ENGINEERING DEVELOPMENT OF COAL-FIRED HIGH PERFORMANCE POWER SYSTEMS

PHASE II

Topical Report

Selective Non-Catalytic Reduction System Development

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Abstract

The current computational fluid dynamics modeling technique is capable of identifying the optimal reagent injector locations for SNCR systems. However, this technique cannot quantify NOx reduction and ammonia slip. ABB carried out a research project to investigate various computational fluid dynamics (CFD) models and the chemical kinetics of nitrogen species during coal combustion. An enhanced computational model was developed by integrating CFD and chemical kinetics to predict the overall performance of SNCR systems. The model was validated using data collected from a large-scale experimental test facility.

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Executive Summary

Most of the available computational models for SNCR systems are capable of identifying injection parameters such as spray droplet size, injection angles and velocity. These results allow identification of the appropriate injection locations based on the temperature window and mixing for effective dispersion of the reagent. However, in order to quantify NOx reduction and estimate the potential for ammonia slip, a kinetic model must be coupled with the mixing predictions.

Typically, reaction mechanisms for SNCR consist of over 100 elementary steps occurring between approximately 30 different species. Trying to model a mechanism of this size is not practical. This ABB project incorporated development of a simplified global kinetics model capable of predicting the overall performance of SNCR systems including NOx reduction and ammonia slip. The model was validated using data collected from a large-scale experimental test facility.

The model developed under this project can be utilized for the SNCR system design applicable to HIPPS. The HITAF design in the HIPPS project includes low NOx firing system in the coal combustor and both selective non-catalytic reduction (SNCR) downstream of the radiant heating section and selective catalytic reduction in a lower temperature zone. The performance of the SNCR will dictate the capacity and capital cost requirements of the SCR.

Introduction

Selective Non-Catalytic Reduction (SNCR) is a technology which can be used to reduce the concentration of NOx formed by more than 50% under favorable conditions. During 1994, ABB began an effort to develop a model to predict the performance of SNCR systems for industrial-scale boilers. A CFD code, FLUENT, was successfully used to model the fluid dynamics and heat transfer occurring in a VU-40 with SNCR, including injection, dispersion, and evaporation of the reagent. The CFD code was shown to be sensitive to injection parameters such as spray droplet injection angles and velocity. The result was a model which allowed for the determination of the appropriate injector locations (based on the temperature window and mixing) as well as the optimization of other parameters which affect the ability of the reagent to disperse effectively throughout the upper furnace flue gases. There was, however, no means of quantifying the actual NOx reduction which would occur for this optimal system design nor was there any ability to estimate the potential for ammonia slip. This type of information can only be determined through the use of a kinetic model.

The NOx reduction chemistry occurring in an SNCR system has typically been modeled in bulk assuming a completely stirred reactor (CSTR) operating isothermally at the average cavity temperature. The trouble with this approach is that the reagent is rarely completely mixed within the SNCR cavity and that cavity is not usually maintained at a constant temperature. By integrating a kinetic model with a CFD code, each computational cell in the

domain is treated as a CSTR. Each cell may differ from its neighbors with respect to temperature and species concentrations. This allows for a more accurate representation of the chemical reactions occurring in the SNCR cavity of a furnace. The addition of kinetics to the model allows for the optimization of other SNCR system related parameters such as the normal stoichiometric ratio of reagent to in-furnace NOx (NSR).

In order to design a commercial SNCR system, a model must be applied to locate injectors for the reagent and to predict the overall system performance including NOx reduction and ammonia slip. The goal of this ABB project was to continue the work begun in 1994 on the development of such a system model. The main objectives of the project were the development of a suitable kinetic subroutine and the incorporation of that subroutine into the CFD code utilized in 1994 for the fluid and thermal dynamic modeling.

