).

The few companies that manufacture machine made table and kitchenware and certain industrial products such as light and electric components, used primarily gas-fueled large furnaces (typically of 100 to 200 TPD capacity). Their furnaces are more similar to Container and Fiber Glass types.

Incandescent light bulbs are made on high speed ribbon machines, where a ribbon of glass is pulled from the furnace and caused to flow over a moving air source and under a forming mold. A moving bubble of glass is formed in the ribbon, and enclosed by the moving mold to form the bulb shape. The mold opens, and the bulb is allowed to cool while still attached to the ribbon. After cooling, the bulb is knocked off the ribbon and annealed. Production rates exceed 1500 pieces per minute.

Fluorescent light bulbs are made from glass tubing. Molten glass is allowed to flow through an orifice with a restriction in the center so that the glass flow forms a tubular rather than a solid shape. While still soft, the tube is bent from the vertical to the horizontal direction, is rotated to maintain eccentricity, and is pulled over a series of cooling rollers until it can be cut to size.

Future Issues

The glass industry is very sensitive to operating costs. Of the total operating costs of the U.S. glass industry about 55 percent is for materials, 30 percent for labor, and 15 percent for energy. High capacity utilization generally brings about lower unit energy consumption and improved productivity factors.

Many new technologies have helped the glass industry to become more competitive in the last two decades. However, most of these innovations have involved either the fabrication of glass products, or finishing operations that add substantial value to the products.

Electric energy is used in significant amounts for mechanical drives, temperature "boosting" in the melting step, and downstream operations such as tempering and annealing. Energy substitution methods are always of interest by the Glass Industry.

From a business point of view, the Flat and Fiber glass industries are tied to the overall U. S. economic climate. Commercial, Educational and Residential construction as well as Automotive purchases dominate changes in their production shipments. Container business will relate more to changes in consumer packaging and product preferences.

International trade significantly affects only the Flat and Pressed and Blown glass segments. Containers and Fibers face very few imports because of excessive transportation costs. The proposed North American Free Trade Agreement *NAFTA* will place the U. S. Flat glass industry at a competitive disadvantage. The 20 % tariff by Mexico would be reduced only 2 % per year on imported glass, while the U. S. tariff would be eliminated almost entirely by 1994. A PPG representative projects that " the Mexican Flat glass monopoly

could capture at least 13 % of the overall U. S. market, including 26 % of the market in the Southwest and West."

Similar concern are evident in California where imported Glass Containers can be shipped a relatively short distance from Mexico. California continues to impose stringent environmental requirements and worker compensation laws on their own industries which are not required in Mexico. Two Container factories have been built less than 15 miles south of the California border in the past three years.

Environmental Technologies

NO_x - Oxy Fuel, Ammonia Injection , Gas Reburn

SO_x - Avoid Sulfur containing Fuels, Batch Sulfate alternatives , Add-On Scrubbers

Particulate - Add-Ons (Bag Houses, Electrostatic Precipitators, Scrubbers)

Looking ahead, the Glass Industry's most viable option for long term compliance for NO_x will probably be conversion to 100% oxygen combustion. The feasibility for larger furnaces was verified last year when Gallo Glass converted a 380 Ton / Day regenerative container furnace to 100% Oxy-Fuel. By mid- 1994 they are expected to have all five of their furnaces converted. The implementation of this technology for meeting future environmental compliance will initiate a significant driving force to integrate waste heat recovery schemes - such as batch / cullet preheating, cogeneration, or gas reformer technology.

Although the proposed Energy Tax legislation was recently dropped, some future modifications are expected. For products competing with imports or alternative materials, this tax could have devastating consequences. By example the recent proposal would have **added** approximately \$ 857 for 1 million glass containers vs \$ 365 for the same number of Aluminum cans, except the Aluminum Industry had gained an exemption for this tax.

Industry Segment - Container

SIC Code - 3221

Production Tons / Year - 13.5 million

Selling Value - \$ 4,900,000,000

Gas Use / Year - 80×10^{15} BTU's
@ \$ 3.00 / mcf = \$ 240,000,000 / year

mmBTU / Ton - 4.5 to 6.0 Melting , 7 to 8 mmBTU / Ton Total

Products

Beer Beverage Food Wine Liquor Cosmetics
Household & Industrial

Competition Materials

Plastics Aluminum Steel Paper

Environmental Concerns

Particulate
NOX
SOX

Melting Furnace Types - Typical Size 250 Tons / Day

Regenerative	Side Ports - 45 %
	End Ports - 50 %
All- Electric -	2 % ↓
Oxy-Fuel -	3 % ↑

Major Companies

Owens-Brockway
Anchor Glass
Ball-Incon Glass
Foster Forbes

Industry Segment - Flat / Float

SIC Code - 3211

Production

Tons / Year - 2,200,000

Selling Value \$ 2,700,000,000

**Gas Use / Year - 42×10^{15} BTU's
@ \$ 3.00 / mcf = \$ 125,000,000**

mmBTU / Ton 8 to 10 mmBTU / Ton Melting

Products

**Automotive / Transportation
Construction - Commercial & Residential
Architectural / Furniture**

Competition Materials

High Density Plastics

Environmental Concerns

**NOX
SOX
Particulate**

Melting Furnace Types - Typical Size 400 + Tons / Day

Regenerative Side Ports - 95 %

Major Companies

**AFG Industries
PPG Industries
Ford Motor
Libby-Owens-Ford
Guardian Industries**

Industry Segment - Fiber Glass

SIC Code - Insulation 3229

Textile 3296

Production

Tons / Year - 2,000,000

Selling Value \$ 2,300,000,000

Gas Use / Year 34.2×10^{15} BTU's
@ \$ 3.00 / mcf = \$100,000,000

mmBTU / Ton 6 to 8 mmBTU / Ton Melting
6 to 10 mmBTU / Ton Fiberizing

Insulation

Textile

Products

Blanket
Mat

Reinforcing (chopped)
Textile (Strand)

Competition Materials

Mineral Wool

Polymers

Environmental Concerns

Particulate

Particulate

Melting Furnace Types

Typical Size

75 -100 Tons / Day
95 % -All Electric
5 % - Gas - OxyFuel

100 - 150 Tons / Day
95 % - Gas Recuperative
5 % - Gas - OxyFuel

Major Companies

Certain Teed
Manville
Owens-Corning Fiberglass
PPG Industries

Industry Segment - Press & Blow

SIC Code - 3229

Production

Tons / Year 3,100,000
Selling Value \$ 1,700,000,000
Gas Use / Year 34.2×10^{15} BTU's
@ \$ 3.00 / mcf = \$100,000,000
mmBTU / Ton 12 to 16 mmBTU / Ton Melting

Products

Consumer products

Machine Made

Tableware

Cookware

Ornamental, decorative

Handmade

Tableware

Ornamental

Industrial products

Lighting and electronic Light bulbs Television tubes

Reflectors and other lamp parts

Scientific Products

Tubing, rods Laboratory glasswork

Ophthalmic and instrument lenses

Competition Materials

Plastics , Metals , Stoneware

Environmental Concerns

Particulate

Heavy Metals

NOX

Melting Furnace Types

Typical Size

Direct / Recuperative - 35 %

Regenerative - 60 %

Oxy-Gas - 5 %

Major Companies

Pressed and Blown Glass Tableware and Kitchenware

Anchor Hocking,

Corning Glass,

Indiana Glass Co.

Lenox Crystal,

Libbey Glass,

St. George Crystal

Lighting Products -

Phillips,

GE

Osram Sylvania

Television Tubes - Thompson Consumer Electronics, OI-NEG

Misc - Shott, Kimble

Commercial Glass Compositions

[illegible]

CALCULATIONS INVOLVING IDEAL GAS LAW

The ideal gas law may be employed to find any one of the variables P , V , T , or n from any specified set of three of these. As an illustration, suppose that we want to know what will be the volume occupied by 10 g of oxygen at 25° C and 650 mm Hg pressure. From the data we have that:

$$n = \frac{10}{32} = 0.312 \text{ mole}$$

$$T = 273.2 + 25 = 298.2^\circ \text{ K}$$

$$P = \frac{650}{760} = 0.855 \text{ atm}$$

$$R = 0.0821 \text{ liter} \cdot \text{atm}$$

Insertion of these into $PV = nRT$ equation yields for the volume:

$$\begin{aligned} V &= nRT/P = (0.312 * 0.0821 * 298.2) / 0.855 \\ &= 8.94 \text{ liters} \end{aligned}$$

Similarly, from appropriately specified data the other quantities involved in the ideal gas equation may be found.

DALTON'S LAW OF PARTIAL PRESSURES

It has already been pointed out that different gases introduced into the same container inter diffuse or mix rapidly. Dalton's *law of partial pressures* states that *at constant temperature the total pressure exerted by a mixture of gases in a definite volume is equal to the sum of the individual pressures which each gas would exert if it occupied the same total volume alone.*

In other words,

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots \quad (10)$$

where the individual pressures, P_1 , P_2 , P_3 etc., are termed the *partial pressures* of the respective gases. The partial pressure of each constituent may be thought of as the pressure which that constituent would exert if it were isolated in the same volume and at the same temperature as that of the mixture. In terms of the partial pressures, Dalton's law may be restated as follows:

The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual components of the mixture.

The significance of Dalton's law and of the concept of partial pressures is best brought out by the following example. If we were to take three *liter* flasks filled respectively with hydrogen at 70 mm Hg pressure, carbon monoxide at 500 mm, and nitrogen at 1000 mm, all at the same temperature, and were to force all these gases into a fourth *1-liter* flask, the total pressure within the fourth flask would be

$$\begin{aligned} P &= P_{H_2} + P_{CO} + P_{N_2} \\ &= 70 + 500 + 1000 \\ &= 1570 \text{ mm Hg} \end{aligned}$$

and the pressures of the individual gases within their 1-liter flasks would be the partial pressures of these gases in the mixture.

Consider now a gaseous mixture composed of n_1 moles of one gas, n_2 moles of another gas, and n_3 moles of still a third. Let the total volume be V and the temperature T . If the conditions of pressure and temperature are not too extreme, the ideal gas laws would be valid for each gas in the mixture, and we obtain for the respective partial pressures:

$$P_1 = n_1 RT / V \quad (11a)$$

$$P_2 = n_2 RT / V \quad (11b)$$

$$P_3 = n_3 RT / V \quad (11c)$$

According to Dalton's law the total pressure P thus becomes

$$P = n_1 RT / V + n_2 RT / V + n_3 RT / V$$

$$P = (n_1 + n_2 + n_3) RT / V$$

$$P = n RT / V \quad (12)$$

where $n = (n_1 + n_2 + n_3)$ = total number of moles of gas in the mixture. We see from equation (12), therefore, that the gas laws may be applied to mixtures as well as to pure gases, and in exactly the same way.

On division of equations (11a) - (11c) by equation (12) it is found that

$$P_1 = \frac{n_1}{n} P \quad (13a)$$

$$P_2 = \frac{n_2}{n} P \quad (13b)$$

$$P_3 = \frac{n_3}{n} P \quad (13c)$$

Equations such as (13) are very important in chemical and chemical engineering calculations, for they relate the partial pressure of a gas to the total pressure of the mixture. Since the fractions n_1/n , n_2/n , and n_3/n represent the moles of a particular constituent present in the mixture divided by the total number of moles of all gases present, these quantities are called *mole fractions* and are designated by the respective symbols N_1 , N_2 , N_3 , etc. Of necessity the sum of all the mole fractions for a system will have to be unity, namely,

$$N_1 + N_2 + N_3 + \dots = 1 \quad (14)$$

In terms of these definitions the partial pressure of any component in a gas mixture is equal to the mole fraction of that component multiplied by the total pressure. This is true only when the ideal gas law applies to each constituent of the gas mixture.

8.13 GLASS MANUFACTURING

8.13.1 General¹⁻⁵

Commercially produced glass can be classified as soda-lime, lead, fused silica, borosilicate, or 96 percent silica. Soda-lime glass, since it constitutes 77 percent of total glass production, is discussed here. Soda-lime glass consists of sand, limestone, soda ash, and cullet (broken glass). The manufacture of such glass is in four phases: (1) preparation of raw material, (2) melting in a furnace, (3) forming and (4) finishing. Figure 8.13-1 is a diagram for typical glass manufacturing.

The products of this industry are flat glass, container glass, and pressed and blown glass. The procedures for manufacturing glass are the same for all products except forming and finishing. Container glass and pressed and blown glass, 51 and 25 percent respectively of total soda-lime glass production, use pressing, blowing or pressing and blowing to form the desired product. Flat glass, which is the remainder, is formed by float, drawing or rolling processes.

As the sand, limestone and soda ash raw materials are received, they are crushed and stored in separate elevated bins. These materials are then transferred through a gravity feed system to a weigher and mixer, where the material is mixed with cullet to ensure homogeneous melting. The mixture is conveyed to a batch storage bin where it is held until dropped into the feeder to the melting furnace. All equipment used in handling and preparing the raw material is housed separately from the furnace and is usually referred to as the batch plant. Figure 8.13-2 is a flow diagram of a typical batch plant.

Figure 8.13-1. Typical glass manufacturing process.

Figure 8.13-2. General diagram of a batch plant.

The furnace most commonly used is a continuous regenerative furnace capable of producing between 45 and 272 Mg (50 and 300 tons) of glass per day. A furnace may have either side or end ports that connect brick checkers to the inside of the melter. The purpose of brick checkers (Figures 8.13-3 and 4) is to conserve fuel by collecting furnace exhaust gas heat which, when the air flow is reversed, is used to preheat the furnace combustion air. As material enters the melting furnace through the feeder, it floats on the top of the molten glass already in the furnace. As it melts, it passes to the front of the melter and eventually flows through a throat leading to the refiner. In the refiner, the molten glass is heat conditioned for delivery to the forming process. Figures 8.13-3 and 8.13-4 show side port and end port regenerative furnaces.

After refining, the molten glass leaves the furnace through forehearth (except in the float process, with molten glass moving directly to the tin bath) and goes to be shaped by pressing, blowing, pressing and blowing, drawing, rolling, or floating to produce the desired product. Pressing and blowing are performed mechanically, using blank molds and glass cut into sections (gobs) by a set of shears. In the drawing process, molten glass is drawn upward in a sheet through rollers, with thickness of the sheet determined by the speed of the draw and the configuration of the draw bar. The rolling process is similar to the drawing process except that the glass is drawn horizontally

Figure 8.13-3. Side port continuous regenerative furnace.

Figure 8.13-4. End port continuous regenerative furnace.

on plain or patterned rollers and, for plate glass, requires grinding and polishing. The float process is different, having a molten tin bath over which the glass is drawn and formed into a finely finished surface requiring no grinding or polishing. The end product undergoes finishing (decorating or coating) and annealing (removing unwanted stress areas in the glass) as required, and is then inspected and prepared for shipment to market. Any damaged or undesirable glass is transferred back to the batch plant to be used as cullet.

8.13.2 Emissions and Controls¹⁻⁵

The main pollutant emitted by the batch plant is particulates in the form of dust. This can be controlled with 99 to 100 percent efficiency by enclosing all possible dust sources and using baghouses or cloth filters. Another way to control dust emissions, also with an efficiency approaching 100 percent, is to treat the batch to reduce the amount of fine particles present, by pre-sintering, briquetting, pelletizing, or liquid alkali treatment.

The melting furnace contributes over 99 percent of the total emissions from a glass plant, both particulates and gaseous pollutants. Particulates result from volatilization of materials in the melt that combine with gases and form condensates. These either are collected in the checker work and gas passages or are emitted to the atmosphere. Serious problems arise when the checkers are not properly cleaned, in that slag can form, clog the passages and eventually deteriorate the condition and efficiency of the furnace. Nitrogen oxides form when nitrogen and oxygen react in the high temperatures of the furnace. Sulfur oxides result from the decomposition of the sulfates in the batch and sulfur in the fuel. Proper maintenance and firing of the furnace can control emissions and also add to the efficiency of the furnace and reduce operational costs. Low pressure wet centrifugal scrubbers have been used to control particulate and sulfur oxides, but their inefficiency (approximately 50 percent) indicates their inability to collect particulates of submicron size. High energy venturi scrubbers are approximately 95 percent effective in reducing particulate and sulfur oxide emissions. Their effect on nitrogen oxide emissions is unknown. Baghouses, with up to 99 percent particulate collection efficiency, have been used on small regenerative furnaces, but fabric corrosion requires careful temperature control. Electrostatic precipitators have an efficiency of up to 99 percent in the collection of particulates. Table 8.13-1 lists controlled and uncontrolled emission factors for glass manufacturing. Table 8.13-2 presents particle size distributions and corresponding emission factors for uncontrolled and controlled glass melting furnaces.

Emissions from the forming and finishing phase depend upon the type of glass being manufactured. For container, press, and blow machines, the majority of emissions results from the gob coming into contact with the machine lubricant. Emissions, in the form of a dense white cloud which can exceed 40 percent opacity, are generated by flash vaporization of hydrocarbon greases and oils. Grease and oil lubricants are being replaced by silicone emulsions and water soluble oils, which may virtually eliminate this smoke. For flat glass, the only contributor to air pollutant emissions is gas combustion in the annealing lehr (oven), which is totally enclosed except for product entry and exit openings. Since emissions are small and operational procedures are efficient, no controls are used on flat glass processes.

