NO_x EMISSION CONTROL BY PARTICLE QUENCHING IN AN ADVANCED GLASS MAKING PROCESS

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ABSTRACT

The formation of NO_x in an advanced glass melting (AGM) process has been studied. In this system, methane is combusted with preheated air at near stoichiometric conditions resulting in a potential for production of a high NO_x concentration in the exhaust. The minerals required for glass synthesis are entrained as a high loading concentration of fine particles in the preheated air supply. The particles are heated up in suspension by the combustion products. The thermal time scale for gas-particle heat transfer is chosen to be comparable to or less than NO_x formation kinetic time. This was projected to prevent formation of NO_x at a concentration corresponding to the adiabatic gas phase combustion temperature. The measured NO_x concentration in the glass melter exhaust is found to be significantly below anticipated NSPS requirements. A model is proposed for the processes in the AGM based on a kinetics/transport code. The decreased amount of NO_x formation is attributed to gas/particle thermal quenching effects and, possibly heterogeneous catalytic reduction.

INTRODUCTION

The development of an advanced gas-fired glass melting process (AGM) is being investigated as an alternative to the conventional glass melting furnace which is of the open-hearth type. The advanced glass melter is a technical derivative of a slagging coal combustor developed for magnetohydrodynamic power generation applications [1-3]. A primary goal is to transfer heat very efficiently at high temperatures to entrained glass batch particles. The high particulate loading required for this application presents a unique mechanism for limiting the formation of NO_x.

High temperature reaction of air feed nitrogen and oxygen to primarily form nitric oxide, NO, is a source of potentially high NO_x concentrations in the melt furnace exhaust. NO_x control is achieved in the AGM by using the entrained particulate material as a dispersed heat sink with a very short thermal transient time. Thus, the combustion products are rapidly quenched from the adiabatic temperature at which high NO_x concentrations would normally result to a much lower temperature. For the size particles considered, the thermal quenching is accomplished on a time scale much shorter than the NO_x chemical kinetic formation time.

AGM CONCEPT AND EXPERIMENTAL SYSTEM

In the glass melter design concept, premixed batch materials are injected as fine particles into a high temperature combustion air line and transported in suspension to a high intensity gas burner. The materials are heated very rapidly in suspension in the turbulent flow field in the burner. A converging nozzle at the exit of the burner accelerates the flow and directs it into a melt separation and homogenizing chamber. The hot materials are separated inertially from the combustion gas and deposited on a collecting surface where initial homogenization occurs. The thin liquid layer flows from the collecting surface to a melt reservoir at the bottom of the chamber where additional homogenization can occur. The combustion products exit the melt separation chamber and are ducted to downstream heat recovery equipment for heating the incoming combustion air.

The experimental system used for development testing of the burner configuration and the separation centerbody is schematically shown in Figure 1. The unit consists of a pre-burner, a main combustor, and a glass receiver. The purpose of the gas-fired pre-burner is to simulate the high temperature preheat since there was no source of high temperature preheated air with which the system would normally operate. The fine glass feed particles are introduced downstream of the pre-burner through three injectors to promote thorough mixing with the gas. Initial tests used cullet as the feed material.

Gaseous oxygen is added to the combustion products of the pre-burner for combustion of the fuel added in the main or glass melting burner. Natural gas is introduced through eight radial injectors just upstream of the main burner. A sudden enlargement at the burner entrance creates a strong vortex flow region to promote mixing of the fuel and oxidizer. Combustion takes place with the particles still entrained in the gas. Rapid quenching of the combusted gas by these particles acts to keep the peak temperature down, thus reducing the NO_x formation. A convergent nozzle at the exit of the burner accelerates the flow to the velocity required to accomplish the inertial separation of the particulate material from the combustion products, leading to homogenization and glass formation.

NO_X TEST RESULTS

The NO_X concentration in the burner exhaust gas is strongly influenced by the temperature-time history and the oxygen concentration of the gas. The latter is determined by the gas stoichiometry or the air-fuel equivalence ratio used. The process constraint is to maintain a low oxygen concentration as well as a minimal residence time at the peak temperature, yet provide for rapid heat transfer to the entrained batch material. For these conditions, NO_X concentrations significantly below the equilibrium flame adiabatic stoichiometric level are predicted.

Figure 2 shows the equilibrium concentrations of NO which would be expected in the absence of particle quenching effects. For stoichiometric and fuel rich combustion, the NO equilibrium concentration for various calculated adiabatic flame temperatures reached by combustion with preheated air are indicated. If an emission limit of 4 lbs NO_X/ton glass produced is assumed, then the maximum allowed NO concentration in the exhaust gas is 970 ppm for stoichiometric conditions.