Results and Discussion

Selection of Modeling Approach

Several difficulties are encountered in coupling kinetics with a CFD code. The primary reaction sequences for SNCR are shown in Figure 1. This figure does not show any of the potential side reactions and undesirable competing reactions which contribute to the complexity of the overall SNCR reaction mechanism. Typically, reaction mechanisms for SNCR consist of over 100 elementary steps occurring between approximately 30 different species.[1-3] Trying to model a mechanism of this size in combination with CFD is not currently feasible within the bounds of existing computer resources in terms of both memory and processing capability. Several research institutions are attempting to solve the computational problem of calculating this kind of complex chemistry in turbulent gas flows. Faced with the complexity of this task we are left with the alternative of somehow simplifying the kinetic mechanism.

The first level of simplification would entail the use of a more reduced chemical mechanism, on the order of 40 reaction steps occurring between less than 20 species. The second level of simplification is to reduce the kinetic mechanism to a set of global kinetic equations based on empirical data. Herein, species profiles determined through bench-scale experiments would be fit to a set of 3-5 rate expressions. Where bench scale data did not exist, CHEMKIN[4] modeling of the complete mechanism would be utilized to determine the species profiles. Sensitivity to some of the minor species is lost in this approach. However, it has been shown in the literature that this type of model can describe the influence of major parameters such as the temperature gradient, residence time, and the amount of injected reagent. Also good correlation with experimental data has been shown.[5,6]

Finally, in order to complete the predictions in a reasonable amount of time, the global kinetic model must be employed as a post-processor. Therefore, the fluid flow, heat transfer, and combustion calculations are first solved completely and then turned off prior to applying