TABLE 8.13-1. EMISSION FACTORS FOR GLASS MANUFACTURING^a

EMISSION FACTOR RATING: B

Process	Particulate		Sulfur oxides		Nitrogen oxides		VOC		Carbon monoxide		Lead	
	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton
Raw materials handling ^b (all types of glass)	Neg	Neg	0	0	0	0	0	0	0	0	-	-
Melting furnace ^c												
Container												
Uncontrolled	0.7 (0.4-0.9)	1.4 (0.9-1.9)	1.7 (1.0-2.4)	3.4 (2.0-4.8)	3.1 (1.6-4.5)	6.2 (3.3-9.1)	0.1 (0-0.2)	0.2 (0-0.4)	0.1 (0-0.2)	0.2 (0-0.5)	-	-
W/low energy scrubber ^d	0.4	0.7	0.9	1.7	3.1	6.2	0.1	0.2	0.1	0.2	-	-
W/venturi scrubber ^e	<0.1	0.1	0.1	0.2	3.1	6.2	0.1	0.2	0.1	0.2	-	-
W/baghouse ^f	Neg	Neg	1.7	3.4	3.1	6.2	0.1	0.2	0.1	0.2	-	-
W/electrostatic precipitator ^g	Neg	Neg	1.7	3.4	3.1	6.2	0.1	0.2	0.1	0.2	-	-
Flat												
Uncontrolled	1.0 (0.4-1.6)	2.0 (0.8-3.2)	1.5 (1.1-1.9)	3.0 (2.2-3.8)	4.0 (2.8-5.2)	8.0 (5.6-10.4)	<0.1	<0.1	<0.1	<0.1	-	-
W/low-energy scrubber ^d	0.5	1.0	0.8	1.5	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
W/venturi scrubber ^e	Neg	Neg	0.1	0.2	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
W/baghouse ^f	Neg	Neg	1.5	3.0	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
W/electrostatic precipitator ^g	Neg	Neg	1.5	3.0	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
Pressed and blown												
Uncontrolled	8.7 (0.5-12.6)	17.4 (1.0-25.1)	2.8 (0.5-5.4)	5.6 (1.1-10.9)	4.3 (0.4-10.0)	8.5 (0.8-20.0)	0.2 (0.1-0.3)	0.3 (0.1-1.0)	0.1 (0.1-0.2)	0.2 (0.1-0.3)	-	-
W/low energy scrubber ^d	4.2	8.4	1.3	2.7	4.3	8.5	0.2	0.3	0.1	0.2	-	-
W/venturi scrubber ^e	0.5	0.9	0.1	0.3	4.3	8.5	0.2	0.3	0.1	0.2	-	-
W/baghouse ^f	0.1	0.2	2.8	5.6	4.3	8.5	0.2	0.3	0.1	0.2	-	-
W/electrostatic precipitator ^g	0.1	0.2	2.8	5.6	4.3	8.5	0.2	0.3	0.1	0.2	-	-
Forming and finishing												
Container ^{h,j}	Neg	Neg	Neg	Neg	Neg	Neg	4.4	8.7	Neg	Neg	-	-
Flat	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	-	-
Pressed and blown ^{h,j}	Neg	Neg	Neg	Neg	Neg	Neg	4.5	9.0	Neg	Neg	-	-
Lead glass manufacturing, all processes ^k	-	-	-	-	-	-	-	-	-	-	2.5	5

^aReferences 2-3, 5. Dash = no available data. Neg = negligible. Ranges in parentheses, where available. Expressed as kg/Hg (lb/ton) of glass produced.

^bNot separated into types of glass produced, since batch preparation is the same for all types. Particulate emissions are negligible because almost all plants utilize some form of control (i.e., baghouses, scrubbers, centrifugal collectors).

^cControl efficiencies for the various devices are applied only to the average emission factor.

^dApproximately 52% efficiency in reducing particulate and sulfur oxides emissions. Effect on nitrogen oxides is unknown.

^eApproximately 95% efficiency in reducing particulate and sulfur oxide emissions. Effect on nitrogen oxides is unknown.

^fApproximately 99% efficiency in reducing particulate emissions.

^gCalculated using data for furnaces melting soda lime and lead glasses. No data available for borosilicate or opal glasses.

^hOrganic emissions are from decorating process. Can be controlled by incineration, absorption or condensation, but efficiencies are not known.

^jFor container and pressed and blown glass, tin chloride, hydrated tin chloride and hydrogen chloride are also emitted during surface treatment process at a rate of <0.1 kg/Hg (0.2 lb/ton) each.

^kReferences 6-7. Particulate containing 23% lead.

Figure 8.13-5. Particle size distributions and emission factors for glass melting furnace exhaust.

TABLE 8.13-2. PARTICLE SIZE DISTRIBUTIONS AND EMISSION FACTORS FOR UNCONTROLLED AND CONTROLLED MELTING FURNACES IN GLASS MANUFACTURING^a

Emission Factor Rating: E			
Aerodynamic particle diameter, um	Particle size distribution ^b		Size specific emission factor, kg/Mg ^c
	Uncontrolled	ESP Controlled ^d	Uncontrolled
2.5	91	53	0.64
6.0	93	66	0.65
10	95	75	0.66

^aReferences 8-11.

^bCumulative weight % of particles < corresponding particle size.

^cBased on mass particulate emission factor of 0.7 kg/Mg glass produced, from Table 8.13-1. Size specific emission factor = mass particulate emission factor x particle size distribution, %/100. After ESP control, size specific emission factors are negligible.

^dReference 8-9. Based on a single test.

TABLE 8.13-1. EMISSION FACTORS FOR GLASS MANUFACTURING^a

EMISSION FACTOR RATING: B

Process	Particulate		Sulfur oxides		Nitrogen oxides		VOC		Carbon monoxide		Lead	
	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton	kg/Hg	lb/ton
Raw materials handling ^b (all types of glass)	Neg	Neg	0	0	0	0	0	0	0	0	-	-
Melting furnace ^c												
Container												
Uncontrolled	0.7 (0.4-0.9)	1.4 (0.9-1.9)	1.7 (1.0-2.4)	3.4 (2.0-4.8)	3.1 (1.6-4.5)	6.2 (3.3-9.1)	0.1 (0-0.2)	0.2 (0-0.4)	0.1 (0-0.2)	0.2 (0-0.5)	-	-
W/low energy scrubber ^d	0.4	0.7	0.9	1.7	3.1	6.2	0.1	0.2	0.1	0.2	-	-
W/venturi scrubber ^e	<0.1	0.1	0.1	0.2	3.1	6.2	0.1	0.2	0.1	0.2	-	-
W/baghouse ^f	Neg	Neg	1.7	3.4	3.1	6.2	0.1	0.2	0.1	0.2	-	-
W/electrostatic precipitator ^g	Neg	Neg	1.7	3.4	3.1	6.2	0.1	0.2	0.1	0.2	-	-
Flat												
Uncontrolled	1.0 (0.4-1.6)	2.0 (0.8-3.2)	1.5 (1.1-1.9)	3.0 (2.2-3.8)	4.0 (2.8-5.2)	8.0 (5.6-10.4)	<0.1	<0.1	<0.1	<0.1	-	-
W/low-energy scrubber ^d	0.5	1.0	0.8	1.5	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
W/venturi scrubber ^e	Neg	Neg	0.1	0.2	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
W/baghouse ^f	Neg	Neg	1.5	3.0	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
W/electrostatic precipitator ^g	Neg	Neg	1.5	3.0	4.0	8.0	<0.1	<0.1	<0.1	<0.1	-	-
Pressed and blown												
Uncontrolled	8.7 (0.5-12.6)	17.4 (1.0-25.1)	2.8 (0.5-5.4)	5.6 (1.1-10.9)	4.3 (0.4-10.0)	8.5 (0.8-20.0)	0.2 (0.1-0.3)	0.3 (0.1-1.0)	0.1 (0.1-0.2)	0.2 (0.1-0.3)	-	-
W/low energy scrubber ^d	4.2	8.4	1.3	2.7	4.3	8.5	0.2	0.3	0.1	0.2	-	-
W/venturi scrubber ^e	0.5	0.9	0.1	0.3	4.3	8.5	0.2	0.3	0.1	0.2	-	-
W/baghouse ^f	0.1	0.2	2.8	5.6	4.3	8.5	0.2	0.3	0.1	0.2	-	-
W/electrostatic precipitator ^g	0.1	0.2	2.8	5.6	4.3	8.5	0.2	0.3	0.1	0.2	-	-
Forming and finishing												
Container ^{h,j}	Neg	Neg	Neg	Neg	Neg	Neg	4.4	8.7	Neg	Neg	-	-
Flat	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	-	-
Pressed and blown ^{h,j}	Neg	Neg	Neg	Neg	Neg	Neg	4.5	9.0	Neg	Neg	-	-
Lead glass manufacturing, all processes ^k	-	-	-	-	-	-	-	-	-	-	2.5	5

^aReferences 2-3, 5. Dash = no available data. Neg = negligible. Ranges in parentheses, where available. Expressed as kg/Hg (lb/ton) of glass produced.

^bNot separated into types of glass produced, since batch preparation is the same for all types. Particulate emissions are negligible because almost all plants utilize some form of control (i.e., baghouses, scrubbers, centrifugal collectors).

^cControl efficiencies for the various devices are applied only to the average emission factor.

^dApproximately 52% efficiency in reducing particulate and sulfur oxides emissions. Effect on nitrogen oxides is unknown.

^eApproximately 95% efficiency in reducing particulate and sulfur oxide emissions. Effect on nitrogen oxides is unknown.

^fApproximately 99% efficiency in reducing particulate emissions.

^gCalculated using data for furnaces melting soda lime and lead glasses. No data available for borosilicate or opal glasses.

^hOrganic emissions are from decorating process. Can be controlled by incineration, absorption or condensation, but efficiencies are not known.

ⁱFor container and pressed and blown glass, tin chloride, hydrated tin chloride and hydrogen chloride are also emitted during surface treatment process at a rate of <0.1 kg/Hg (0.2 lb/ton) each.

^kReferences 6-7. Particulate containing 23% lead.

References for Section 8.13

1. J. A. Danielson, (ed.), Air Pollution Engineering Manual, 2nd Ed., AP-40, U. S. Environmental Protection Agency, Research Triangle Park, NC, May 1973. Out of Print.
2. Richard B. Reznik, Source Assessment: Flat Glass Manufacturing Plants, EPA-600/20-76-032b, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1976.
3. J. R. Schorr, et al., Source Assessment: Glass Container Manufacturing Plants, EPA-600/2-76-269, U. S. Environmental Protection Agency, Washington, DC, October 1976.
4. A. B. Tripler, Jr. and G. R. Smithson, Jr., A Review of Air Pollution Problems and Control in the Ceramic Industries, Battelle Memorial Institute, Columbus, OH, presented at the 72nd Annual Meeting of the American Ceramic Society, May 1970.
5. J. R. Schorr, et al., Source Assessment: Pressed and Blown Glass Manufacturing Plants, EPA-600/77-005, U. S. Environmental Protection Agency, Washington, DC, January 1977.
6. Control Techniques for Lead Air Emissions, EPA-450/2-77-012, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1977.
7. Confidential test data, Pedco-Environmental Specialists, Inc., Cincinnati, OH.
8. H. J. Taback, Fine Particle Emissions from Stationary and Miscellaneous Sources in the South Coast Air Basin, PB-293-923, National Technical Information Service, Springfield, VA, February 1979.
9. Emission test data from Environmental Assessment Data Systems, Fine Particle Emission Information System (FPEIS), Series Report No. 219, U. S. Environmental Protection Agency, Research Triangle Park, NC, June 1983.
10. Environmental Assessment Data Systems, op. cit., Series No. 223.
11. Environmental Assessment Data Systems, op. cit., Series No. 225.

Particulate Reduction From Various Type of
Glass Furnaces

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Glass production facilities present unique air pollution air control problems. Emissions from many glass processes contain extremely small particulate that is difficult to collect and handle. The overall composition of the off-take emission can vary greatly because of difference in processes, batch mixtures, and fuel quality. As more is learned about the potential dangers of various off-take gasses, stricter regulations are being imposed to limit acid gas and particulate emissions.

This paper discusses the technique used to reduce glass furnace particulate emissions.

Introduction

For many years the emission from a glass melting furnace was thought to be an insignificant health hazard. Tall stacks or ejector stacks were used to disperse the particulate which created the impression that a health hazard did not exist. The dispersing techniques reduced the concentration of the emission so that the stack opacity was quite low. Low stack opacity meant low public pressure to reduce the mass emission. This attitude still prevails in many parts of the world.

Obviously, what is emitted is equally or more important than stack opacity. Glass melting furnaces can emit very small, and in certain cases very hazardous materials. The size of the particulate is very important. Once inhaled, small particles are very difficult to exhale.

The batch materials used in glass production can cause emission of lead oxide, arsenic, sodium silicate, selenium, boron, antimony, chromium and so on. Figure 1 shows a particle size distribution for a soda lime glass furnace, Figure 2 shows the typical mass emission rate for various types of uncontrolled glass furnaces.

Several methods have been used to reduce the emission of these materials from glass melting furnaces. These methods include dispersion, wet scrubbers, electrified filter beds (EFB), fabric filter systems (FF), and dry electrostatic precipitators (EP).

Regulations

Significant acid gas and particulate reduction requirements for glass furnace are less than 30 years old. Even today, regulations in some countries are so lenient, that they may as well be considered non-existent. However, awareness has brought increasingly stricter acid gas and particulate reduction requirements for the glass industry in the United States and most countries.

Figure 3 shows typical U.S. pre-1980 limitations for stationary sources. Most glass furnaces can be operated in a manner to meet these requirements uncontrolled.

The 1980 Clean Air Act reduced these levels to that shown in Figure 4. Additional reduction requirements have been imposed by U.S. State and Local agencies for specific types of emissions as shown in Figure 5. However, world-wide, the regulations vary by a substantial margin. Figure 6 shows some of the recent regulations for various areas around the world.

Dispersion

Tall stacks can be used to provide a natural draft to provide exhaust for a furnace. A natural draft stack for a glass furnace is typically 150ft. (45m) - 250 ft (76m) high. Particulate appears to be dispersed at such heights. The belief was that the relative small amount of particulate was dispersed enough not to pose health or environmental problems.

An alternative to a tall stack is an ejector stack. The ejector stack is much less expensive than the tall stack to install; however, the cost of operation is increased because of the high flow rate the ejector fan needs to provide an adequate furnace draft. A feature of the ejector stack is that the furnace exhaust is diluted. Dilution reduces the exhaust opacity giving the impression of a

clean stack exhaust.

Some ejector designs incorporated additional heat recovery and are part of the reversal system. Of course, neither the tall stack or the ejector system does anything to reduce the mass emission from a glass furnace.

Wet Scrubber Systems

Wet scrubbers were tried briefly to reduce emissions; however, several factors make their use in the glass industry impractical. The most important are particle size, particle solubility, water consumption and water disposal.

Since the glass emission particulate size is so small, a very high pressure drop wet scrubber is required so the equipment can meet today's emission requirements. The pressure required is often impractical and/or consumes a large amount of energy and water.

Some of the materials collected are soluble. A wet scrubber requires disposal of a large quantity of water and the particulate solubility increases the cost of this disposal. Although the initial price of a wet scrubber system is low, the cost of operation is very high.

Electrified Filter Beds (EFB)

EFB's were also tried briefly. Their lower initial cost seemed to present an attractive option. However, the packing proved to be virtually impossible to clean. They provided good short term performance, but required frequent off-line and expensive cleaning.

Fabric Filter Systems

A fabric filter system can provide adequate particulate reduction performance. There are some in use on glass furnaces today. While the purchase price of a fabric filter system can be lower than alternate types of pollution control equipment, several operating conditions can lead one to decide against a baghouse system.

Again, particulate size is a factor. The very small size of glass emissions tend to blind bags, even with bag precoating. Instead of 2-3 year bag life, which would be typical for a coal boiler or waste incineration application, the typical bag life can be as short as 6 months to a year for a glass application.

Bags present much more resistance to flue gas flow than a precipitator system. During operation, the baghouse pressure drop can rise to 6-8 inches w.g. (2.4 - 3.2 m bar) as the bags collect material. After cleaning, it can drop to 1-2 inches w.g. (.1 - .8 m bar). The energy required for this higher pressure drop can result in a substantial annual premium for the baghouse cost of operation. In addition, when the bags are cleaned the rapid pressure drop can make accurate furnace pressure control difficult which can upset the glass quality.

Also, the exhaust gases from a glass furnace is often much hotter than other processes, therefore, there is a much greater risk of exposing the air pollution equipment to high temperature flue gas. A very short upset period can result in substantial damage to a baghouse system.

Bags also present an additional problem. Worn bags and cages are usually considered hazardous waste and must be disposed of in approved hazardous waste facilities.

Electrostatic Precipitator

Electrostatic precipitator (EP) systems have been proven effective at reducing particulate from glass furnaces. They are by far, the most popular device used on glass furnaces in the world today.

The initial cost of an electrostatic precipitator system may be slightly higher than other types of pollution control equipment. However, the operating and maintenance costs are low enough that the price premium can be paid back in about 2-3 years, depending upon the size of the system. Several furnaces can be connected to a single EP system much easier than with a baghouse system. (Multi-furnace pressure control is more difficult with a baghouse). This tends to normalize the cost of the EP vs. FF systems. A precipitator offers several features that contribute to the lower cost of operation:

System Pressure Loss

The largest energy consumer in an air pollution device is the draft fan. The pressure drop across an E.P. system is typically .5 inches w.g. (1.25 m bar) much less than a baghouse or wet scrubber system. The annual energy savings will be in the tens of thousands of dollars.

Maintenance

Obviously bag replacement and bag precoating are not necessary for an EP. These annual costs are substantial. Typically, the extra maintenance and higher energy costs for a baghouse system will offset the initial price premium for an E.P. system in only two years.

High Temperature Design

As mentioned before, the United McGill E.P. can withstand high temperature upsets, thus avoiding damage for a much longer period than a baghouse system. High temperature operation

can also avoid water consumption. Many furnaces exhaust between 600-900°F (370-483°C). If the duct from the furnace exhaust point to the E.P. inlet is long enough, radiant losses can be high enough so that water cooling is not required. The system price is reduced with the elimination of the cooler and the cost of water consumption is avoided.

Coincidentally, the exhaust temperature of 700-900°F (370-482°C) is a good for SO₂/hydrated lime reaction. If medium SO₂ reduction is required, the higher temperature offers an opportunity for high temperature lime injection. As much as 50% SO₂ reduction can be achieved by dry reaction of hydrated lime and SO₂.