Tests were conducted over a wide range of gas mass flows and feed loadings to determine system performance. While tests without batch material demonstrated that fuel-rich combustion offers the lowest NO_X emission due to lower peak flame temperatures, it leads to a lower thermal efficiency because a portion of the combustion energy of the fuel is not released and made available for melting of the glass in the furnace. As a result, the main furnace is typically operated with excess oxygen, $\phi \sim 1.4$. The temperature of the melt chamber is approximately 2500F. For these conditions, NO_X formation is approximately 1200 ppm prior to particle injection. Since the residence time at peak temperature is short, several milliseconds, the NO_X concentration is less than the equilibrium level shown in Figure 2.

Tests with a four component batch comprising 52% silica, 20% soda ash, 13% calcium carbonate, and 15% cullet demonstrated the AGM's ability to capture, homogenize and fine the molten batch material on the centerbody, producing a fully reacted glass product. As predicted, the NO_X production of the melter is considerably reduced by the quenching of the combustion gas by the batch particles. Batch injection is found to reduce the exhaust gas NO_X level to approximately 250 ppm, corresponding to an NO_X loading of 1 lb/ton glass without flue gas treatment.

KINETICS/TRANSPORT MODEL

The chemical kinetic reaction mechanism used to model AGM combustion consists of 31 chemical species and 146 elementary chemical reactions. The principal reactions for formation and decomposition of thermal NO are:

$$O_2 + M \rightarrow O + O + M$$

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

$$N + OH \rightarrow NO + H$$

The first three reactions, where M is a third body (usually N_2), represent the important and well known Zeldovich mechanism of atomic exchange reactions. The code utilizes experimentally measured reaction rate parameters or the results of thermodynamic calculations if experimental data are not available. The numerical technique used in these calculations is described by Reference 4.

A thermodynamic equilibrium code is initially used to determine the composition of vitiated air from the combustion of air/CH_4 at T ~ 2500K in the pre-burner. These species account for approximately 40% of the total concentration of initial molecular constituents in the main combustor. Given these values and the concentration of added O_2 and CH_4 necessary to obtain the desired air/fuel ratio, the kinetic model is used to obtain the temporal dependence of key reaction species as a function of initial temperature. Figure 3 shows calculated temporal profiles for T = 1500K and a stoichiometric air/fuel ratio. Following an ignition delay of about 1.6 ms, a peak flame temperature of approximately 2350K is attained. The e-fold NO formation time is ~ 3.0 ms. The corresponding NO mass fraction, 0.003, is in good agreement with thermodynamic equilibrium calculations shown in Figure 4. This value is somewhat higher than the AGM test results, but this is attributed to a lower gas temperature in the glass melter.

The kinetic code is modified to include the effects of solid particles and the calculations are repeated. As Figure 3 indicates, the addition of solid particles reduces the NO_x concentration from approximately 2000 ppm to 750 ppm, a factor of ~2.5. The AGM test results show still lower NO_x concentrations in the furnace exhaust, but the general conclusion remains that NO_x control is achieved by using entrained particulates as a dispersed heat sink with a short thermal transient time. Some errors are introduced in the kinetic calculations due to the difficulty of simulating the process which causes ignition, namely, the expansion of gases into a dump combustor, as well as the use of a flameholder, creating recirculation zones which result in bulk flow and mixing of combusted and uncombusted gases. This is analogous to the experimental situation where ignition would also not take place if methane was to be injected into the gas stream without provisions for flameholding.

A numerical simulation model treating transport processes in the AGM is used to describe NO_x formation and decomposition during rapid gas cool down by suspended batch material. The code is 1-D and calculates the temperatures and velocities of gas and particles along the length of the combustor. It assumes that all the particles are entrained in the gas and do not come into contact with each other in the combustor. Gas properties are calculated based on its chemical composition. The batch composition and the gas flow rates were selected to simulate the performance of the AGM. The program starts calculations at the location where particles are injected into the gas and it follows the temperature and velocity of gas and particles as they move along the combustor till the particles separate on the target.

Figure 5 shows the temperature profiles in the combustor section. Cold batch particles (sand, cullet, soda, and lime; batch flow rate=0.12 kg/s) were injected into hot gas coming from the vitiation burner (0.11 kg/s). The particle temperature rises at a rate dependent on the particle size. The flow rates of oxygen and natural gas were 0.037 and 0.0083 kg/s, respectively. The hot combustion gas is initially quenched very rapidly due to the high heat transfer rate from the gas to small particles. The gas temperature exhibits two subsequent sharp drops when oxygen and secondary methane are added to the gas stream. The calculation indicates that the gas cools from its peak temperature to 800-900K in about 12 ms.