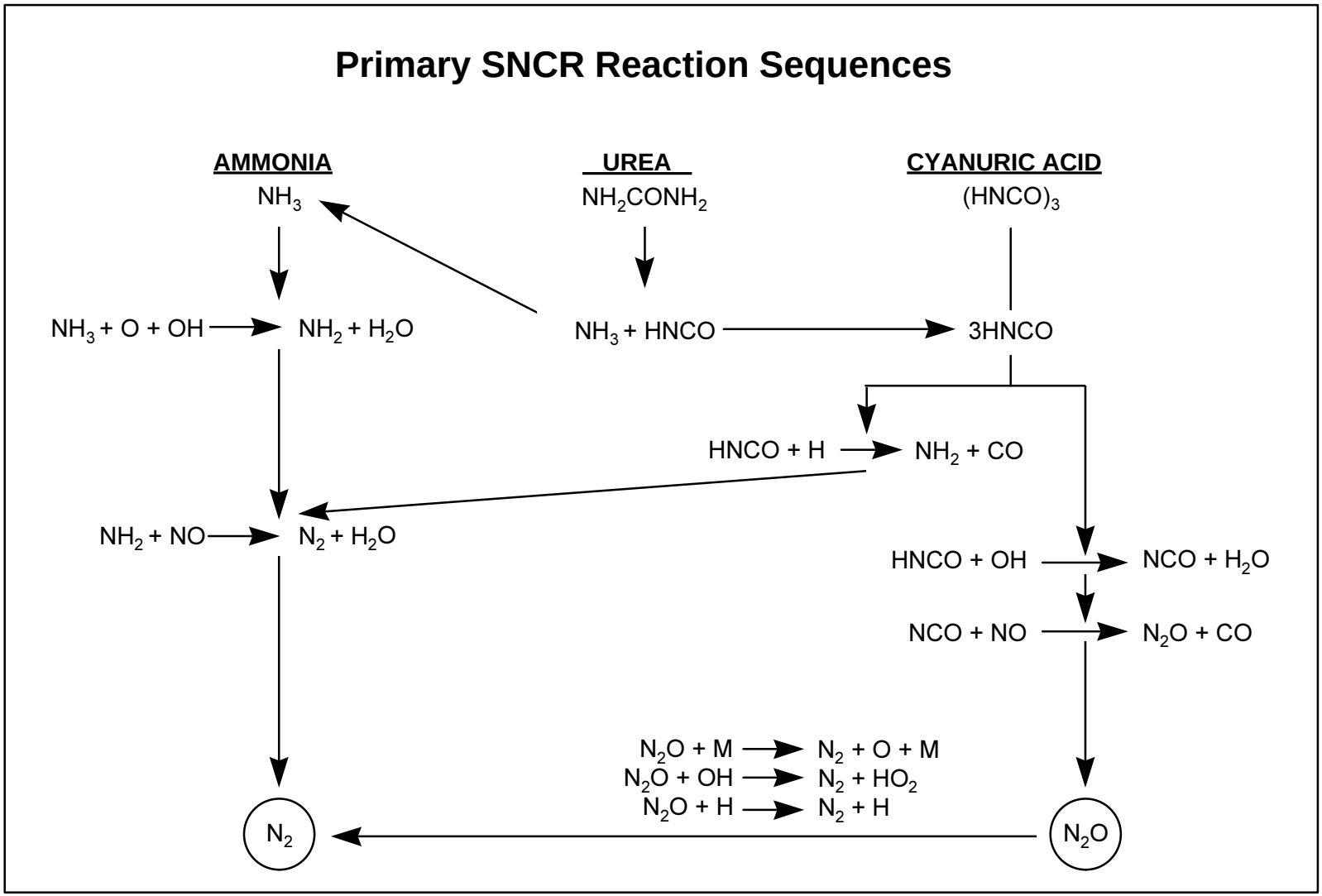

Primary SNCR Reaction Sequences
AMMONIA
NH3
UREA
NH2CONH2
CYANURIC ACID
(HNCO)3
NH3 + O + OH → NH2 + H2O
NH3 + HNCO → 3HNCO
HNCO + H → NH2 + CO
NH2 + NO → N2 + H2O
HNCO + OH → NCO + H2O
NCO + NO → N2O + CO
N2O + M → N2 + O + M
N2O + OH → N2 + HO2
N2O + H → N2 + H
N2
N2O

FIGURE 1

the SNCR kinetic model. This approach is already employed in FLUENT for the prediction of NOx formation from combustion. The danger in this simplification is that the reagent penetration is determined without the effect of reactivity. This could potentially cause the model to under predict the rate of NOx reduction and over predict the amount of ammonia slip, since it would theoretically allow for more unreacted reagent to be present in the cooler backpass area of the furnace. These possible shortcomings are somewhat acceptable since both error on the side of caution.

Test Conditions

Because there was not detailed full-scale SNCR test data available for use in the validation of the kinetic model, it was necessary to find other data suitable for this purpose. In 1991, the SNCR process was investigated by PPL through a series of tests performed in the Boiler Simulation Facility (BSF). Testing was performed at different boiler loads and excess air levels using both front and side wall urea injection. High, mid and low NSR conditions were all evaluated. Spatially resolved NOx, O2, CO and temperature profiles were obtained. The exit species concentrations (including NH_3) were also measured.

As our goal was to examine the sensitivity of the SNCR global kinetic subroutine and not validate the ability of FLUENT itself to perform combustion calculations on tangentially fired PC boilers (which is the within the scope of other efforts at PPL), we chose to model the BSF for only one set of firing conditions, but validate the model for three cases each with a different NSR.

Kinetic Model Development

Significant research concerning SNCR kinetics and modeling has been conducted at the Technical University of Denmark. Researchers from this university have published a technical paper describing the application of a global kinetic model for ammonia-based SNCR which consists of two equations.[6] The model was applied to the prediction of SNCR systems in a both a 12 MW fluidized bed boiler and in a pilot scale coal fired boiler. The model showed good agreement with experimental data for the fluidized bed boiler. After extensive literature review, the rate expressions from this work were selected and used to develop our global rate expressions for application in this project. Relevant equations are shown below:

$$r_{NH3\ to\ N2} = k_{NH3\ to\ N2}\,[NH3]\,[NO] \quad (1)$$

$$r_{NH3\ to\ NO} = k_{NH3\ to\ NO}\,[NH3] \quad (2)$$

where:

$$k_{NH3\ to\ N2} = 2.45 \times 10^{14} \exp(-29400/T)\ m^3\ mol^{-1}\ s^{-1} \quad (3)$$

$$k_{NH3\ to\ NO} = 2.21 \times 10^{14} \exp(-38160/T)\ s^{-1} \quad (4)$$

Suitable rate expressions for urea decomposition were not found in the literature, however, data sufficient for the purpose of correlating a rate expression was located. At temperatures above 200 ^{o}C, one mole of urea rapidly decomposes to form one mole of HNCO and one

mole of NH_3. In the temperature range where the injection takes place, this conversion is complete.

Following the urea decomposition, NH_3 reacts in the same manner as if it had been injected alone. This leaves only the HNCO global kinetic expressions unknown. CHEMKIN was used to simulate the HNCO chemistry using the complete mechanism of Miller and Bowman.[8] Global rate expressions for the reduction and oxidation pathways were correlated based on the resulting species profiles.

After the global kinetic expressions were developed, it was necessary to incorporate them into the FLUENT CFD code. In order to perform this in the most efficient manner, Fluent, Inc. was contracted for this task. It was necessary to thoroughly debug the code at PPL before it would run in a satisfactory manner.

SNCR Model Validation

In order to ascertain whether or not the combined CFD and kinetic model could quantitatively predict SNCR system performance, a validation study was performed using data from the BSF SNCR testing conducted in 1991, as discussed previously in this report.

Comparisons with the BSF experimental data indicated that the upper furnace temperatures resulting from the CFD combustion, flow and heat transfer calculations were too high. Consequently, the predicted species concentrations were also incorrect. Since the goal of the project was to validate the kinetic sub-model, not the FLUENT-CFD code, it was determined that the best approach was to patch new initial conditions to the inlet plane of the upper furnace model, imposed on the normalized profiles predicted by the lower furnace model, such that the upper furnace CFD model predictions agreed well with the conditions observed in the test facility for our selected base case Three cases (differing in NSR) were modeled and the kinetic rate constants calibrated in order to best fit the test data obtained in the field. Since the global kinetic rate constants for the ammonia pathway were previously validated by other researchers and known to result in reasonable predictions, only the rate constants associated with the HNCO pathway were adjusted.

A comparison of the experimental BSF data with the results of the calibration/validation calculations are shown in Figure 2. The outlet NO predicted for all three cases reasonably agreed with the experimental data. Ammonia slip for the low and middle NSRs was also reasonably predicted. The ammonia slip for the higher NSR case was not accurately predicted. It is possible that the experimental value is in error since ammonia slip is difficult to measure. However, the model result is also suspicious in that it predicts a simple linear trend in ammonia slip with increasing NSR. Figures 3, 4, and 5 show the profiles of NO, NH_3, and HNCO at the centerline of the upper furnace model and at the centerline of the SNCR cavity in plan view for the middle NSR case.