The recognition of the hazards of glass emissions and United McGill's many years of experience, led to the installation of two precipitator systems at a glass plant in New Jersey in 1973. Since that time the United McGill precipitator system has been installed on over 120 glass melting furnaces world wide.

Oxygen Fuel Firing

Recent requirements to further reduce emissions from glass furnaces, particularly NO_x, have resulted in a great deal of interest in 100% oxygen firing. Very good results have been achieved in NO_x reduction, improved glass quality, furnace cost reduction, and a potential waste disposal cost reduction.

Oxygen firing substantially reduces the volume of gas exiting a glass furnace. However, as reported in the November 1991 Glass Problems Conference by Gallo Glass and Carr Lowry, the

mass emissions of particulate and SO_2 are not significantly changed. In addition, since there is no heat recovery, the flue gas exits the furnace around 2200-2600°F (1200-1427°C) with 50-60% water vapor. The concentration of particulate is high, therefore the opacity is also high. Pollution control equipment may be required for an O_2 fired furnace depending upon the prevailing regulations.

If an air pollution system is necessary, the flue gas must be cooled before entering a precipitator or baghouse system. Cooling with water is not usually advisable because the moisture content is already high. Cooling with dilution air will reduce the moisture content, however, the flue gas volume will be increased. The net result is that the flue gas volume is lower than with a conventionally fired furnace, but the mass emission rate will be about the same. Air Pollution equipment will be as necessary as with a conventional fired furnace. Since the flow rate is less, it is likely that the pollution control equipment can be smaller.

Fundamentals of Precipitator Operation

Particle collection with an E.P. is relatively simple. It consists of attraction of charged particles to an opposite polarity. United McGill Corporation has developed a unique E.P. design that is well suited for collection of particulate from a glass furnace. Particles are charged by passing them through an ionized gas. The ionized gas, or corona, is made by a high voltage, direct current source in a gas stream. In a precipitator, the high voltage potential is usually applied to small diameter wires or, as in the case of the United McGill E.P., plates with sharp needles attached to the leading and trailing edges. This is typically called the discharge grid or discharge plate. The opposite polarity is called the collector plate.

The high voltage results in a high electric field near the corona emitter. The area of the corona glow discharge contains excited free electrons and positive ions that are a result of electron impact ionization. Dust passing through this corona region captures the free electrons or positive ions. The dust particles in turn become charged by the accumulation of like charges.

Subsequently, the charged dust particles migrate to the opposite polarity of the power source. In practice, the particles are allowed to agglomerate for a period of time. Then the plates are "rapped" to knock sheets of collected material into hoppers below the plates.

Some of the unique features of the United McGill design are:

1. The gas is ionized using sharp needles attached to a discharge plate. Because of the sharp points, ionization occurs at a relatively low voltage, 20-30 KV. This lower voltage saves energy costs, reduces insulator maintenance costs, and permits more collection area per volume of equipment. The needle plate design also broadens the usable dust resistivity range for efficient operation. More details about this will be covered later.
2. Particle charging is random. Particles will be charged both positively and negatively. Therefore the discharge plate in the United McGill E.P. will collect as well as the collection plate. This effectively increases the collection area per volume by about 30%.
3. Both the collection and discharge surfaces in the United McGill design are made of heavy, 13 gauge, corten steel plate. The result is that the system is rated 850°F (454°C) continuous duty. This protects the equipment for prolonged upset conditions that would cause substantial damage to other equipment designs.
4. Glass dust can be "mechanically sticky" and once agglomerated can be difficult to release. The United McGill rapper design has proven to provide the effective

energy to release glass dust without severe re-intrainment.

E.P. Efficiency

The efficiency of an E.P. system has been described by the Deutsch-Anderson equation:

$$\text{efficiency} = 1 - e^{-(A/Q \times 4)} \quad (1)$$

Where:

$$\text{efficiency} = (1 - \text{outlet/inlet}) \times 100$$

$$Q = \text{gas rate (ACFM)}$$

$$W = \text{migration velocity (ft./min.)}$$

$$A = \text{collection area (ft}^2\text{) or plate area}$$

Thus, for a given E.P. size and operating condition, if the migration velocity is known the efficiency is known. In real life though, the migration velocity is dependent on a great number of parameters.

Temperature, moisture, chemical composition, and particle size will vary the migration velocity enough that use of the equation is quite risky.

On the other hand if data is collected for a specific process, then the relationship can be used to help size equipment. For a specific process, the migration velocity can be considered a constant. A/Q is defined as specific collection area (SCA). If this is done, it can be shown that the mass emission is an exponential function of the collection area and the gas flow rate.

$$\text{Efficiency} = 1 - K_1 e^{-SCA} \quad (2)$$

$$\text{Reworking this relationship: Outlet} = K_2 e^{-SCA} \quad (3)$$

Given the flow rate, and desired outlet, the size of the precipitator can be found for the specific process. United McGill's procedure is to segregate data and plot information from as many common sources as possible. For example, E-glass data or container glass data and so on. The

collection of this data is used to select the optimum E.P. size. This method eliminates the risk of a judgmental selection of migration velocity in the Deutsch Anderson equation. Fig 3 shows a typical SCA curve.

Factors that effect E.P. Performance

The emissions from glass melting furnaces are relatively constant over prolonged periods. Therefore the performance from an E.P. system will be good also so long as the recommended maintenance is performed. However, batch changes can effect the chemical composition of the exhaust gas. Such a chemical change can alter the resistivity of the collected dust.

Usually, a minor change in the dust resistivity is not significant and does not significantly alter an EP's performance. However, there is a limit. Too high or too low a dust resistivity will reduce E.P. performance. If the resistivity is too high, the collected particles retain too much of their charge and cause back corona . Back corona will inhibit the applied voltage and the ability to charge particles. Back corona is characterized by very low voltage and high current meter readings. If the resistivity is too low the particles discharge too quickly and retrain into the gas stream. Dust with too low a resistivity is characterized by higher than usual d.c. voltage, and high current.

The needle plate design of the United McGill E.P. can provide excellent performance collecting dust with resistivity from $8(10)^4$ to $5(10)^{11}$ ohm - centimeters. The needle plate design has demonstrated the ability to provide good performance over a broader range than other EP designs.

Figures 4-6 show three typical dust analysis from various glass furnace emissions. The data show the dust from batch A can be collected over the entire range; however, the performance will be better above 300°F (149°C). Dust from batch B should be collected at less than 300°F (149°C) or greater than 600°F (316°C).

To avoid operation in an undesirable range, it is important to know the characteristics of the dust. If a batch change is made on an existing E.P. system, data should be taken to determine if a temperature change should be made to maintain optimum E.P. performance. Usually it is a matter of comparing previous E.P. operating voltage and current data with the new data. If there is a large change, the matter should be pursued.

Maintenance

Operation of a glass melting furnace is different than most other manufacturing processes. First the process is relatively hot and second the process is continuous. Unless the end of a campaign is near, shutting down for maintenance is not an option. Therefore ancillary equipment must have high reliability. There are several features of an E.P. that should be included with each system. Some of the most important are:

- High temperature structural design

- Insulated hoppers and chambers

- Isolated insulator compartments

- Quick access for inspection and maintenance

- Flow Modeling

Conclusion

The small particle size, and the material emitted from glass furnaces are hazardous to human health. It is our moral obligation to minimize their emission. The electrostatic precipitator has proven to be an effective device to collect glass furnace emissions. The E.P. has proven to have long term performance with minimal required maintenance.

DJK:sap:7094G.1

Figure 1

Test Conditions:

1. Test Location: Precipitator System Inlet.
2. Flue Gas Temperature at Test Location: 730°F (388°C).
3. No Pretreatment.

Test #1 8-27-77

Greater than 14.86 microns	100 % less than
7.98 to 14.86 microns	87.89 % less than
3.61 to 7.98 microns	75.42 % less than
2.22 to 3.61 microns	63.34 % less than
1.11 to 2.22 microns	53.21 % less than
.566 to 1.11 microns	15.98 % less than
Less than .566 microns	24.56 % less than

Test #2 8-27-77

Greater than 14.98 microns	100 % less than
8.05 to 14.98 microns	89.57 % less than
3.64 to 8.05 microns	76.1 % less than
2.24 to 3.64 microns	64.52 % less than
1.12 to 2.24 microns	55.54 % less than
.570 to 1.12 microns	43.96 % less than
Less than .570 microns	28.13 % less than

Test #3

Greater than 13.42 microns	100 % less than
7.21 to 13.42 microns	89.62 % less than
3.26 to 7.21 microns	77.28 % less than
2.00 to 3.26 microns	64.2 % less than
1.00 to 2.00 microns	55.07 % less than
.511 to 1.00 microns	44.7 % less than
Less than .511 microns	32.11 % less than

Figure 2

Typical Mass Emission Rate for Uncontrolled Glass Furnaces

Glass Industry Segment	Typical Production Rate		Particulate Emission Factor		Particulate Emission from Typical Furnace	
	(mt/d)	(tons/day)	(g/mt)	(lb/ton)	(kg/hr)	(lb/hr)
Flat Glass	300	330	0.75	1.5	10.3	18.75
Container Glass	127	140	0.75	1.5	3.97	8.8
Pressed and Blown (excluding textile fiberglass)	91	100	0.75	1.5	2.84	6.3
Textile Fiberglass	73	80	2.0	4.0	6.08	13.33
Wood Fiberglass	136	150	2.0	4.0	11.33	25

mt/d = metric tons per day

g/mt = grams per metric ton

Figure 3

TYPICAL PRE-1980 PARTICULATE LIMITATIONS FOR EXISTING STATIONARY SOURCES

Process Weight Rate		Illinois, Indiana, Ohio and Oklahoma		California		New Jersey		New York		Pennsylvania		West Virginia	
kg/hr	lb/hr	kg/hr	lb/hr	kg/hr	lb/hr	kg/hr	lb/hr	kg/hr	lb/hr	kg/hr	lb/hr	kg/hr	lb/hr
0.45	1	1.9	(4.1)	1.9	(4.1)	2.5	(5.5)	1.7	(3.8)	1.8	(3.9)	4.5	(10)
0.91	2	3.0	(6.5)	2.7	(5.9)	2.7	(6.0)	2.7	(6.0)	2.4	(5.3)		
1.36	3	3.9	(8.6)	3.4	(7.4)	2.9	(6.4)	3.5	(7.8)	2.8	(6.2)		
1.82	4	4.7	(10.4)	4.0	(8.7)	3.1	(6.9)	4.3	(9.5)	3.2	(7.0)		
2.27	5	5.5	(12.1)	4.5	(10.0)	3.4	(7.4)	5.0	(11.0)	3.5	(7.7)		
2.72	6	6.2	(13.6)	5.1	(11.3)	3.6	(7.9)	5.6	(12.4)	3.8	(8.3)	7.3	(16)
3.18	7	6.9	(15.1)	5.7	(12.5)	3.8	(8.4)	6.2	(13.7)	4.0	(8.9)		
3.64	8	7.5	(16.5)	6.2	(13.7)	4.0	(8.8)	6.8	(15.0)	4.3	(9.4)		
4.09	9	8.1	(17.9)	6.8	(15.0)	4.2	(9.3)	7.4	(16.2)	4.5	(9.9)		
4.55	10	8.7	(19.2)	7.4	(16.2)	4.5	(9.8)	7.9	(17.4)	4.7	(10.3)		
5.0	11	9.3	(20.4)	10.1	(22.2)	4.7	(10.3)	8.4	(18.5)	4.9	(10.8)	10.0	(22)
5.45	12	9.9	(21.7)			4.9	(10.8)	8.9	(19.6)	5.1	(11.2)		
5.91	13	10.4	(22.9)			5.1	(11.2)	9.4	(20.7)	5.2	(11.5)		
6.36	14	10.9	(24.0)			5.3	(11.7)	9.9	(21.8)	5.4	(11.9)		
6.82	15	11.5	(25.2)			5.5	(12.2)	10.4	(22.8)	5.6	(12.3)		
7.27	16	12.0	(26.3)			5.8	(12.7)	10.8	(23.8)	5.7	(12.6)		

Figure 4

Approximate 1980 New Source PM-10 Requirements

<u>Type of Glass</u>	<u>Allowed Emission Gas Fired</u>		<u>Allowed Emission Oil Fired</u>	
	<u>(lbs/T)</u>	<u>g/KG</u>	<u>(lbs/T)</u>	<u>g/Kg</u>
Borosilicate pressed and blown	1	0.5	1.3	0.65
Container	1	0.5	0.26	0.13
Soda lime pressed and blown	0.2	0.1	0.26	0.13
Textile	0.5	0.25	0.65	0.33
Wool fiberglass	0.5	0.25	0.65	0.33
Flat Glass	0.45	0.23	0.45	0.23

Figure 5

Typical Recent Additional Requirements for New Sources (USA)

	<u>Outlet</u>
Lead Glass	0.005 grains/DSCF (12.3 mg/Nm ³)
SO ₂	80-85% Reduction
HF	95+ % Reduction
B ₂ O ₃ (E-Glass)	< 10% opacity
B ₂ O ₃ (Hard Borosilicate Glass)	< 20% opacity

Figure 6

Recent Non-USA Allowed Emission for Glass Furnaces - (New Source)		
Country	Particulate grains/DSCF	Particulate (mg/Nm ³)
Austria	0.012	(30)
Belgium	0.02	(50)
Brazil	0.02	(50)
Chile	0.04	(100)
England	0.02	(50)
France	0.02	(50)
Germany	0.02	(50)
Japan	0.02	(50)
Korea	0.02	(50)
Mexico	1.0	(250)
Thailand	0.06	(150)
U.S.	* See below	

* Rate is by glass type, and furnace pull rate. Usual range is 0.005 for lead glass to 0.03 for an oxy-fuel furnace.

Application of Gas Reburning Technology to Glass Furnaces for NO_x Emissions Control

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Abstract

Like many other high-temperature industrial processes, glass furnaces produce high concentrations of oxides of nitrogen (NO_x) due to the high combustion temperatures required to process the glass batch raw materials. Since increasingly stringent air quality regulations are forcing the glass industry to reduce emissions of NO_x, there is significant interest in technologies which can be applied to glass furnaces to achieve high levels of emissions control cost effectively. For glass furnaces, available options for NO_x control are either very expensive or have the potential to negatively impact the process. Gas Reburning is a NO_x control technology which has successfully been demonstrated on utility boilers to provide moderate to high NO_x removal efficiencies at a moderate cost per ton of NO_x abated. This paper describes the results of a study to assess the potential for and economics of applying gas reburning technology to industrial glass furnaces. Model furnaces were defined for glass furnaces employed in the manufacturing of flat, container, and fiber glass to permit a detailed evaluation of reburning technology. Conceptual reburning system designs for each model plant were developed to permit the process performance and costs to be established. Chemical kinetic and heat transfer models were used, respectively, to assess the potential reductions in NO_x emissions achievable and to evaluate the impacts of the reburning process on the overall furnace thermal efficiency. Costs for application of reburning technology to glass furnaces were developed and compared to other available technologies for control of NO_x emissions.

Introduction

Gas Reburning is a NO_x control technology which can be used to control emissions from virtually any continuous emission source. It is not fuel specific and can be applied to equipment fired with coal, oil, gas, biomass or waste fuels. Some of the principal applications where gas reburning can effectively be applied are: utility boilers, industrial boilers, process heaters, incinerators, furnaces, and kilns. A significant amount of the work on the reburning process to date has focused on coal fired utility boilers. This emphasis has been due to concern over acid gases (NO_x and SO₂) and the need for control of acid rain precursors from these systems.

This paper summarizes the results of a feasibility study funded by the Gas Research Institute to evaluate the potential for the application of gas reburning to glass furnaces. Glass furnaces produce high concentrations of oxides of nitrogen (NO_x) due to the high combustion temperatures required to melt the glass batch materials. Increasingly stringent air quality regulations are forcing the glass industry to reduce emissions of NO_x . Two NO_x control technologies that result in moderate, 40 to 50 percent, reductions at relatively low cost are low- NO_x burners (LNB) and Oxygen Enriched Air Staging (OEAS). Two technologies capable of achieving high, 85 to 90 percent, reductions in NO_x emissions are Selective Catalytic Reduction (SCR) and Oxy-Fuel. However, SCR has very high capital costs and Oxy-Fuel has very high operating costs, resulting in a high overall annualized cost of control for these technologies. Further, SCR is poorly suited to glass furnaces because the alkalis present in the exhaust gas can rapidly poison the catalyst. As demonstrated in this paper, gas reburning is a technology which can be applied to glass furnaces to achieve NO_x emissions levels potentially similar to Oxy-Fuel with a cost effectiveness equivalent to LNB and OEAS on an annualized cost per ton of NO_x abated basis.

The gas reburning process, as shown in Figure 1, divides the chemical pathway into three zones. The first zone is the primary zone where fuel and air are burned under normal conditions. In the second zone, a small amount of natural gas is injected downstream of the primary combustion zone to drive the overall stoichiometry slightly fuel rich. Depending upon the primary zone combustion stoichiometry, the amount of fuel required is 10 to 20 percent of the primary zone fuel. Hydrocarbon radicals formed from natural gas in the fuel rich reburning zone, primarily CH species, react with NO formed in the primary zone to form other reduced nitrogen species such as HCN and NH_3 . Once formed, these species rapidly react with the remaining primary NO molecules to form molecular nitrogen (N_2). Following the reburning zone, additional combustion air is injected to complete oxidation of the reburning fuel. In the burnout zone, any remaining reduced nitrogen species are converted to molecular nitrogen or back to NO. High combustion gas temperatures and high primary NO_x concentrations can improve the NO_x reduction achievable with gas reburning. If gas reburning can be accomplished under nearly isothermal conditions and at residence times of roughly half a second, significant NO_x reductions (greater than 80 percent) are theoretically possible. Glass furnaces appear to be good candidates for a successful installation of gas reburning because of their large post melter cavities (furnace ports and regenerator crown). Overall, NO_x reductions of up to 85 percent have been estimated for glass furnaces using empirical and computational modelling tools.