At a distance of 1.2 meters from the particle injection location combustion takes place and the gas temperature sharply increases. The particle temperature also rises, but the rate is slower due to particle inertia. By the time the gas exits the combustor, 40 ms after particle injection, the temperature of the gas and the majority of the particles is almost equal, about 1800K. The only exception are the soda particles which due to their large size (150 micron diameter) and, thus, their large thermal inertia, are unable to follow the gas temperature as closely.

A question not presently addressed by the model is the suggestion of NO_x control by heterogeneous catalytic reduction. Evidence for such processes is provided by studies of the reduction of NO by H_2 over a Rh/SiO_2 catalyst [5] and of the decomposition of nitrous oxide on magnesium oxide and cupric oxide [6]. In addition, specific gas-surface interactions have been reported for NO and SO_2 with constituents typically found in entrained fly ash from coal combustion [7]. The effect of batch particle surface absorption sites for catalytic reduction and enhanced NO_x control in the AGM process requires additional analysis.

SUMMARY

The measured NO_x concentration in the advanced glass melter exhaust gas is significantly below anticipated NSPS requirements. This is attributed to gas/particle thermal quenching effects. NO_x formation in the high temperature post-flame gases is chosen to occur over a time scale of several milliseconds, whereas heat transfer takes place on a shorter time scale resulting in significantly lower NO_x emissions than the equilibrium level for adiabatic gas combustion.

ACKNOWLEDGEMENTS

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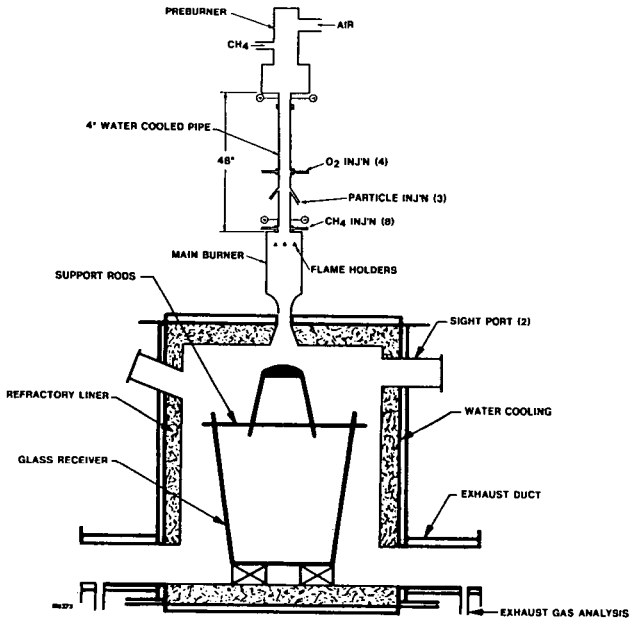


Figure 1 Schematic of AGM Experimental Set-up

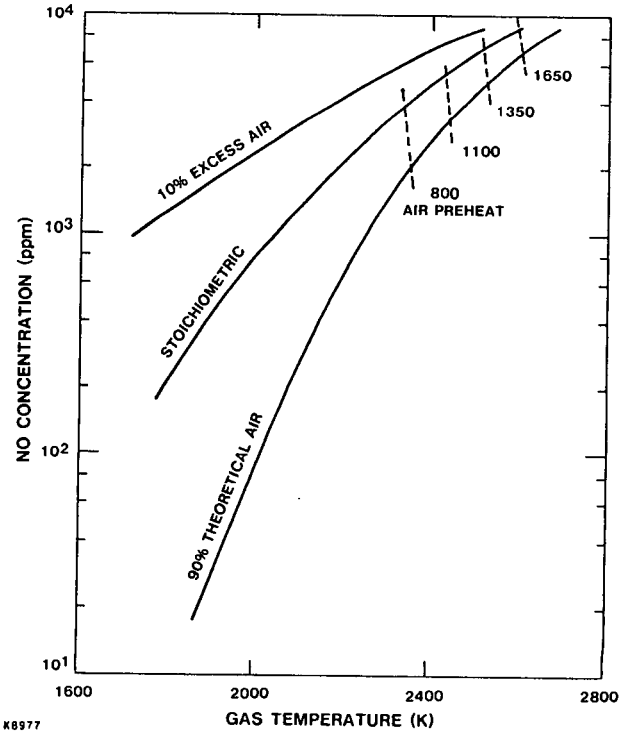
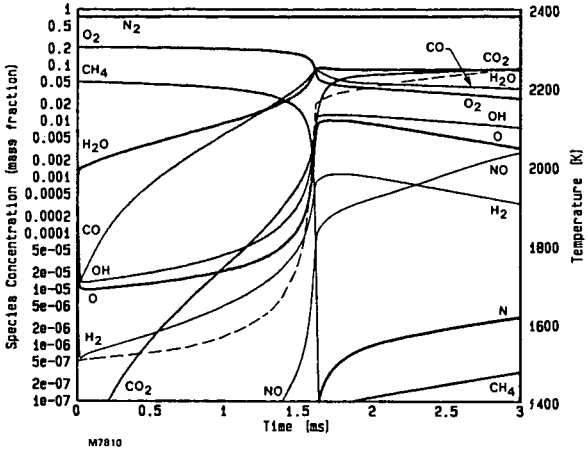