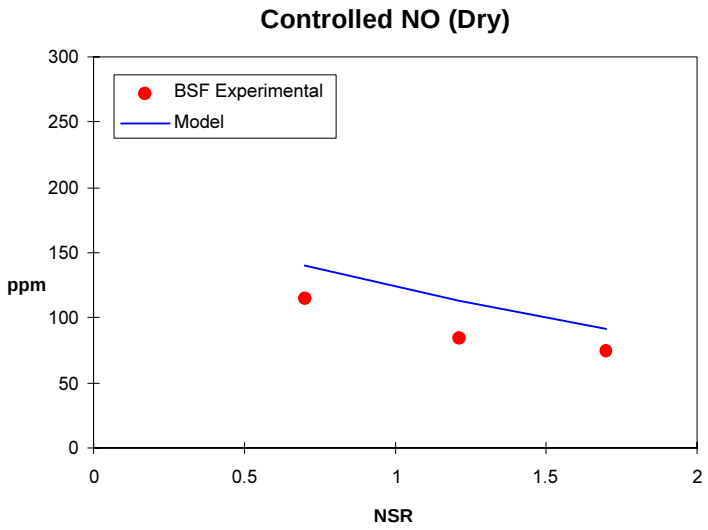
SNCR Parametric Studies

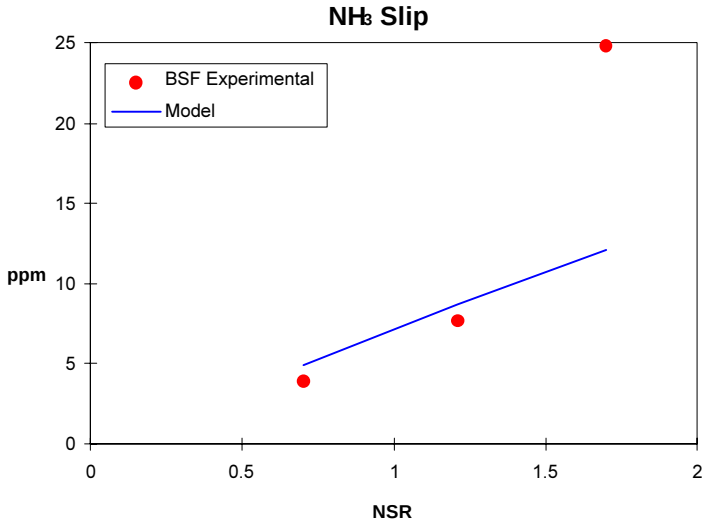
In order to evaluate the sensitivity of the SNCR CFD and Kinetic Model a series of parametric studies were performed. The variables examined were temperature, inlet NO, and inlet O2. The complete test matrix is shown in Figure 6. The predicted trends for NO reduction were compared to those reported in the literature[2] (no suitable data was found in the literature for comparison with the predicted trends of NH_3 slip). The results predicted by our model are in fairly good agreement with these published trends except, however, for the predictions at high temperature. At temperatures above 1900 ^oF the model over predicts NO reduction indicating a need for further investigation of the HNCO rate constants.

Conclusions

The model developed under this program can be utilized for the SNCR system design applicable to HIPPS. In order to apply the current model to performance predictions for a full-scale unit a CFD model of that unit (including combustion) must be completed. Further, it is necessary to supply realistic boundary conditions at the inlet to the model. These boundary conditions must include temperature, velocity, O_2, N_2, CO, CO_2, H_2O, and NO. These values may be obtained from another CFD model or from field data. The predictions are more accurate if profiles of these variables (with the velocity resolved into it u, v, and w components) are used instead of simply the average values at the inlet. If the profiles are unknown for the specific unit, normalized profiles from another unit can be applied if the other unit is sufficiently similar in geometry and firing conditions.