There are several potential approaches for application of gas reburning to glass furnaces. In the approach used in this study, it was assumed that the reburning fuel would be injected into the ports opposite the firing side to avoid major impacts on the heat distribution above the melt. For glass furnaces with sufficient gas residence time between the reburning fuel injection point and the heat recovery device (i.e. regenerator or recuperator), the burnout air would be injected just upstream of the heat recovery device. This makes gas reburning an attractive technology for retrofit applications since the modifications necessary to install the technology are minimized. Application of reburning during a furnace rebuild offers the potential for minimizing the impacts of reburning on furnace thermal performance and for increasing NO_x reductions. For example, regenerators can be redesigned to substantially improve recovery of the reburning fuel heat content, and to implement advanced versions of the reburning process.

The objective of this feasibility study has been to assess the potential for successful application of gas reburning to control NO_x emissions from glass furnaces used in the manufacture of container, flat and fiber glass. The overall effort was focused on retrofit applications since this is believed to be the current market. Conceptual designs were developed for retrofitting reburning systems on

three model furnaces: a 500 ton per day flat glass furnace, a 250 ton per day container glass furnace, and a 125 ton per day fiber glass plant. Next, the impacts of reburning on the overall thermal efficiency and NO_x emissions for each furnace were evaluated using computerized computational process models. Finally, the cost effectiveness of gas reburning technology was calculated and compared to other available NO_x control technologies. The results of this assessment for the flat and container glass furnaces are summarized in the following sections since these plants represent the majority of the glass manufacturing industry. Further details on the feasibility study and the results for the fiber glass plant are found elsewhere¹.

Model Glass Furnaces

Model glass furnaces were developed to permit evaluation of gas reburning for a representative cross section of equipment used in the United States. Model furnaces representing the two main types of glass manufacturing processes—flat and container glass—were defined based upon information in the open literature and discussions with industry experts and glass furnace manufacturers. The model furnace definitions included furnace size, operating parameters, and NO_x emissions. Furnace sizes were selected based upon averages of those used in industry and to allow comparison to the EPA Alternative Control Technology Document for NO_x emissions from glass manufacturing². The model furnaces are briefly described below.

Flat Glass Model Furnace

Flat glass manufacturing accounts for approximately 20 percent of the glass produced in the United States. Most of the furnaces utilize the float glass method rather than the energy and labor intensive rolled glass method. Furnaces producing flat glass are generally much larger than their container and fiber glass counterparts, with production ranging from 300 to 1000 tons per day. For the flat glass model furnace, a production rate of 500 tons per day has been assumed.

To maintain high temperatures in the melter and to improve thermal efficiency, flat glass furnaces utilize regenerators to recover heat from the melter flue gases and to provide high air preheat temperatures. The products of combustion pass through a "regenerator", which typically consists of a stack of refractory bricks, transferring heat to the bricks. Every 15 to 20 minutes, the firing and exhaust ports are reversed. Combustion air passing through the regenerators on the reverse cycle is preheated to high temperatures.

Figure 2 shows a plan view of the flat glass model furnace. The furnace is of the side port design with twin regenerators. The burners are fired perpendicular to the direction of glass melt flow. Firing sides (six port) are assumed to switch every 20 minutes to maintain air preheat. The furnace thermal efficiency is 6.0 million Btus of natural gas per ton of melted glass. The average combustion air preheat temperature is 2300°F. The gas temperature is 2850°F at the exhaust ports. Baseline NO_x emissions are assumed to be 14 pounds of NO_2 per ton of glass melted, which corresponds to 1,839 ppm NO (dry, corrected to 3 percent O_2).

Container Glass Model Furnace

Container glass furnaces produce approximately 65 percent of all the glass manufactured in the United States. The majority of these furnaces utilize natural gas in addition to electric boosting to achieve high pull rates. Two primary furnace designs, side and end port, are utilized in container glass manufacturing. An end port design, shown in Figure 3, was chosen for the container glass

model furnace since this is a common firing configuration, and since the model flat glass furnace is of the side port design.

The container glass model furnace uses regenerators and produces 250 ton per day of glass at a furnace firing rate of 4.2 million Btu per ton of glass melted. In addition to firing natural gas, approximately 1750 kW of electric boosting is used. Over the cycle, the average air preheat temperature is 2100°F, and the average exhaust gas temperature at the exhausting port is 2700°F. NO_x emissions are 7 lb NO₂ per ton of melted glass or 1,287 ppm NO (dry, 3 percent O₂).

Gas Reburning Evaluation Methodology

To estimate gas reburning performance on the model furnaces, a methodology consisting of the following steps was followed: (1) critical parameters needed to optimize reburning performance on glass furnaces were identified, (2) conceptual reburning system designs were developed for the model furnaces, (2) heat transfer and mass balances were calculated to establish overall gas and air temperatures throughout the furnace, and (3) the temperature predictions and a reburning process kinetic model were used to estimate the potential reductions in NO_x emissions achievable with gas reburning.

Reburning Process

For application to glass furnaces, the overall reburning process can be divided conceptually into three zones as shown in Figure 4:

- *Primary Zone:* In this zone, fuel and air are fired through the existing burners on the furnace at normal or slightly reduced primary fuel stoichiometry. The level of NO_x exiting the zone is the input to the reburning process.
- *Reburning Zone:* The reburning fuel is injected downstream of the primary zone to create a fuel rich, NO_x reduction zone. NO_x from the primary zone reacts with hydrocarbon fragments formed during oxidation of the reburning fuel and is reduced to molecular nitrogen.
- *Burnout Zone:* In this final zone, air is added to produce overall fuel lean conditions and oxidize carbon monoxide and any remaining fuel fragments exiting the reburning zone.

Extensive bench and pilot scale research programs have been conducted by EER under funding from U.S. Environmental Protection Agency, the Gas Research Institute, and the U.S. Department of Energy. These studies have quantified the impact of process parameters on reburning effectiveness and provided scaling methodologies. Although a wide range of process parameters influence overall NO_x reductions and must be specified in a reburning application, fortunately, not all of the parameters are of first order importance. The reburning process is primarily controlled by the stoichiometric ratios of the primary, reburning, and burnout zones (SR₁, SR₂, and SR₃), reburning zone fuel mixing, temperature and initial NO_x level. Long zone residence times, hot combustion gases, and high initial NO_x all work to enhance the NO_x reduction achievable with gas reburning. These characteristics are well matched in glass furnaces.

Conceptual Designs

Conceptual designs for a gas reburning system for the model furnaces were first developed to insure adequate reburning zone access along the gas path. By determining where the reburning fuel and overfire air injectors can practically be placed, a more realistic assessment of the time-temperature history of the reburning zone can be established. In addition, development of the conceptual designs permits a more accurate estimate of the capital costs for retrofitting the model furnaces with a reburning system.

The first step in the conceptual design process is development of material balances for baseline and reburning operation. For reburning, the primary design criterion is to achieve a stoichiometry in the reburning zone of about 0.90. This stoichiometry generally results in optimum NO_x reduction at minimum reburning fuel usage. In this study, it was assumed that the reburning fuel would be added immediately downstream of the melter in the port neck to minimize impacts of reburning on the melt. It may be possible to inject the reburning fuel into the end of the melter region; however, this possibility would need to be evaluated on a site specific basis.

Reburning fuel injection downstream of the melt can decrease the overall furnace efficiency if the added heat input is not fully recovered in the regenerators. Therefore, to minimize the amount of reburning fuel injected and the impact on furnace efficiency, the primary stoichiometry should be minimized. For this study, the primary zone stoichiometry has been assumed to be 1.01 during reburning operation. It is expected that this level can, on average, be achievable on most glass furnaces, but may require some optimization of the melter firing rate and distribution. On furnaces where it is not possible to modify the melter stoichiometry without impacting the melter operation or glass quality, additional reburning fuel would be needed to offset the higher oxygen content of the flue gas. Recovery of the reburning fuel energy in the regenerators is expected to result in higher air preheat temperatures and lower primary fuel consumption, which can offset the reburning fuel consumption.

The reburning process design involves utilizing empirical correlations of jet behavior in conjunction with process design parameters (zone residence times and temperatures) to specify the number, location, and size of the reburning fuel and overfire air injectors. The correlations are used to specify injection systems which are expected to provide rapid mixing of the reburning and overfire air jets with the main flue gases. Rapid mixing of the reburning gas and overfire air are necessary to minimize chemistry delay times due to mixing. In the conceptual designs, a dedicated fan was assumed to be required for the overfire air, which is at ambient temperatures.

Thermal Analysis

An overall heat transfer model of a glass furnace was developed to provide information about the potential impacts of reburning on refractory, gas and process temperatures, and on energy requirements. Specifically, the desired information is the amount of energy associated with the reburning fuel which is absorbed by the checkers, and the magnitude of any changes in the gas and brick temperatures. The temperature profiles through the regenerators are also of interest to characterize any potential changes in the normal operating profile.

The processes considered in the thermal analysis model are illustrated in Figure 5. The thermal model calculates the mass and energy content of the gas stream as it passes through the furnace, from the entrance to the air preheat regenerator to the exit of the flue gas regenerator from known, measured process variables. The thermal analysis model also includes a time-dependent one-dimensional regenerator model and a simplified radiant equilibrium model of the melter.

Specification of the furnace fuel efficiency and exhaust port excess oxygen allows fuel and combustion air flow rates to be calculated.

Heat transfer in the regenerators is calculated using a numerical algorithm in which the gas and brick temperatures are determined as a function of distance along the regenerator length and time through the regenerator cycle³. Both convective and radiative contributions to heat transfer are considered. The radiative contribution is calculated using a radiative heat transfer coefficient³. The gas radiative properties are calculated using a polynomial curve fit⁴. The convective heat transfer coefficient is calculated by iteration to satisfy the boundary conditions. Heat loss from the furnace and air in-leakage to the regenerator are also considered by the model.

Thermal analyses were performed for both baseline and reburning operating conditions. For simplicity, the regenerator convective scale factor, the fractional heat loss in the regenerator, and the total heat loss in the melter were specified to be equal to the baseline operation values. The chief variation in operation due to reburning is the introduction of reburning fuel and overfire air. These input streams are located downstream of the melter, and so represent energy which may be lost unless recovered in the regenerator.

NO_x Performance Estimates

The potential NO_x reductions achievable with gas reburning were estimated using a computational chemical kinetic, time dependent model of the reburning process. The kinetic model consists of 52 species and 200 elementary reactions. The code is assembled into a series of well stirred and plug flow reactors which represent the various zones associated with the reburning process. The reburning fuel and overfire air streams are injected into their respective reactors at a specified rate over a specified period of time. The mass flow rates and temperature profiles in the reburning fuel and overfire air reactors are specified based upon the results of the process design and thermal performance analysis.

Gas Reburning Performance Impacts

Applying the methodology described in the previous section, conceptual gas reburning systems were developed for the model furnaces. In the approach selected, reburning fuel is introduced at the furnace port location and burnout air through multiple flush wall nozzles just above the regenerator packing. The effects of these design modifications were evaluated with the thermal analysis and kinetic models described in the preceding section. Key results are summarized in Table 1. Details of the results for the container glass model furnace are described in the following sections.

Thermal Impacts

The predicted impacts of reburning on overall mass flow rates and gas path temperatures for the container glass furnace are shown in Figure 6. Regenerator temperatures (brick and gas path) are slightly elevated (150°F) relative to baseline due to the introduction of burnout air. The increased heat input to the flue gas regenerator also increases the air preheat to the primary zone by about 150°F. This increase in air preheat energy is offset by a slight decrease in mass flow due to the reduced air flow (necessary to keep primary stoichiometry, and subsequent reburning fuel requirements, as low as possible). As a result, the primary fuel flow decreases slightly from 1992 lb/hr (baseline). The reburning fuel needed for attaining the proper reburning zone stoichiometry raises the total fuel consumption to about 7.5 percent.

Figure 7 shows a comparison between the mean flue gas temperature profile in the regenerator for baseline and reburning conditions. The difference between the baseline and reburning temperatures is smaller at the regenerator entrance and increases as it reaches the exit. The average increase is expected to be approximately 250°F. Exhaust gas residence time in the checkers is about 2.5 seconds.

The effects of temperature elevation and alternating oxidizing and reducing gases on refractory lifetime are a practical consideration for reburning design retrofits. Near the top of the checkerwork, brick temperatures increase by about 100°F due to reburn. Like the gas temperatures, the magnitude of the change in temperature increases further down in the checkerwork. At the top elevation, only the first 3.5 feet of regenerator packing exceed the baseline maximum temperature.

NO_x Control

The reburning gas path temperature profile developed in the thermal analysis was used to estimate the potential NO_x control achievable with gas reburning using a kinetic model of the reburning process, in the absence of mixing processes. For the container glass furnace, the key model inputs were:

•	Primary NO _x	7 lb/ton (1193 ppm, wet, 0 %O ₂)
•	Reburning Fuel Injection Temperature	2850°F
•	Reburning Zone Residence Time	0.7 seconds
•	Reburning Zone Stoichiometry	0.90
•	Burnout Air Injection Temperature	2783°F

The gas temperature at the point of reburning fuel injection and the gas temperature at the burnout air injection point were based upon the thermal model results. To calculate the reburning fuel average residence time, it was assumed that the volume occupied by the combustion gas was equal to the port flue volume plus one half of the regenerator crown volume (to one foot above the checkerwork). This assumption was based upon the results of a two-dimensional computational fluid dynamics model which indicate that major stream tubes occupy about half of the regenerator crown and that a significant recirculation zone occupies the remainder of the headspace.

For the container glass furnace, Figure 8 presents NO, HCN, NH₃ concentrations in the reburning and overfire air zones as a function of time. During reburn fuel injection, NO_x emissions decrease rapidly, and then slower as the initial hydrocarbon radical pool is consumed. Some HCN, NH₃ remains following the reburning zone. However, at these temperatures, NH₃ or HCN do not survive the burnout air injection step. For nominal conditions, the idealized kinetic model predicts that NO emissions will be reduced from 1193 to 116 ppm, a 90 percent reduction.

Sensitivity studies, summarized in Figure 11, show the impact of reburning zone residence time and overfire air injection temperature on final NO_x. As the reburning zone residence time increases from 0.5 to 0.9, the estimated NO_x reduction efficiency improves slightly from 90 to 91 percent. As the temperature at the overfire air injection point increases from 2700°F to 2800°F, the NO reduction efficiency falls from 92 percent to 90 percent.

Reburning Fuel mixing is a potentially limiting factor, and the reductions estimated by the kinetic model are usually optimistic. By comparing kinetic modeling predictions to bench and full-scale data, it is possible to adjust the kinetic predictions for the impacts of reburning fuel and overfire air mixing. Based upon this comparison, it was estimated, conservatively, that 80 percent reduction

should be achievable for the container glass model furnace after scaling the predictions for mixing effects.

Economic Evaluation

The conceptual designs and performance estimates were used to establish the capital and operating costs, and cost-effectiveness for application of gas reburning to glass furnaces. The cost effectiveness of gas reburning was then compared with that of other commercial NO_x control technologies. Typical installed costs for oxygen enriched air staging (OEAS), low NO_x burners (LNB) and Oxy-Fuel were developed and used in conjunction with estimated operating costs and estimated NO_x removal levels to determine the cost of control in dollars per ton of NO₂ removed.

Capital Costs

Reburning: Based upon the conceptual design developed for the model glass furnaces, the reburning system is composed of the reburning and overfire air injectors, associated duct work and flow control valves, and process controls. It was assumed that natural gas was available on site, and would be supplied from the main furnace supply line and piped to the gas jets on the ports. A dedicated burnout air fan is needed to provide air to the refractory injectors penetrating the regenerator side wall. Trickle cooling air can be provided to the nozzles when they are out of service. A line item based cost of the equipment was developed for each model plant. For the flat glass plant, the reburn capital cost was estimated to be \$719,000. For the container glass plant, the reburn capital cost was estimated to be \$475,000.

Oxygen Enriched Air Staging: Oxygen enriched air staging extracts preheated combustion air from the furnace's regenerator and re-injects it with additional oxygen downstream of the primary combustion zone. Combustion Tec Incorporated has participated in the installation of OEAS at two glass plants in California and Texas. NO_x reductions exceeding 50 percent are reported. Combustion Tec⁵ has estimated that for a 250 ton per day end port furnace, the capital cost would be approximately \$353,000. Scaled costs for the larger side port furnace were estimated to be \$535,000.

Low NO_x Burners: Low-NO_x burners are generally an attractive option for low to moderate NO_x removal efficiencies because of their low cost. The installed cost will depend largely upon the number of ports retrofitted with the burners. The EPA ACT² document provides costs for retrofitting low-NO_x burners to glass furnaces, but acknowledges that they may be inaccurate since they were scaled from a 32 ton per day furnace. A cost estimate was obtained from Teichmann⁶ for their Sorg Cascade Burner System applied to a 242 ton per day end port furnace and a side port furnace. Scaled capital costs for the model furnaces were estimated at \$241,000 for the flat glass furnace and \$159,000 for the container glass furnace.

Oxy-Fuel: Oxy-Fuel systems reduce thermal NO_x formation by firing with pure oxygen rather than air. NO_x reductions for natural gas fired furnaces of up to 90 percent have been achieved. For Oxy-Fuel systems, two situations are possible. In the first situation, the plant is forced to shutdown and rebuild the furnace before its useful life is over. In this case, the cost of the melter rebuild is the installed cost. In the second case, it is assumed that a rebuild is scheduled, and that a capital cost savings results from not constructing the regenerators. Estimated scaled costs, based on Union Carbide⁷ and EPA data, for a forced Oxy-Fuel conversion were \$1,427,000 for the flat glass furnace and \$941,000 for the container glass furnace. For Oxy-Fuel conversion performed at a scheduled rebuild, the credit for the flat glass furnace was estimated at \$750,000, and the credit

for the container glass furnace was estimated at \$495,000. These estimates do not include the cost of an oxygen plant; it is assumed that oxygen will be bulk purchased at bulk commodity prices.