Figure 2 Calculated Equilibrium NO Concentrations for Various Stoichiometries and Gas Temperatures

(a)



(b)

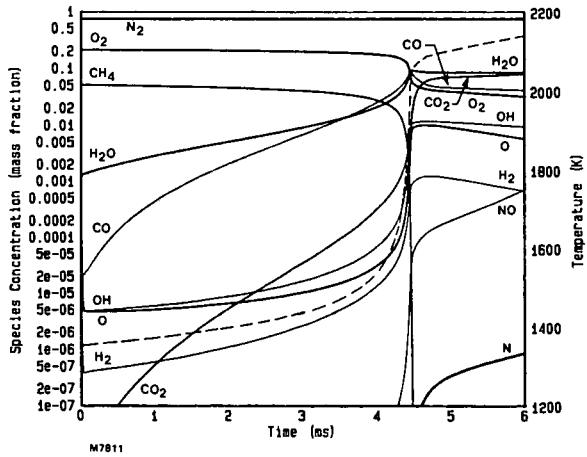


Figure 3 Combustion Species Temporal Profiles
(Dashed Line Shows Temperature Profile)
(a) Without Solid Particles
(b) With Solid Particles

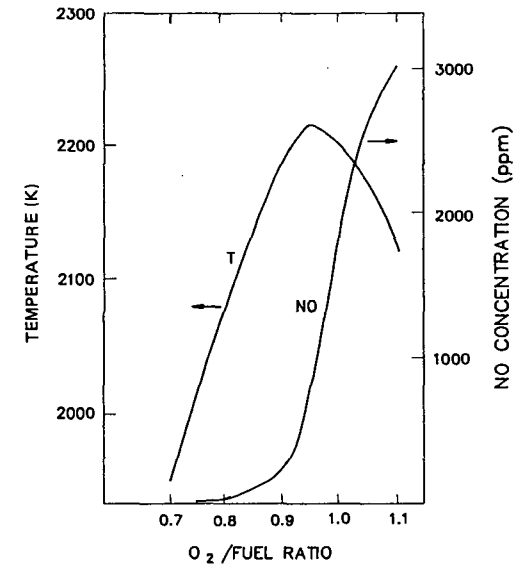


Figure 4 Equilibrium Calculation of Temperature and [NO] as a Function of the Oxygen/Fuel Ratio

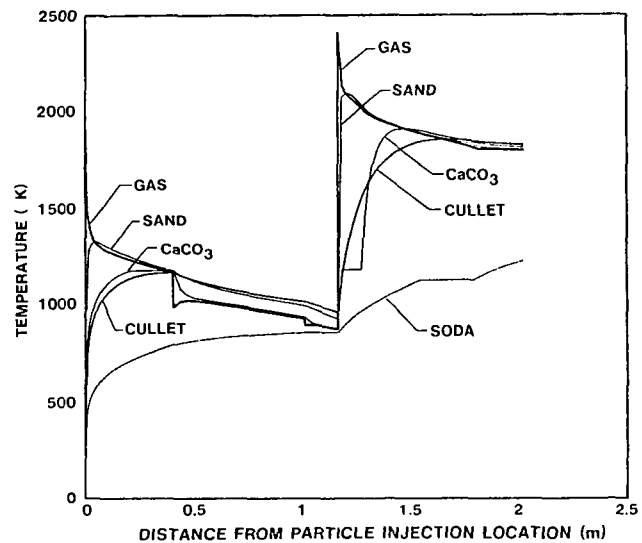


Figure 5 Temperature Profiles in Glass Melter