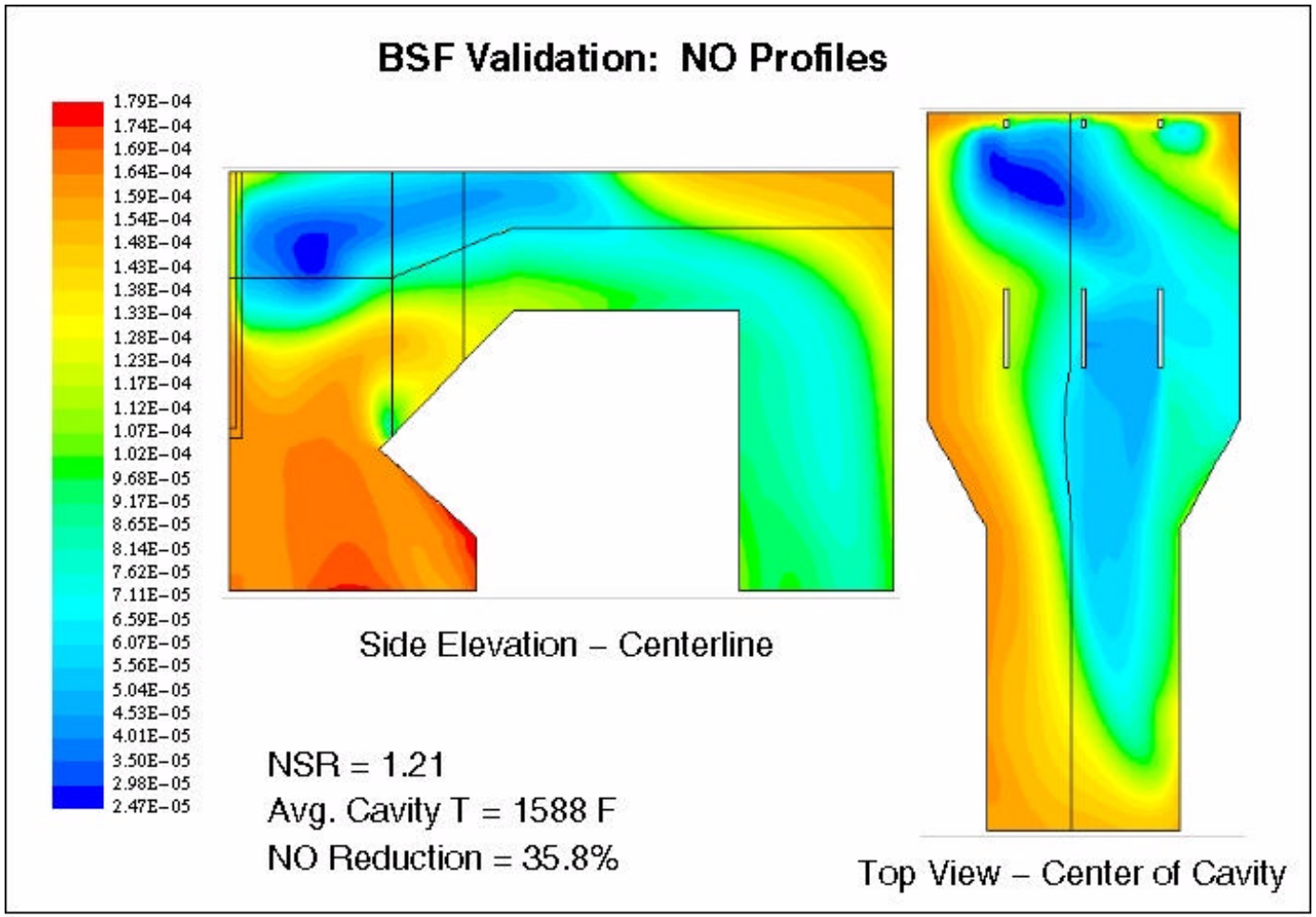
BSF Validation Results





Cavity Temperature: 1588 °F
Inlet NO: 175 ppm
Inlet O_2: 2.7 % (mole basis)