Operating Costs

Each of the four NO_x control technologies have operating costs which impact the overall process economics. The main costs associated with operating the various NO_x control technologies are:

- Changes in fuel consumption, and the cost of fuel
- Cost to maintain the NO_x control equipment
- Cost of oxygen for Oxy-Fuel and OEAS technologies

Two of the four technologies impact glass furnace fuel efficiency: gas reburning and Oxy-Fuel. As shown previously, fuel consumption for gas reburning application is expected to increase by 7 to 8-1/2 percent, depending upon furnace type. Oxy-Fuel on the other hand results in a 15 percent decrease in fuel consumption for regenerative furnaces. The extent to which these changes in fuel consumption impact the operating costs, depends upon the cost of natural gas. Since the cost of natural gas varies by region in the United States, a nominal gas price of \$3.50 was used in the operating cost estimates for these technologies, and the impact of price was evaluated by varying it from \$1.50 to \$5.00 per million Btu.

The Oxy-Fuel and OEAS technologies require oxygen. Oxy-Fuel technology uses only oxygen to burn the fuel. In operation of OEAS, 3 to 5 percent of the total oxidant is oxygen. The cost of oxygen is generally reported to be 0.15 \$/100 ft³ (40 \$/ton), but it can vary as well. For the cost analysis, 40 \$/ton was used as the nominal case.

NO_x Reduction Performance

Gas reburning NO_x reductions at each of the model furnaces were estimated based on computational modeling and empirical data. An 80 percent reduction was projected for the container and flat glass furnaces. For OEAS, a 50 percent reduction from 6 lb/ton has been shown at an Anchor Glass Plant in California. Therefore, a 50 percent removal was used for the model glass furnaces. For Oxy-Fuel, a 90 percent reduction in NO_x emissions was used. This value is consistent with recent field data⁸ and the EPA ACT document. For low NO_x burners, data provided by Teichmann indicate that a 40 percent reduction is possible when the initial NO_x emission level is 4.5 lb/ton.

Cost Comparison

Cost effectiveness was calculated by summing the annualized capital cost with the annual operating costs, and dividing by the tons of NO₂ removed per year – \$/ton NO₂. To annualize capital cost, a capital recovery factor is calculated based on an estimated interest rate and life of the equipment. For this analysis, the interest rate (i) is assumed to be 10 percent. Useful equipment life estimates are based on the EPA ACT document, as well as on comments from industry, and were assumed to be 2 and 8 years for container and flat glass, respectively.

Figures 10 through 12 show the calculated cost of control for each NO_x control technology for the estimate flat and container glass model furnaces. Variations in the estimates take into account a -15/+30 estimated error in capital costs. Overall, the cost effectiveness of gas reburn, OEAS, and low-NO_x burners are similar, but gas reburning has significantly lower final NO_x emissions.

Oxy-Fuel (either with or without a scheduled rebuild) is significantly less cost effective than the other technologies; however, it does result in the lowest emission rate. In the case of the container furnace, gas reburning reduces NO_x emissions to 1.4 lb/ton at a cost effectiveness of 1300 \$/ton NO_x removed when the initial NO_x is at 7 lb/ton. Oxy-Fuel achieves NO_x control levels of 0.7 lb/ton more than reburning at a cost effectiveness of between 3200 and 4500 \$/ton. Thus Oxy-Fuel removes 10 percent more NO_x at a cost effectiveness factor 2.5 to 3.5 times higher.

Because the furnace thermal efficiency is impacted by both gas reburning and Oxy-Fuel, the cost of natural gas will influence the cost of control for these technologies as shown in Figure 13. Natural gas in Southern California is available at \$3–4 per million Btu to bulk (non core) users, and is generally one of the more expensive areas for natural gas in the United States. As shown in Figure 13, even at \$5 per million Btu, the cost effectiveness of gas reburning is still a factor of two better than Oxy-Fuel when a rebuild is scheduled.

Conclusions

A feasibility study has been performed to evaluate the effectiveness of gas reburning for NO_x control from glass furnaces. In the feasibility study, preliminary conceptual designs have been prepared for application of gas reburning to model glass furnaces representing typical furnaces used in the manufacturing of container and flat glass. Computational models have been used to evaluate the impacts of gas reburning on NO_x emissions, and on furnace fuel usage and temperatures. The results of these models indicate that 80 percent NO_x control is expected to be achievable on most flat and container glass furnaces. In retrofit applications, gas reburning is expected to result in an increase in furnace fuel consumption and slightly elevated regenerator temperatures. These impacts can potentially be mitigated during a rebuild by optimization of the regenerator design.

To evaluate the cost effectiveness of gas reburning in comparison to other NO_x control technologies, capital and operating costs were developed for gas reburning, low-NO_x burners, oxygen-enriched air staging, and Oxy-Fuel technologies. For both flat and container glass plants, estimates of capital and operating costs indicate that while gas reburn, OEAS, and LNB have similar cost effectiveness, gas reburning results in significantly lower final emissions than the other two technologies. If an additional 10 percent reduction is required, Oxy-Fuel may be utilized, but at a significantly higher annualized and operating cost. The application of gas reburning during a furnace rebuild could incorporate regenerator designs which reduce the fuel penalty expected with retrofit application. During rebuild, slightly higher regenerator construction costs would be expected for use of higher temperature refractory ratings in the upper elevations, brick configurations for enhanced heat transfer, and more massive structures.

An advanced gas reburning development plan incorporating regenerator design enhancements is being developed. The concept is directed at substantially reducing the fuel penalty and increasing the NO_x control efficiency to 90%. The concept features the combined use of selective non-catalytic reduction (SNCR) and gas reburning to attain 90 percent NO_x control, and improvements in radiative and convective heat transfer in both the melter and regenerator.

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References

1. Pont, J., et al. *Glass Tank NO_x Emission Control with Gas Reburn*, GRI Report No. GRI-94/0018.2, March 1994.
2. *Alternative Control Techniques Document—Control of NO_x Emissions from Glass Manufacturing (Second Draft)*, U.S. Environmental Protection Agency, February 1993.
3. Hausen, H. *Heat Transfer in Counterflow, Parallel Flow, and Cross Flow*, translated from the German by M. S. Sayer, translation edited by A. J. Willmott, McGraw-Hill Book Company, New York, 1983.
4. Smith, T. F., Z. F. Shen, and J. N. Friedman. *Evaluation of Coefficients for the Weighted Sum of Gray Gases Model*, Transactions of the ASME, Vol. 104, November 1982, pp. 602-608.
5. Personal Conversation with Michael Joshi of Combustion Tec, November 5, 1993.
6. Personal Correspondence from Ronald Moore, Teichmann/Sorg Group, Ltd, July 1, 1993.
7. Delano, M. A. *Preliminary Economic Analysis of 100 Percent Oxygen Enriched Glass Melters*, Union Carbide Corporation, Linde Division.
8. Tuson, G., R. Higdon and D. Moore, D. *100% Oxygen Fired Regenerative Container Glass Melters*, Presented at the 52nd Conference on Glass Problems, University of Illinois at Urbana-Champaign, November, 1991.

TABLE 1. IMPACT OF GAS REBURNING ON MODEL FURNACE PERFORMANCE.

Model Furnace	Container Glass Furnace	Flat Glass Furnace
Furnace Parameters:		
Furnace Production Rate (tons per day)	250	500
Firing Configuration	End Port	Side Port
Number of Firing Ports	1	6
Burner per port	3	2
Fossil Furnace Efficiency (mmBtu/ton)	4.2	6
Electric Boosting (kW)	1,750	0
NO _x Emissions (lb NO ₂ per ton glass)	7	14
Furnace Temperatures (°F):		
Combustion Average Air	2,100	2,550
Combustion Products:		
Exhaust Port	2,700	2,850
Regenerator Average Exit	850	700
Performance Estimates:		
NO _x Control (%)	90-93	89-90
Fuel Increase (%)	12.2	12.2
Maximum Refractory $\Delta T(^{\circ}F)$	100	140

Figure 1. Overview of gas reburning process.

Figure 2. Plan view of flat glass model furnace.

Figure 3. Plan view of container glass model furnace.

Figure 4. Approach for applying gas reburning to glass furnaces.

Figure 5. Overview of glass furnace thermal analysis model.

Figure 6. Impact of reburning on thermal performance of container furnace.

Figure 7. Container furnace regenerator temperature profile.

Figure 8. Kinetic model predictions for container glass model furnace.

Figure 9. Impact of reburn zone residence time and overfire air injection temperature on predicted NO_x emissions for container furnace.

Figure 10. Cost of control for container glass furnace (7 lb/ton initial NO_x).

Figure 11. Cost of control for container glass furnace (4.5 lb/ton initial NO_x).

Figure 12. Cost of control for flat glass furnace.

Figure 13. Impact of natural gas cost on cost of control for container glass furnace.

OxyFuel Glass Furnaces & Air Pollution Control Systems

Pure oxygen based combustion has been around for many years and is becoming widely accepted in the glass industry. It enables glass producers to pull more glass, melt batch with less fuel, reduce the cost of a furnace, remove costly regenerators and recuperators, and reduce a furnace's exhaust flow rate. With all of these new benefits comes a new set of emissions concerns and problems. This paper will address these concerns and explore the technologies available to solve the problems.

Objectives in Converting to OxyFuel Firing

Glass producers are constantly looking for ways to produce quality glass in the shortest amount of time with the least amount of fuel. By pulling more glass more efficiently, they can make more money. Combine this objective with ever tightening environmental regulations, and OxyFuel firing can be an attractive alternative to conventional firing.

The EPA has six criteria pollutants that must be regulated under Title I of the Federal Clean Air Act Amendment of 1990. The monitored pollutants are oxides of sulfur (SO_x), carbon monoxide (CO), oxides of nitrogen (NO_x), particulate matter less than 10 microns (PM_{10}), ozone (NO_x or VOC), and lead. Sections of the country have been classified as either attainment or nonattainment zones. Attainment zones are areas that are currently below the regulatory levels of these six pollutants. Non-attainment zones are above the regulated levels of the pollutants. There are five types of non-attainment zones: marginal, moderate, serious, severe, and extreme.

In severe or extreme non-attainment zones, such as New Jersey and the south coast of California, the highest priority is reducing NO_x emissions from furnace exhaust. In these zones, a Reasonably Achievable Control Technology (RACT) is required. For glass manufacturers, RACT calls for reducing NO_x , which is a precursor to ground level ozone, PM_{10} , and SO_x , which is a precursor to PM_{10} . OxyFuel firing can be a glass manufacturer's best retrofit alternative for NO_x reduction because it increases process quality and productivity while lowering costs.

The Chemistry of OxyFuel Combustion

In furnaces with conventional firing, the oxygen required for combustion comes from air, a large percentage of which is nitrogen. Since nitrogen does not aid in the combustion process, melting a quantity of glass requires a larger volume of air than it would of pure oxygen. The large quantity of nitrogen is what forms the oxides of nitrogen which help create brown, ground level ozone or smog. Oxygen based combustion nearly eliminates the nitrogen component, substantially reducing the flue gas emissions. NO_x can still form at the furnace burners from tramp nitrogen, but this quantity is minimal.

Air based combustion -For every 1 unit of natural gas used in combustion, there are roughly 8 units of nitrogen and 2 units of oxygen. The end result is close to 11 units of combustion.

The equation is as follows:

Oxygen based combustion -For perfect combustion, every 1 unit of natural gas requires 2 units of oxygen. The end result is 3 units of combustion.

Reducing combustion units from 11 to 3 results in a 72 percent decrease in flue gas volume. Oxygen based combustion also offers a fuel savings of one third. The resultant flue gas reduction is then as high as 82 percent. The moisture as a percent of the total volume would be 67 percent, as opposed to 1015 percent in air fired furnace exhausts.

Regenerative, Recuperative, and OxyFuel Furnace Conditions

Converting to OxyFuel firing substantially changes the characteristics of the exhaust gases. Regenerative furnaces typically have a flue gas temperature of 600 - 900°F (315 - 480 °C) at the furnace exhaust off take. The moisture in the gas is 810 percent. Recuperative furnaces experience slightly higher off take temperatures of 1100 - 1700 °F (593 - 926 °C) and moisture of about 12 15 percent. OxyFuel furnaces, without a heat recovery system, exhaust 2200 - 2600 °F (1204 - 1426 °C) flue gas with 55 - 67 percent moisture. With such drastic changes in exhaust conditions, alternative methods of handling the flue gas must be considered.

Flue Gas Handling and Control

Cooling the Exhaust Gas

From an emissions control standpoint, the extremely high temperature from an OxyFuel furnace is the greatest concern. Downstream ductwork and air pollution control equipment are typically constructed of carbon steel or ASTM A588 steel, which cannot withstand such severe conditions. The flue gas could be cooled by injecting atomized water into the duct work immediately following the off take. But adding water at this point increases the moisture to upwards of 7580 percent by volume, depending on the amount of temperature reduction. In glass applications especially, particulate from a furnace tends to adhere to the surfaces it comes in contact with. The increase in moisture will only worsen this effect. The operational problems associated with high moisture and the expense of high temperature steels required for water cooling far outweigh any benefit of the cooling itself.

With the switch to OxyFuel combustion, heat recovery equipment is no longer needed to preheat combustion air. The expensive replacement of regenerator refractories and recuperator flues have come to an end. The fuel saved by preheating the combustion air makes these replacements justifiable. With OxyFuel furnaces, the exhaust temperatures seem ideal for heat recovery; however, the dust loading can foul the heat exchanger medium. Plus, any acids present in the flue gas will condense on the equipment. In the case of E Glass, the volatilized boron can condense and harden with the consistency of cement on any surface it contacts. It appears that the cost of cleaning the heat exchange equipment, combined with the cost of future replacement, outweighs any benefit of recovering heat from the flue gas because most glass plants have no use for the heat.

Another option is to cool the flue gas by adding dilution air to the system. Although it adds to the overall flow volume, dilution air performs two very important tasks. First, the flue gas will receive the cooling needed for downstream equipment at little or no cost. Second, the percent moisture will decrease as the quantity of dilution air increases. Dilution air may enter through a refractory section of duct, which costs less than the high temperature steels required for water cooling. The air will quickly cool the gas through high temperature condensation zones encountered in some glass batches.

If cooling is done exclusively with dilution air, the flue gas volume may increase to the point that sizing emissions control equipment for this large flow becomes quite costly. An alternative method is to use both dilution air and water cooling. The combination of the two cooling methods creates a more desirable flue gas which is easier to handle. The dilution air can be injected as the flue gas exits the furnace, effectively cooling the gas to 800 - 950°F (426 - 510 °C) and reducing the moisture from 65

percent to about 14 percent by volume. Reducing the temperature any further with dilution air substantially increases the volume and the size of the emissions control equipment.

The lower temperature range permits the use of a lower cost steel, such as ASTM A588 or carbon steel, instead of stainless steel ductwork. If acid gas control is not an issue, the temperature may be reduced further with water. A cooling chamber equipped with atomizing water nozzles can be installed down stream of the dilution air. The nozzles inject a fine mist of water into the gas stream, and the chamber provides residence time to allow any water droplets to evaporate completely before exiting the chamber. This minimal water injection will increase the moisture to only about 25 - 30 percent. These moisture levels are easily tolerated in any down stream equipment, compared to the 80 percent moisture.

Acid Gas Control

In non-attainment zones, regulations often require the reduction of acid gases such as sulfur by-products (SO_x). This is done by injecting a base or reagent into the flue gas to react with the acid to form a salt. Several reagents are available for acid gas removal. The most commonly used reagents are calcium hydroxide, sodium carbonate, and sodium hydroxide. Calcium hydroxide (hydrated lime) can be used as a dry powder for relatively low efficiencies or as a wet slurry for slightly higher removal. Dry lime can remove 40 - 55 percent of SO_x , and a wet slurry can remove 60 - 70 percent. Sodium carbonate or soda ash (Na_2CO_3) is possibly the most common reagent because of its availability at glass plants. Soda ash is mixed as a solution and sprayed as a fine mist into the flue gas. Performance in the 80 - 85 per cent range is obtainable for SO_x scrubbing. Sodium hydroxide (NaOH) is a corrosive liquid, but when mixed with water it can reduce SO_x by as much as 85 - 90 percent.

The following table summarizes the percent removals available with the most widely used reagents on various acids.

Removal Efficiencies

	HCl	SO_2	HF	B_2O_3
Hydrated Lime	90 %	55 %	95 %	60 %
Sodium Carbonate	90 - 95 %	80 %	95 %	85 %
Sodium Hydroxide	90 - 95 %	85 %	98 %	85 - 90 %

As you can see from the table, very strong acids such as HCl and HF can be removed relatively easily with any base; however, weaker acids such as SO_x and B_2O_3 are best removed with a stronger reagent, typically with a sodium base.

Several factors should be considered when selecting a reagent. The level of acid reduction that is required will depend on the location of a glass plant. Low levels of reduction can be accomplished with hydrated lime and high levels with soda ash or sodium hydroxide. A plant must have a method of disposing of the reacted salts. Often, reacted lime may be disposed of in a landfill. Since sodium based reagents are leachable, they can have higher disposal costs in certain geographical locations. Depending on the batch materials, reacted sorbents may be recycled as a glass batch component. Reacted soda ash (sodium sulfate) is most often a recyclable reagent.

The spray dry process is similar to that of a water evaporative cooling chamber. A scrubbing chamber is a large segment of duct which is situated in a vertical position. The flue gas enters one end and is injected with the reagent solution or slurry. The reagent enters the chamber as an atomized substance through a high pressure nozzle in a spray lance. The base is then given adequate time to react with the acids present. As the reagent and acids react, a salt by-product will precipitate out of the flue gas.

The chamber should be sized to cool the gas stream to a preset temperature, usually 350 - 400°F (176 - 204 °C). (If lower temperatures are required, the presence of a cold spot in downstream equipment could create corrosion from any residual acids still in the gas stream.) The closer to the acid dew point the flue gas gets, the greater the acid reduction. By the time the gas reaches the other end of the chamber, the solution droplets are evaporated and a dry particulate exits for collection in a particulate control device. This type of acid gas control is typically referred to as semidry scrubbing, and SO_x reductions are typically 80-85 percent.

In territories with less stringent acid reduction requirements, a dry reagent, such as hydrated lime or dry sodium carbonate, is simply blown into the ductwork for the SO_x. The dry powder is given retention time in a reaction chamber, and the particulate is then collected in a downstream control device. With dry injection, there are usually several temperature windows where reduction efficiencies of 50-60 percent are often achievable at 600 - 1000 °F (315 - 537 °C) and at 250 - 400 °F (121 - 204°C). The drawback to this type of acid removal is that another chamber is needed to get the flue gas to the optimum injection temperature. There are numerous other methods of reducing acid gas, and each should be analyzed according to the types of acids present and the reduction requirements stated in the emissions permit.

The injection of a dry reagent requires a minimal amount of equipment. A silo for storage of the sorbent will be followed by a small fan for conveying the powder into the duct. A chamber for the reaction of the acids will be followed by a particulate control device. When a solution or slurry mixture is required, the quantity of reagent preparation equipment will increase slightly. In the case of soda ash, an on-site batch silo may be tapped and the reagent transferred to a preparation station. This station consists of a tank to mix the solution, a tank for storing the material, and pumps for transferring water and the solution into the scrubbing chamber. This chamber will be upstream of a particulate collection device.

Particulate Control

Converting a furnace to OxyFuel firing substantially reduces the amount of particulate. Typical reductions are as follows: 30 percent reduction for soda lime glass, 30 - 50 percent for borosilicate based glass, and 60 - 70 percent for lead glass furnaces.

These numbers can be misleading from a particulate control aspect. For example, Plant 1 is conventionally fired with a regenerative heat recovery system. The furnace produces 100 pounds per hour of particulate (45 kg/hr), 80 percent of which could fall out or fill the regenerator bricks. That leaves 20 pounds per hour (9 kg/hr) carrying over to the particulate control device, in this case an electrostatic precipitator (EP). If the furnace were converted to OxyFuel firing, it would emit less particulate because less batch material is used, combustion is more efficient, and lower flow volumes carry less particulate out of the glass furnace. Oxygen suppliers show particulate reductions of 40 - 50 percent, but that reduction is typically the heavier dust that falls out in flue tunnels. The dust that is removed by an EP is microscopic in size, and the 20 pounds per hour (9 kg/hr) will still be present at the off take. It is this quantity of particulate that the glass producer must be concerned with instead of the reductions that occur upstream. Often, the quantity of particulate going to the EP per ton of glass produced can increase. Measured particulate on two glass furnaces increased from 0.75 to 1.3 pounds per ton and 0.884 to 1.19 pounds per ton. One reason for this increase could be that the lack of a regenerative section allowed heavier dust to fall out in the brick refractory.

The two forms of particulate control used most often in the glass industry are fabric filters and electrostatic precipitators. A fabric filter consists of a compartment of bags which act as the filter medium. It provides excellent collection efficiency because of the filter cake medium through which the particulate must pass in order to be cleaned. When acid gas reduction is required, this filter cake acts as a second reaction zone, where excess reagent from previous alkali injection is layered on the bag. This

reagent layer will react again with leftover acids, usually resulting in a higher acid reduction than with an EP.

There are, however, a few limitations that fabric filters have on oxygen based systems. The lack of a primary heat exchanger on the furnace delivers high temperature, high moisture flue gas to down stream equipment. If any of the cooling methods prior to the fabric filter fail, the bags will probably have to be replaced. Because of the changing conditions on the bag surface, fabric filter systems operate under various pressure drops. Therefore, controlling furnace pressure with a fan on the clean side of a fabric filter can be more complicated than with an EP. Glass dust is typically a microscopic material. Even with precise bag selection, the glass dust can permeate the bag material, hindering the ability of the air to pass through the bag. This phenomenon is referred to as "blinding" the bag and can result in bag failure, which leads to replacement. Often, bags last less than 1 year. Some have lasted as little as 6 weeks.

An electrostatic precipitator uses a series of high voltage electrodes to ionize the particulate in the gas stream. An electrode has an applied voltage of 25 - 30 kilovolts D.C. Depending on the charge it receives, the particulate is attracted to a collection plate with an opposite charge. EPs are the most widely used particulate control devices in the glass industry. Furnace pressure control is relatively simple because an EP provides a constant, low pressure drop, typically less than 0.5 inch (1.25 mbar) of water column across the EP chamber. EPs fabricated of carbon steel or ASTM A588 steel can operate at temperatures as high as 850°F (454°C) continuously. An EP is much more forgiving in case of a temperature upset or an increase in moisture, whereas a fabric filter's bag material can be destroyed and require costly replacement.

Furnaces with Pollution Control Equipment Presently in Operation

Many glass companies that are converting to oxy fuel firing already have a particulate control device in operation. These companies have been concerned about how the reduced flow will affect the operation of the existing equipment. Experience to date has shown that a conventionally fired system converted to Oxy-Fuel can operate at about 50 - 60 percent of the original flow volume. This volume takes into account dilution cooling to approximately 900°F (480°C) and water cooling to approximately 400°F (204°C).

A lower flow volume in the same size duct can result in dust fallout in the duct running from the furnace to the particulate control equipment. This fallout occurs because of the reduced gas velocity. Prior to conversion, the velocity was capable of carrying the dust to the EP. If the duct size is not reduced, the dust could lie in the bottom of the duct until the effective diameter is reduced and the velocity increases to carry the dust to the EP.

Pollution control devices are sized primarily by the flow volume entering the system. In the case of a fabric filter, the system is sized by the air-to-cloth ratio. This ratio is derived by dividing the flow volume by the total square feet of bag material through which the flow must pass. Ratios are typically in the range of 2:1 to 4:1. It is obvious that as flow reduces, the air-to-cloth ratio reduces, thus making the existing filter more efficient in removing particulate.

EP's are also sized according to flow volume. The term used to size an EP is specific collection area (SCA). The SCA is obtained by dividing the total collection area of the EP by the total volume flow. The higher the SCA, the greater the collection efficiencies are for a specific system. Another sizing criteria of an EP is the flow through velocity, which is determined by dividing the flow volume by the cross sectional area of the EP inlet. The velocity has great bearing on the dust collection and its ability to be removed properly from the collection surfaces. When a velocity is too high, the dust which is removed during rapping can become re-entrained in the gas stream and exit out the stack. This re-entrainment can result in temporary opacity spikes. When a furnace is converted to OxyFuel firing, the resultant decrease

in flow creates a lower velocity and a higher SCA. With these two factors taken into account, the existing EP becomes more conservative and should create a more efficient system overall.

With all forms of particulate control, there is an industrial fan to either push or pull the gas through the equipment. The size of the fan should be checked to ensure that it operates within the new specified ranges. Often, there is an automatic damper to control the static pressure across the system. With the oxygen conversion, the reduction of flow may require the damper to be closed to a point at which the fan is running at inefficient conditions. A variable speed drive could be added to increase fan efficiency and decrease operating costs.

Conclusions

OxyFuel firing of glass melting furnaces has forced us to address a new set of emissions concerns. Because of the extremely high temperatures and an usually high moisture content, the flue gas can seem complicated at first. Using different cooling scenarios and sizing criteria can make these emissions easier to handle and control. The application of acid gas removal and subsequent particulate control to flue gas streams is still complicated, but it is becoming easier as we gain more experience and increase our understanding of OxyFuel combustion.

Particulate and Acid Gas Reduction Oxygen-Fired Furnace

Acid Scrubbing with a Solution

NOxOUT[®] PROCESS DESCRIPTION

The NOxOUT[®] Process is a post-combustion NOx reduction method that reduces NOx through a controlled injection of NOxOUT A or other NOxOUT reagents into the combustion gas path of fossil-fired and waste-fired boilers, furnaces, incinerators, or heaters. NOxOUT A is a 50% urea solution plus a small amount of additives for scale and corrosion control. This reagent is readily available and requires no special safety precautions for handling.

The use of urea for control of oxides of nitrogen was developed under the sponsorship of the Electric Power Research Institute (EPRI) between 1976 and 1981. Nalco Fuel Tech is EPRI's exclusive licensing agent for the urea based technology. These early investigations provided fundamental thermodynamic and kinetic information of the NOx-urea reaction chemistry and identified some traces of by-products. The predominant overall reaction is described as:

Though some trace quantities of ammonia and carbon monoxide may form, the quantities of these can often be controlled through application know-how.

The NOx removal efficiency and reagent utilization are related by a variable known as Normalized Stoichiometric Ratio (NSR). This ratio is defined as shown below. NOxOUT A utilization is equal to the NOx reduction divided by NSR.

$$\text{NSR} = \frac{\text{Actual Molar Ratio of Reagent to Inlet NOx}}{\text{Stoichiometric Molar Ratio of Reagent to Inlet NOx}}$$

Nalco Fuel Tech has expanded the technology by developing chemical injection hardware, widening the applicable temperature range, and process control expertise required for commercial applications. Nalco Fuel Tech's licensing agreement with EPRI, combined with its successful in-house developments, is marketed commercially under the trade name NOxOUT[®].

Two key parameters that affect the process performance are flue gas temperature and the reagent distribution. The NOx reducing reaction is temperature sensitive; by-product emissions become significant at lower than the optimum temperature range while chemical utilization and NOx reduction decrease at higher than the optimum. This optimum temperature range is specific to each application. The reagent needs to be distributed within this optimum temperature zone to obtain the best performance. Typically, the distribution is more difficult for large units and for units with high flue gas velocity.

The NOxOUT® Process is designed with the aid of computational fluid dynamics (CFD) and chemical kinetic model (CKM) in addition to results from field tests. The CFD model simulates flue gas flows and temperature inside a unit while the CKM calculates the reaction between urea and NOx based on temperature and flow information from CFD. A combination of these two models determines the optimum temperature region and the optimum injection strategy to distribute the reagent. With an ability to estimate NOx reduction, a model study can be performed to determine if an application is a right fit for the process.

The reagent distribution is facilitated by chemical injectors developed by Nalco Fuel Tech. Utilizing pressurized air, these injectors atomize and direct the NOxOUT reagents into the combustion gas path. The droplet size distribution and spray coverage developed by the injectors promote efficient contact between the NOxOUT reagents and the NOx in the flue gas.

The NOxOUT® Process provides effective boiler load following capabilities. Through the computer modelling, an injection strategy is developed that makes use of multilevel injection, control of reagent concentration, droplet size and spray patterns, and the chemical enhancers.

Several years of field testing indicate that the NOxOUT® Process is applicable on various types of units firing many different fuels. The process was successfully proven on units fired with coal, oil, gas, wood or municipal solid or hazardous waste. These units varied in size and type: package boilers, process heaters, incinerators, circulating or bubbling fluidized beds, waste heat boilers, utility boilers. By virtue of being a post-combustion process, unit size and type and fuel type have some, but no a major effect on the process.

There are substantial benefits gained from the application of the NOxOUT® Process compared to first generation NOx control technologies, such as ammonia injection. These benefits are briefly summarized below:

- Use of non-toxic, non-hazardous chemicals.
- Potentially lower capital cost due to the lack of large system compressors and elimination of anhydrous ammonia storage, handling, and safety equipment.
- Lower operating costs resulting primarily from minimization of gas (steam or compressed air) requirements.
- Inherently more effective control of spray patterns and chemical distribution for better mixing with the use of liquid rather than gas-based reagents, thereby resulting in better chemical utilization.
- Chemical enhancers which can be used to improve control of potential by-product generation while reducing NOx over an expanded temperature range.

NOxOUT® LT PROCESS DESCRIPTION

The NOxOUT® Process is a post-combustion NOx reduction method that reduces NOx through a controlled injection of NOxOUT LT or other NOxOUT reagents into the combustion gas path of fossil-fired and waste-fired boilers, furnaces, incinerators, or heaters. NOxOUT LT is a 32.5% urea solution plus a small amount of additives for scale and corrosion control. This reagent is readily available and requires no special safety precautions for handling.

The use of urea for control of oxides of nitrogen was developed under the sponsorship of the Electric Power Research Institute (EPRI) between 1976 and 1981. Nalco Fuel Tech is EPRI's exclusive licensing agent for the urea based technology. These early investigations provided fundamental thermodynamic and kinetic information of the NOx-urea reaction chemistry and identified some traces of by-products. The predominant overall reaction is described as:

Though some trace quantities of ammonia and carbon monoxide may form, the quantities of these can often be controlled through application know-how.

The NOx removal efficiency and reagent utilization are related by a variable known as Normalized Stoichiometric Ratio (NSR). This ratio is defined as shown below. NOxOUT LT utilization is equal to the NOx reduction divided by NSR.

$$\text{NSR} = \frac{\text{Actual Molar Ratio of Reagent to Inlet NOx}}{\text{Stoichiometric Molar Ratio of Reagent to Inlet NOx}}$$

Nalco Fuel Tech has expanded the technology by developing chemical injection hardware, widening the applicable temperature range, and process control expertise required for commercial applications. Nalco Fuel Tech's licensing agreement with EPRI, combined with its successful in-house developments, is marketed commercially under the trade name NOxOUT®.

Two key parameters that affect the process performance are flue gas temperature and the reagent distribution. The NOx reducing reaction is temperature sensitive; by-product emissions become significant at lower than the optimum temperature range while chemical utilization and NOx reduction decrease at higher than the optimum. This optimum temperature range is specific to each application. The reagent needs to be distributed within this optimum temperature zone to obtain the best performance. Typically, the distribution is more difficult for large units and for units with high flue gas velocity.

The NOxOUT[®] Process is designed with the aid of computational fluid dynamics (CFD) and chemical kinetic model (CKM) in addition to results from field tests. The CFD model simulates flue gas flows and temperature inside a unit while the CKM calculates the reaction between urea and NOx based on temperature and flow information from CFD. A combination of these two models determines the optimum temperature region and the optimum injection strategy to distribute the reagent. With an ability to estimate NOx reduction, a model study can be performed to determine if an application is a right fit for the process.

The reagent distribution is facilitated by chemical injectors developed by Nalco Fuel Tech. Utilizing pressurized air, these injectors atomize and direct the NOxOUT reagents into the combustion gas path. The droplet size distribution and spray coverage developed by the injectors promote efficient contact between the NOxOUT reagents and the NOx in the flue gas.

The NOxOUT[®] Process provides effective boiler load following capabilities. Through the computer modelling, an injection strategy is developed that makes use of multilevel injection, control of reagent concentration, droplet size and spray patterns, and the chemical enhancers.

Several years of field testing indicate that the NOxOUT[®] Process is applicable on various types of units firing many different fuels. The process was successfully proven on units fired with coal, oil, gas, wood or municipal solid or hazardous waste. These units varied in size and type: package boilers, process heaters, incinerators, circulating or bubbling fluidized beds, waste heat boilers, utility boilers. By virtue of being a post-combustion process, unit size and type and fuel type have some, but not a major effect on the process.

There are substantial benefits gained from the application of the NOxOUT[®] Process compared to first generation NOx control technologies, such as ammonia injection. These benefits are briefly summarized below:

- Use of non-toxic, non-hazardous chemicals.
- Potentially lower capital cost due to the lack of large system compressors and elimination of anhydrous ammonia storage, handling, and safety equipment.
- Lower operating costs resulting primarily from minimization of gas (steam or compressed air) requirements.
- Inherently more effective control of spray patterns and chemical distribution for better mixing with the use of liquid rather than gas-based reagents, thereby resulting in better chemical utilization.
- Chemical enhancers which can be used to improve control of potential by-product generation while reducing NOx over an expanded temperature range.

Standard NOxOUT[®] LT System Description

The NOxOUT[®] process incorporates a reagent storage and delivery system to inject the NOxOUT LT solution into the combustion gases of the boiler. Concentrated NOxOUT LT solution (32% urea) is delivered by truck and transferred into the chemical Storage Tank. The chemical in the Storage Tank then gravity-feeds into the LT Metering Kit.

The LT Metering Kit is a self-contained system used to supply mixed NOxOUT LT to each Distribution Panel. The unit is prepackaged and shop tested and includes a chemical metering pump, turbine pump to supply water pressure boost, an in-line mixer, and a local control panel. At the discharge of the boost pump is a recirculation loop with a manual regulating valve to properly control the flow and pressures to the injectors. In addition, the module contains all necessary valves, check valves, water strainer, flow transmitters, pressure and flow switches and stainless steel piping/tubing to make it a self-contained metering and pumping system.

NOx reduction is a function of the chemical feed rate, which is controlled by varying the speed of the metering pumps through a 4-20 mA signal. Control for the Metering Module is provided at the Local Control Panel or the Plant DCS (or NFT supplied Remote Controller). The system will operate in local or remote mode. In the local mode, instrumentation and electrical control is performed at the module. In the remote mode, control is performed from the Plant DCS. The Module also has a hand/auto mode associated with the metering pump and the water boost pump. In any mode, the pumps will shutdown for low air pressure, low chemical flow, or low water flow. A low tank level alarm will shut the Metering Module down in the Auto Mode. The flow control for the metering pump also has a local and remote mode. In the remote mode, the metering pump receives a 4-20mA signal from the Plant DCS which controls the pump motor speed. This controls the chemical feed rate. In the local mode, metering pump control is performed at the local control panel using the digital flow controller. The Plant Control signal is disabled. Chemical totalization is provided on the flow indicator.

Mixed NOxOUT LT is transported from the Metering Pump to the Distribution Panel (located on the front of the cabinet), which channel the NOxOUT LT mixture to each injector. Each Panel consists of flow meters, balancing valves and regulators which accurately control and display the chemical and atomizing air to each injector. Also contained on these panels are the necessary manual ball valves, gauges and stainless steel tubing required to adequately control the NOxOUT LT injection process.

The injectors consist of an atomizing chamber in which the air and NOxOUT LT mixture first meet. The mixed chemical deflects off an internal orifice plate while being continuously atomized in the chamber by the addition of plant air (up to 80 psig may be necessary) which is the atomizing medium. The atomized chemical then flows through the injector tube to the nozzle. The nozzle is specially designed and characterized to meet the appropriate plant conditions. This is done by detailed computer analysis of the temperature, combustion and gas

velocity profiles in the boiler. The atomized NOxOUT LT reagent then enters the boiler and mixes with the boiler flue gas to form nitrogen, carbon dioxide and water. Air is required for cooling at any time the injectors are in operation and not retracted from the boiler. The injectors are equipped with quick disconnects and hydraulic hoses for flexibility and ease of maintenance.

The final addition to the injector is an outer cooling air jacket. This shield is ceramic coated and is attached to the atomizing chamber. Plant air is feed into the coolant air jacket at low volume and pressure. The air acts as a coolant for the nozzle and the jacket minimizes direct contact between the corrosive flue gas and the injector. This maximizes the useful life of the nozzle in a hostile environment.

Injectors not expected to be used for extended periods of time should be withdrawn from the boiler and placed on standby to eliminate the possibility of damage from corrosion and overheating. Injectors out-of-service for short periods of time eg: several hours, can be left in place provided cooling and atomizing air flows are maintained. In the event of loss of cooling/atomizing air, the injectors should be withdrawn from the boiler as quickly as possible. The cooling air jacket should provide sufficient protection if the injectors are withdrawn within a few minutes of loss of air flow. Also, as an option, Nalco Fuel Tech can supply an Injector Automatic Retract System, which by receipt of a signal the air-over-spring mechanism can retract/insert the injector(s).

Loss of mixed chemical flow to the injectors is not considered to be a problem as long as air flow is maintained. However, in the event of loss of mixed chemical flow, it is desirable to purge the liquid lines with water to avoid overheating and decomposition of NOxOUT LT within the injector and/or nozzle. Such decomposition products could ultimately plug the nozzle orifice. Also, the water flush eliminates the possibility of chemical crystallization in the transfer lines, when the system is down. The system is set up with the appropriate valving to allow for an automatic water flush.

WELD TO DUCT - DESIGN D

TYPICAL APPLICATION: INCINERATORS, DUCTS, KILNS, CO BOILERS

NOTE

- 1) THIS IS A SUGGESTED DESIGN FOR TYPICAL APPLICATIONS. ACTUAL PENETRATION DESIGN FOR SPECIFIC APPLICATION BY CUSTOMER.
- 2) NOT TO SCALE.

DESIGNS REPRESENTED ON THIS DRAWING ARE THE PROPERTY OF NALCO FUEL TECH. ALL RIGHTS ARE RESERVED. ANY USE OTHER THAN THAT DESCRIBED IN THE CUSTOMER CONTRACT REQUIRES WRITTEN PERMISSION. REVISED 3/15/94

DWG. NO.

I-4

NALCO/FUELTECH

P.O. BOX 3031 NAPERVILLE, ILLINOIS 60566-7031

NOTES

- 1) DELETED
- 2) AIR PRESSURE SWITCH IS SKID MOUNTED.
- 3) PORTAFEED OPTION RECOMMENDED FOR APPLICATIONS <3 GPH. STANDARD 6000 GAL. STORAGE TANK RECOMMENDED FOR APPLICATIONS >3 GPH. INSULATION AND HEAT TRACE ALSO AVAILABLE AS OPTIONAL; PER SITE CONDITIONS.
- 4) FLOW RATE DEPENDS ON TRUCK DELIVERY PUMP CAPACITY.
- 5) FLOW RATES AND CAPACITIES ARE SITE SPECIFIC.
- 6) INJECTORS SUPPLIED WITH STEEL BRAIDED FLEX HOSE AND DOUBLE CHECKED QUICK DISCONNECTS.
- 7) Z PURGE KIT OPTIONAL.
- 8) REFERENCE DETAIL DRAWING FOR SKID SIZE AND EQUIPMENT OPTIONS.
- 9) PROVIDE BACKFLOW PREVENTION PER APPLICABLE CODES.
- 10) SLC CONTROLLER (MOUNTED ON LOCAL PANEL) AND/OR LCR REMOTE PANEL OPTIONAL.
- 11) OPTIONAL SOLENOID VALVES ALLOW INDEPENDENT LEVEL CONTROL.
- 12) MODULES AVAILABLE WITH DISTRIBUTION PANELS TO SERVE 1, 2, 3 OR 4 INJECTORS.

PORTAFEED

TYPE: STAINLESS STEEL
CAPACITY: 400 GALLON
SEE NOTE 3

STORAGE TANK

TYPE: FIBERGLASS REINFORCED VINYLESTER, VERTICAL
CAPACITY: 6000 GALLON
DESIGN PRESSURE: ATM
DESIGN TEMPERATURE: 120°F
SEE NOTE 3

METERING PUMP (1)

TYPE: HYDRAULIC DIAPHRAGM
CAPACITY: 15 GPH
MAX DISCHARGE PRESS= 130 PSIG
DRIVE: 1/2 HP, VARIABLE SPEED

WATER BOOST PUMP (1)

TYPE: TURBINE
CAPACITY: 4 GPM
MAX DISCHARGE PRESS = 130 PSIG
DRIVE: 1.5 HP

	1	2	3	4	5	6	7
FLUID	NOxOUT A	NOxOUT A	DIL WATER	AIR	DIL NOxOUT A	AIR	DIL NOxOUT A
DESIGN FLOW	NOTE 4	0-15 GPH	4 GPM	40 SCFM	0-4 GPM	6-8 SCFM	.5-1.5 GPM
TEMPERATURE, DEG F	>35°F	>35°F	70	70	>35°F	70	>35°F
PRESSURE, PSIG			30 (MIN.)	80-120		30-60	
DENSITY, LBS/GAL	9.17	9.17	8.34				
NOTES	4	5	5,9	5	5	5	5,6

NOxOUT LT MODULE
32% NOxOUT A P&ID

DWG. NO.

B-7

NALCO/FUELTECH

P.O. BOX 3031 NAPERVILLE, ILLINOIS 60566-7031

Standard NOxOUT[®] System Description

The NOxOUT[®] process incorporates a reagent storage and delivery system to inject the NOxOUT A solution into the combustion gases of the boiler. Concentrated NOxOUT A solution (50% urea) is delivered by truck and transferred into the chemical Storage Tank.

The chemical Storage Tank is typically a closed top vertical tank, fabricated of fiberglass reinforced polyester and premium grand vinylester resin. It is designed per ASTM D3299-88. The tank is supplied with level indicator, thermocouple, manway, vent, internal dow pipe, external fill pipe, ladder, hold down and lifting lugs, and necessary connections and isolation valves. Site conditions will determine the connections and isolating valves. Site conditions will also determine the need for heat trace, insulation, and seismic qualifications.

The Circulation Module serves the NOxOUT[®] process in a dual role. While its primary purpose is to supply the chemical NOxOUT A to the Metering Modules, it has a secondary purpose of keeping the chemical at a temperature above 80°F, through constant circulation and, if necessary, a circulation heater. The Module is skid mounted and fully shop tested. It consists of redundant centrifugal pumps, an electric in-line heater, a flowmeter, a duplex strainer, one self-contained control panel, and all associated stainless steel pipe, tubing, valves and instrumentation.

The control panel consists of local controls for the Circulation Module. The heater is controlled by a thermostat and is preset to a temperature of 80°F. When the pump is running, and the temperature falls below the setpoint, the heater will automatically activate. The circulation pump should run at all times. The pressure indicators will show if the system is not running properly. There are temperature and pressure indicators, and a flow meter/indicator for monitoring the correct system operation. The local control panel will also digitally show the tank level and temperature.

The Metering Module is a skid mounted unit used to supply mixed NOxOUT A to each Distribution Module. The unit is prepackaged and shop tested and includes a chemical metering pump, turbine pump to supply water pressure boost, an in-line mixer, and a local control panel. At the discharge of the boost pump is a recirculation loop with a manual regulating valve to properly control the flow and pressures to the injectors. In addition, the module contains all necessary valves, check valves, water strainer, flow transmitters, pressure and flow switches and stainless steel piping/tubing to make it a self-contained metering and pumping system. At a minimum, redundant pumps with motors is suggested. In some cases, a completely redundant Metering Module is preferred. For situations where chemical biasing/Independent Level Control is required, the controls and pumping system will be designed for independent chemical injection to each level of operation.

NOx reduction is a function of the chemical feed rate, which is controlled by varying the speed of the metering pumps through a 4-20 mA signal. Control for the Metering Module is provided at the Local Control Panel or the Plant DCS (or NFT supplied Master Control Module - PLC). The system will operate in local or remote mode. In the local mode, instrumentation and electrical control is performed at the module. In the remote mode, control is performed from the Plant DCS. The Module also has a hand/auto mode associated with the metering pump and the water boost pump. When the system is in auto and is turned off, the chemical pump will stop, the chemical valve closes and an automatic water flush occurs. In any mode, the pumps will shutdown for low air pressure, low chemical flow, or low water flow. A low tank level alarm will shut the Metering Module down in the Auto Mode. The flow control for the metering pump also has a local and remote mode. In the remote mode, the metering pump receives a 4-20mA signal from the Plant DCS which controls the pump motor speed. This controls the chemical feed rate. In the local mode, metering pump control is performed at the local control panel using the digital flow controller. The Plant Control signal is disabled. Chemical totalization is provided on the flow indicator.

Mixed NOxOUT A is transported from the Metering Module to the Distribution Modules, which channel the NOxOUT A mixture to each injector. Each Module consists of flow meters, balancing valves and regulators which accurately control and display the chemical and atomizing air to each injector. Also contained on these modules are the necessary manual ball valves, gauges and stainless steel tubing required to adequately control the NOxOUT A injection process.

The injectors consist of an atomizing chamber in which the air and NOxOUT A mixture first meet. The mixed chemical deflects off an internal orifice plate while being continuously atomized in the chamber by the addition of plant air (up to 80 psig may be necessary) which is the atomizing medium. The atomized chemical then flows through the injector tube to the nozzle. The nozzle is specially designed and characterized to meet the appropriate plant conditions. This is done by detailed computer analysis of the temperature, combustion and gas velocity profiles in the boiler. The atomized NOxOUT A reagent then enters the boiler and mixes with the boiler flue gas to form nitrogen, carbon dioxide and water. Air is required for cooling at any time the injectors are in operation and not retracted from the boiler. The injectors are equipped with quick disconnects and hydraulic hoses for flexibility and ease of maintenance.

The final addition to the injector is an outer cooling air jacket. This shield is ceramic coated and is attached to the atomizing chamber. Plant air is feed into the coolant air jacket at low volume and pressure. The air acts as a coolant for the nozzle and the jacket minimizes direct contact between the corrosive flue gas and the injector. This maximizes the useful life of the nozzle in a hostile environment.

Calculated Effects of Residence Time on NO_x Reduction with Urea Injection (10).

Effects of Initial NO_x Level on SNCR Performance at Pilot Scale (11).

Formation of Ammonium Sulfate and Ammonium Bisulfate.

Figure C-9
Post-Retrofit Performance with Urea,

SNCR Process Description

(a) Temperature = 1600°F; Initial NO = 125 ppm; N/NO_x = 2

(b) Temperature = 1600°F; Initial NO = 250 ppm; N/NO_x = 2

Effects of Methane Additive with Urea Injection on NO, NO₂, and N₂O (8).

Effect of Transport Air Flow on SNCR Performance with Urea Injection (2).

Utility-Scale SNCR Ammonia Slip Performance.

Tradeoff Between Achievable NO Reduction and NH_3 Slip at Full Load in the First Inspection Cavity (6).

THERMAL DeNO_x[®] NO_x Reduction Performance, LADWP Haynes Unit 4,
Oil Fuel (24).

NO_x Reductions Using UREA

*This information was generated for the Glass Packaging Institute
for presentation to the SCAQMD to challenge regulations proposed
to require UREA injection in Oxy-Fuel Furnaces for ultra-low NO_x emissions.*

SNCR

The chemistry involved in SNCR processes is becoming moderately well understood and can be generalized by two overall paths (see attachment diagram). These paths are dictated by whether the SNCR chemical decomposes to NH₂ or cyanic acid (HNCO). The primary decomposition product of ammonia (NH₃) is NH₂. NO_x reduction occurs by a reaction between nitric oxide (NO) and NH₂, which ideally forms water (H₂O) and nitrogen (N₂). Secondly, the overall path can be somewhat different for cyanuric acid HNCO₃. HNCO₃ initially decomposes to isocyanic or HNCO, in which case NCO can be a major intermediate. The NCO can then react with NO to form N₂O and carbon monoxide (CO). Depending on the temperature, the N₂O will decompose to N₂ or be emitted as a byproduct of the SNCR process. Urea is thought to be a hybrid between NH₃ and HNCO₃, with decomposition yielding NH₃ and HNCO. Thus, it is recognized that N₂O is one of the byproducts of Urea based SNCR.

In SNCR applications, reaction gasses are introduced in a water solution. Unfortunately, the inherent water evaporation lowers the gas temperatures and makes it difficult to obtain homogeneous mixing. At higher temperatures, the rate of a competing reaction for direct oxidation, which actually *forms* NO_x ($2\text{NH}_3 + 5/2 \text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$) becomes significant. At low temperatures NH₃ will pass through without reaction as "slip" and create other serious problems. Some suppliers try to remedy this situation with the addition of costly "enhancers" for Urea. This increases the reagent costs for operating a Urea system, and unfortunately NH₃ slip is not eliminated.

Ammonia injection is not an option for Glass Manufacturers. Leaks and spills from NH₃ storage tanks and piping are safety concerns because liquid or highly concentrated ammonia vapor is **extremely** hazardous. The Occupational Safety and Health Administration standard limits occupational exposure of only 50 ppm for an 8 hour period. Glass factory employees and surrounding neighbors are expected to express concern about the large quantities of ammonia used. It is questionable whether or not glass manufacturers will be able to obtain appropriate permits to receive, store, and consume large quantities ammonia in urban facilities.

Urea

The Electric Power Research Institute (EPRI) sponsored research from 1976 to 1981 primarily utilizing Urea for NO_x control; this research lead to a number of Patents for Utility Boiler applications. To address some of the handling concerns associated with ammonia, a water solution with ~50 % Urea content is used. The reaction chemistry is represented by:

Process chemistry determines the NO_x reduction potential of Urea. Vendors typically state consumption of 1 Mole Urea to 2 Moles NO_x ($\text{N}/\text{NO} = 1.0$). Experience in actual practice to maximize NO_x reduction percentages is significantly higher (generally in the range of $\text{N}/\text{NO} = 1.5 - 2.5$).

Although Urea appears to be a simple process, optimizing a Urea system's performance involves the challenge of understanding its dependence on a number of parameters. Achievable NO_x reductions with Urea have been highly site specific. Operating conditions, process parameters, and injection system design are the major factors that impact Urea performance:

- Physical location of optimum temperature range
- Initial NO_x Levels and quantity of gases to be treated
- The amount and concentration of Urea solution (N/NO molar ratio)
- Injection method and Mixing variables
- Nature of temperature gradients throughout the reaction zones
- Residence Times available in the reaction temperature range
- Additives and/or Concentration of Trace Gas Species (e.g., CO , $\text{SO}_2 / \text{SO}_3$, NH_3)

The effects of these operating prerequisites for Urea process performance are highly interrelated. Any out of control variable can result in reduced performance. Initial NO_x reduction performance degrades with lower NO_x concentrations. As initial NO_x levels decrease below a certain threshold, the optimum reaction temperature also changes. Thus, it is not possible to consider each item individually in order to define the optimum conditions for a specific unit. Instead, all operating conditions must be considered together as a whole.

Increasing the amount of chemical used (i.e., N/NO ratio) will increase the NO_x reduction up to a point. This point varies with the unit and the extent of mixing in the furnace, but is generally in the range of $\text{N}/\text{NO} = 1.5 - 2.5$. With higher inputs there are diminishing returns in NO_x reduction, and a significant increase in other undesirable gas species being formed.

To date, Urea has only been used for NO_x reductions in:

1. Large Air-Fired Utility Boilers
2. Wood Waste Incinerators
3. Refinery Carbon Monoxide Boilers
4. Small Co-Generation Boilers

No applications, tests, trials, or studies have been made for Oxy-Fuel Glass Furnaces. Until recently NALCO was unaware of the presence of NaOH , $\text{SO}_2 / \text{SO}_3$ / and Sulfates in the application proposed by the SCAQMD.

Injection System Design

The impact of injection system design on Urea performance in an Oxy-Fuel furnace exhaust has yet to be determined. The main challenges in applying Urea at full scale are (1) finding the appropriate temperature window over the load range, and (2) mixing the chemical with the flue gas. The location of the temperature window and access to it determine whether Urea is feasible for a given application. Changing furnace loads (products of combustion and Calcination volumes) in a fixed cross section exhaust duct will result in a different temperature at each point in the exhaust.

Temperature measurements within candidate units must be made to determine whether the 1600 - 2100 °F temperature window is accessible, and how it moves as a function of unit's operating variables. Additives can lower the effective temperature window, including H₂, CO, and oxygenated hydrocarbons. However, other handling and safety issues should be apparent for the use of these chemicals. In order to effect adequate mixing of the injected chemical with the flue gas, systems employ various approaches. Low and High energy injection systems are available, but no direct comparison of performance is available for duct applications. These can be categorized into the following three basic injection mechanisms:

Mechanical Distribution - A large grid located throughout the exhaust cross section physically distributes the chemical to numerous small orifices used to mix the chemical with the flue gas. High temperatures present internal cooling concerns, and material selections have not been investigated for a Glass Furnace exhaust.

Liquid Droplet Injection - An atomizer, either through the furnace wall or through a limited number of lances in the furnace, using droplet momentum as the primary source of energy to entrain flue gas and distribute the chemical throughout the exhaust flow.

Transport Gas/Jet Mixing - A separate transport gas (air or steam) provides the energy to mix the chemical by entrainment of the flue gas into the transport gas jet. Utility Boilers have large scale turbulent structures that exist in the furnace tube section which contribute to mixing. Glass furnaces are not equipped with these types of structures.

Glass furnace exhaust systems typically are designed for flow velocities above 50 ft. per sec. Reaction times are required for Urea between 0.5 and 1 second. This will require flue lengths of an additional 25 to 50 feet after reasonable mixing is accomplished, and after additional flue construction is provided for an upstream temperature quench system. It is questionable if sufficient site space will be available for this yet-to-be designed system.

N₂O (Nitrous Oxide) Emissions

Serious questions have been raised regarding N₂O for some time. The U.S. EPA sponsored a workshop with industry and researchers on N₂O emissions from combustion processed in February, 1986. Many concerns regarding N₂O raised uncertainties with the use of Urea for NO_x control. While it is currently not subject to regulation in the United States, some states do require utilities to consider the environmental impact of N₂O production as an added cost penalty when selecting technologies for new power plants.

With Urea injection, norminally 15 - 25% of the reduced NO_x appears in the reaction products as N₂O. With Urea, the peak conversion to N₂O appears to be at the same temperature as peak NO_x reduction. N₂O measurements taken during the San Diego Gas & Electric Urea demonstration yielded N₂O levels of 12 - 17 % of the NO_x reduced.

Nitrous oxide (N₂O) with a concentration of only about 0.31 parts per million by volume is the most abundant atmospheric nitrogen species after molecular nitrogen (N₂). Measurements indicate that atmospheric concentrations of N₂O are increasing at a rate of about 0.2 to 0.3 % per Year.⁶

Nitrous oxide is an important atmospheric constituent for two reasons - it is a greenhouse gas that traps Earth emitted infrared or heat energy, and it leads to the chemical destruction of stratospheric ozone. Nitrous oxide is a very long lived gas with an atmospheric lifetime of about 150 years. A single N_2O molecule has the comparable greenhouse warming potential of about 250 Carbon Dioxide molecules. Being stable in the troposphere, N_2O is transported to the stratosphere where it is the largest source of NO.

NO is the primary species responsible for establishing the equilibrium stratospheric O_3 (Ozone) concentration. Stratospheric ozone absorbs solar ultraviolet radiation and shields the Earth's surface from this biologically lethal radiation. Hence, N_2O is both a greenhouse gas and an Ozone depleter.

The photosynthesis of NO_2 is responsible for about 90% of its destruction to the production of NO, which leads to the chemical destruction of stratospheric ozone (O_3) through the nitrogen oxide catalytic cycle.

The net reaction of these reactions is: $O_3 + O \rightarrow 2O_2$. This Nitrogen Oxide Catalytic Cycle is responsible for about 70 % of the global chemical destruction of stratospheric Ozone.

N_2O formation is always significantly higher with Urea than other SNCR schemes. This hurts process end users in two ways. The NO converted to N_2O with Urea injection is not reduced to innocuous N_2 as the chemistry implies. Therefore NO reductions to N_2 are over stated by as much as 12 - 40 %. Most regulators are becoming aware of this conversion. Though they have not yet enacted rules clarifying what NO reduction consists of, it is being suggested that conversion of $NO \rightarrow N_2O$ (another oxide) will not be acceptable - which they should recognize as a noxious species.

In the context of Global warming, it is of interest to note that the recycling of glass containers significantly reduces the amount of CO_2 produced in manufacturing glass from natural raw materials. For each 100 tons per day of cullet remelted (~ 40% of a typical 25 ton/day container furnace), the combination of reduced products of combustion and fewer raw material carbonates results in a net reduction of 17.8 Tons of CO_2 emissions per day.

CO (Carbon Monoxide) Formation

In addition to N_2O formation, carbon monoxide (CO) has been shown to be a byproduct of Urea injection. The Urea chemistry responsible for increased CO is due to the following reaction where the intermediate species HCNO is a precursor:

Conversion of NO_x with SNCR processes increases with temperature up to approximately 990 °C (1800 °F) as demonstrated by the results of a pilot scale test. Formation of N_2O also increases with temperature.

Past efforts to reduce NO_x have avoided techniques which might increase CO emissions. High flue gas CO can impact the temperature window and the system performance. The presence of CO has a major impact on SNCR system performance (removal efficiency, NH_3 slip, and N_2O levels). Operating with an excess of O_2 to reduce this concern would increase costs, hinder the SNCR reactions, and potentially change the balance between SO_2 and SO_3 .

NH_3 Slip

Urea process performance is generally determined by comparing the percentage NO_x reduction to the NH_3 slip for a given reagent injection at a given load. There is normally a tradeoff between NO_x reduction and slip. Thus, in order to achieve a higher NO_x reduction, one must be willing to accept the consequences of higher NH_3 slip. NH_3 emissions are of serious concern for the following reasons:

Regulatory requirements are expected to limit NH_3 emissions.

The potential exists for reactions with SO_3 , which could foul down stream heat transfer surfaces and CEMS equipment.

The potent odor is objectionable to surrounding neighbors.

Plume visibility problems can result from ambient reactions with Sulfur Oxides in the plume gas.

NH_3 slip is generally not regulated in the United States, primarily because no reliable continuous emission monitor exists for ammonia. The one exception is in the Los Angeles Basin, where utilities with SNCR systems are committed to maintaining slip below 20 ppm (based on occasional checks using wet chemistry to measure ammonia).

Ammonia slip from the Urea system can react with trace species and ash in the flue gas. Ammonia reacts with SO_3 to form sulfates, sulfites, and bisulfates - which can lead to exhaust system deposition and plugging. Ammonia also reacts with HCl to form solid ammonium chloride, which is often visible as a detached plume. Finally, ammonia slip may be absorbed onto the collected particulate causing potential problems to workers handling the ash and companies trying to reuse or sell it.

Downstream reactions occur between ammonia slip from the Urea process and SO_3 , HCl, and particulate in the flue gas. In fact, these reactions and the impact of reaction products may dictate the level of ammonia slip that can be tolerated for a given system.

Oil fired operations, generating SO_x , using Urea have confirmed additional concerns with NH_3 slip. Ammonium Sulfate $[(\text{NH}_4)_2\text{SO}_4]$ deposits in the exhaust section and particulate matter (PM) emissions may result from NH_3 slip with the use of sulfur bearing fuel oil.³ This is of specific concern for SO_x from glass furnaces. It is understood that the Flat Glass furnaces using Ammonia injection are continuously battling this problem.

All Container Glass furnaces must use sulfates in the batch, which results in some SO_2 emissions. Like the pass-through "slip" of NH_3 , there will be some SO_2 slip through SO_x control exhaust systems. SO_3 reacts with NH_3 slip to form a Sulfite, Ammonium BiSulfate (ABS) or Ammonium Sulfate, as shown in the following reactions:

The high H_2O content of Oxy-Fuel exhaust gases will force this reaction toward the ABS, with conversion rates as high as 91 % of the NH_3 slip.⁵ This material causes buildup problems in particulate control systems. The temperature region in which these reactions take place is a function of flue gas SO_3 content and NH_3 slip. These reactions generally take place below 500 °F and can lead to deposition and plugging.

The material has a sticky nature (a melting temperature of 298 °F vs. 1623 °F for Sodium Sulfate) which can "blind" bag houses or attach itself to collector plates of Electrostatic precipitators. This property will **reduce capture efficiency** of particulate control equipment. Incidentally, this same reaction is a major reason that SCR materials foul, even after particulate control systems.

Present SO_x add-on controls require a lower temperature than that of Urea NO_x control. The presence of SO_2 with Urea may play a significant role in increasing the generation of N_2O .¹⁰

It must be recognized that trials to date with Urea have been on relatively stable operating Utility Boilers. Glass Furnaces have significant differences, including variable firing rates (combustion exhaust volume), glass pull rate changes (CO_2 volume changes from virgin raw materials), and the presence of other gas species (SO_2 / Sulfates / NaOH).

Oxy-Fuel Exhaust Gas

The H_2O content of products of combustion from Air / Natural Gas in Container Glass Furnaces is approximately 15 - 18 % vs. 46 - 50 % for Oxy-Fuel. This significantly higher H_2O content must question any extrapolation of exhaust reaction data / results from Air-Fuel to Oxy-Fuel applications.

Specific concerns which have not been addressed for this high H_2O content include:

1. Absence of N_2 increases the partial pressure for all other gas species present
2. SO_2 / SO_3 equilibrium mechanisms have not been studied
3. Influence of OH^- relative to N_2O formation
4. Urea's decomposition equilibrium between ($2\text{NH}_2 + \text{CO}$) vs. ($\text{NH}_3 + \text{HNCO}$)
5. NH_3 preference reactions between SO_3 and NaOH

The exhaust conditions from Oxy-Fuel glass furnaces have a number of problems for add on controls, especially SNCR. Exhaust ducting from the melter will have some site space constraints when considering a sequence for 1) temperature reduction 2) NO_x , 3) SO_x , and 4) Particulate Control. The future economic viability of Oxy-Fuel melting may depend upon waste heat recovery of the hot exhaust gases. Research projects have started to address this issue, but no scheme has been installed on an operation Oxy-Fuel furnace, much less proven in practice. Requirements to use SNCR could hinder or prevent these energy conservation efforts by dictating exhaust system layouts in restricted available space. Batch/Cullet preheating equipment being developed in Europe would not be adaptable to SNCR.

Beyond the issue of concerns with atomized water being injected into a Refractory lined duct, the exhaust injection control will have a direct influence on Furnace pressure control. The issue of furnace pressure is very critical for Oxy-Fuel refractory life issues. Furnace pressure variations greater than 0.005"

W. C. are unacceptable. Since both CO and N₂O generation are temperature dependent, water based Urea injection will have varying conditions for chemical reactions as the flue gas temperature drops.

NO emission variations from Oxy-Fuel Glass Furnaces have not been characterized to potentially design Urea injection control algorithms. If the rate of Urea injection does not match the concentration of NO, the level of undesirable species (NH₃, CO, N₂O) will increase.

Costs

Capital and operating costs for Urea systems are dependent on system complexity and size, and are highly site specific. Primary operating costs include the following:

- Receiving and unloading labor costs

- Chemical and water consumption costs (Present and Future estimates)

- The production of compressed air and / or steam for mixing

- Clean water issues for diluting the Urea solution prior to injection

- The change in temperature conditions associated with evaporating a diluted aqueous solution

Costs on a pure chemical basis are nominally \$200 / ton for Urea. Proprietary mixtures are more.

\$200 / ton Urea translates to \$3.00 / lb.- mole Nitrogen. Using a N / NO ratio of 1.5 to 2.5, a reduction of NO_x from 1.2 to 0.8 lb. per ton of glass would result in the **material operating cost** of \$4,800 per ton of NO_x reduced. Operation of compressors or boilers for carrier gas generation (25 scfm @ 80 psi) and water requirements (200 + gph) will result in operating costs ~ \$10 / Hr. For **possibly** obtaining a reduction of 0.4 lb. NO_x per ton of glass on a 250 Ton furnace, this equates to increasing an additional \$ 4,800 per ton; or a total operating cost approaching \$10,000 per ton of NO_x reduced.

No design has been developed for an Oxy-Fuel glass container furnace flue duct for applying Urea injection technology. There are refractory application design concerns of thermal shock for reducing exhaust temperatures to ~2000 °F by water injection. Many site constraint issues will have to be considered as well. Sensors for temperature, lancing positions, flow rate and concentrations measuring devices, and furnace pressure control systems would all have to be developed to obtain a better cost estimate.

Capital costs for adding Urea injection are usually expressed in broad ranges (\$6 to 18 / kW on Utility Boilers). Translating these numbers to the exhaust volume of a 250 ton/day Oxy-Fuel glass furnace, yields figures in the \$400 to \$700 K region. Estimates from NALCO appear low, especially when considering the complexity of space restrictions, ducting requirements, and complex instrumentation requirements.

No economic data has been presented to describe any situation using of Urea for the specific conditions and concerns represented in the exhaust from a Container Glass Furnace. The issues of SO₃ interference and NH₃ slip have been ignored. One possible control scheme for reducing (**not eliminating**) CO, NH₃, and N₂O would necessitate the cost of purchasing and operating a second Continuous Emission Monitor System. Formation of Ammonium BiSulfate would reduce the efficiency of Particulate control, possibly requiring yet another unproven technology to be added to an Oxy-Fuel Furnace.

Conclusions

1. Oxy-Fuel has been successful in reducing NO_x up to 90% from uncontrolled Glass Container furnaces, and is compatible with all glass colors, cullet recycling contents, and necessary production rate flexibility. The inherent ability to minimize NO_x , reduce energy consumption, and satisfy production quality requirements without the generation other hazardous pollutants should qualify Oxy-Fuel conversions as BARCT.
2. Urea has not been used for NO_x control on any Glass Container Furnaces, or any Oxy-Fuel combustion process. Process variability and the presence of SO_x and Sulfates will vary expected conversion efficiencies. Concerns with slip are serious issues, and the formation of Ammonium BiSulfate can reduce the efficiency of particulate control devices.
3. A significant percentage of NO_x reductions from Urea will result in the generation of other undesirable compounds - Carbon Monoxide (CO), Ammonia (NH_3) and Nitrous Oxide (N_2O). These may be regulated to more stringent standards in the future.
4. Ammonia slip and reactions with SO_2 will result in the formation of Ammonium BiSulfates. These are known to foul CEMS and result in measuring accuracy and maintenance problems. The "tacky" nature of this material may create problems with Particulate Control system efficiency. The stack opacity will increase.
5. Requirements for SNCR on exhaust flues of Oxy-Fuel furnaces may prevent making make waste heat recovery schemes economically or technically feasible. This will inhibit or prevent future energy conservation anticipated to evolve with this new melting technology.
6. Vendor stated efficiencies do not recognize the very narrow temperature range required for optimum results. SNCR use of ammonia has many serious drawbacks for the conditions found on glass furnaces, and in almost every category Urea is worse.
7. When installing Urea, secondary emissions, especially ammonia and N_2O , must be considered. NO_x reduction should not be based upon a significant portion being converted to other undesirable compounds (Carbon Monoxide, Nitrous Oxide, Ammonia Slip and Ammonium BiSulfate), especially if these species may be subject to future regulations.
8. Costs have not been well defined for the issues and conditions expected on glass container furnaces. In any event, the vendor costs appear to be too low, and the incremental cost of NO_x control will be much higher than stated.

Natural Gas

(So. Calif. Jan, '93 - Mar '94)

CO	0.0738	N. Gas =	0.04426	22.59311	per Lb. Gas				
H2O	0.0466		Lbs. O2 Comb. Prod. Lbs. CO2 Lbs. H2O Lbs. N2						
H2	0.0053		3.7993 4.7993 4.7820 2.1372 0.6589						
Air	0.0763		Lbs. Air N2						
O2	0.0843		12.5770						
NO	0.0791								
SO2	0.1727								

Lb. / Hr.

Oxygen	85,369	SCFH
	7199	Lb. / Hr.
	2.03	O:GAS Ratio
250	Ton / Day	
35.0%	% Cullet	
3.5%	Batch Moisture	
14.8%	Fusion Loss Factor	
1.2	NOX / Ton	
957	NOX ppm	
1.2	SOX / Ton	
957	SOX ppm (+SO3 ?)	
0.8	Particulate / Ton	
0.018	Particulate gm / scf	
4	NOX / Ton	
842	NOX ppm	

	CO ₂	H ₂ O	CH ₄
CO ₂	30,341	172,710	3539.7
H ₂ O	17,967	102,274	837.1

Total Flow			
Air-Fuel	692,634	3,942,686	53,870
Oxy-Fuel	212,068	1,207,158	17,433

United McGill
66.7 fps

Flue Area	5	15	Sq. Ft.
Flue Vel.	67.1	73.0	fps

2500 Deg. F

w/ Batch Contributions

717	NOX ppm
717	SOX ppm (+SO3 ?)
0.018	Particulate gm / scf

Flue Gas Temperature Reduction to > 2000 Deg. F

w/ Water

w/ Water			Exiting				Water Req.		1,670	Lbs.
Incoming	Lb. / Hr.	BTU/Hr.	- BTU/Hr.	Lb. / Hr.	SCFH	ACFH	/ Hr.	200	Gallons	
CO2	12429	8,178,430	1,888,621	12,429	106,540	504,015				
H2O	4810	6,316,897	1,410,307	6,480	139,094	658,020				
N2	32	21,579	4,667	32	6,077	28,750	654		NOX ppm	
O2	137	83,987	17,983	137	1,619	7,660	654		SOX ppm (+SO3 ?	
NO	13	8,125	1,750	13	158	748	0.015		Particulate gm / scf	
SO2	13	5,416	1,287	13	72	342				
		14,614,434	3,324,614	19,103	253,560	1,199,535				
		33.8%								

w/ Air

Incoming	Lb. / Hr.	Lb. / Hr.	SCFH	ACFH	Air Req. / Hr.	84,118 / 6,418	SCFH Lbs.
CO2	12429	12,429	106,540	504,015			
H2O	4810	4,810	103,242	488,415			
N2	32	32	6,077	28,750	524		NOX ppm
O2	137	137	1,619	7,660	524		SOX ppm (+SO3 ?)
NO	13	13	158	748	0.013		Particulate gm / scf
SO2	13	13	72	342			
Air	-	6,418	84,118	397,941			
		23,851	301,826	1,427,871			

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