FIGURE 2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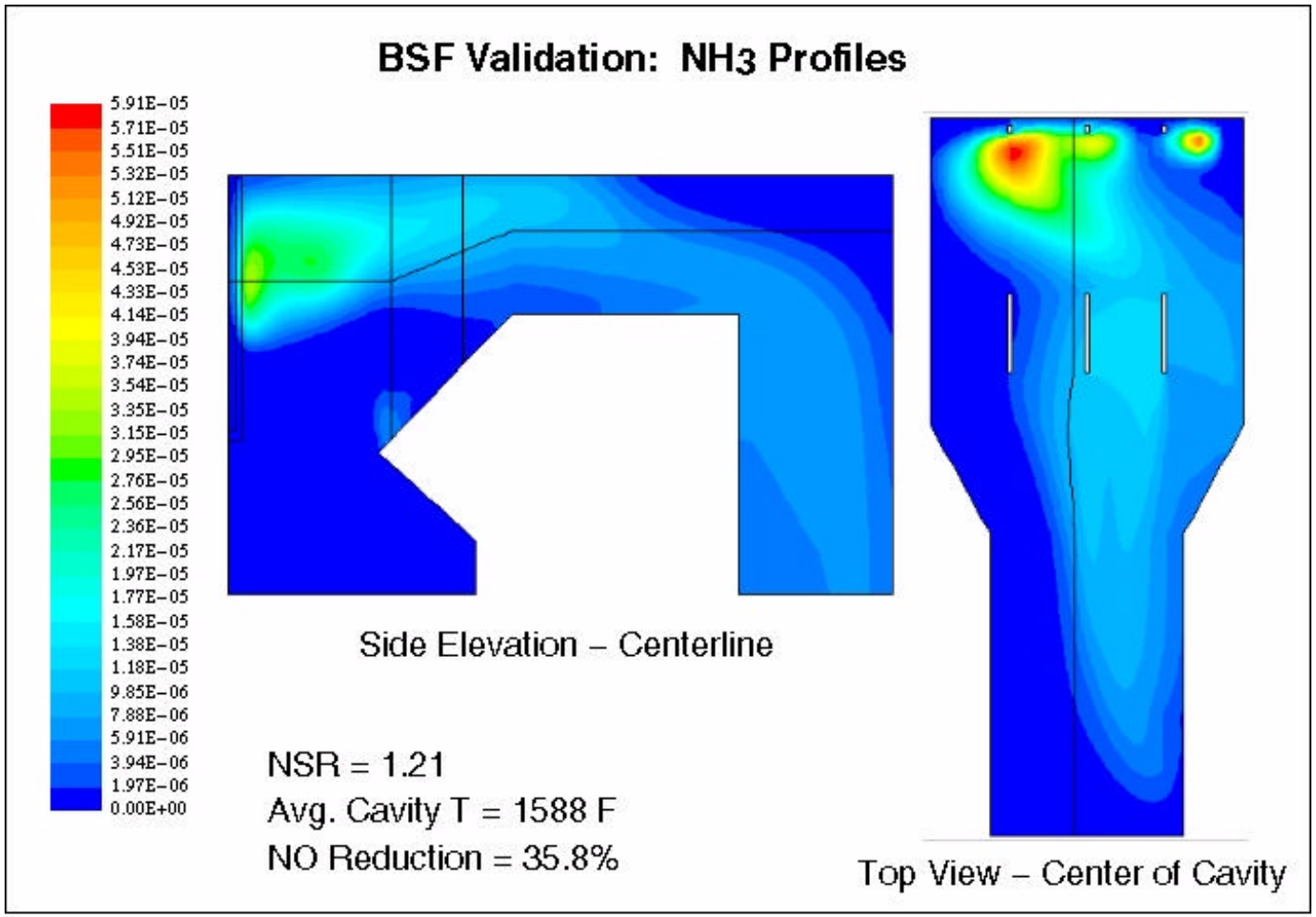
8.65E-05
8.14E-05
7.62E-05
7.11E-05
6.59E-05
6.07E-05
5.56E-05
5.04E-05
4.53E-05
4.01E-05
3.50E-05
2.98E-05
2.47E-05
Side Elevation – Centerline
NSR = 1.21
Avg. Cavity T = 1588 F
NO Reduction = 35.8%
Top View – Center of Cavity

FIGURE 3


BSF Validation: NH3 Profiles
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5.32E-05
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4.73E-05
4.53E-05
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3.94E-05
3.74E-05
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2.95E-05
2.76E-05
2.56E-05
2.36E-05
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1.18E-05
9.85E-06
7.88E-06
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3.94E-06
1.97E-06
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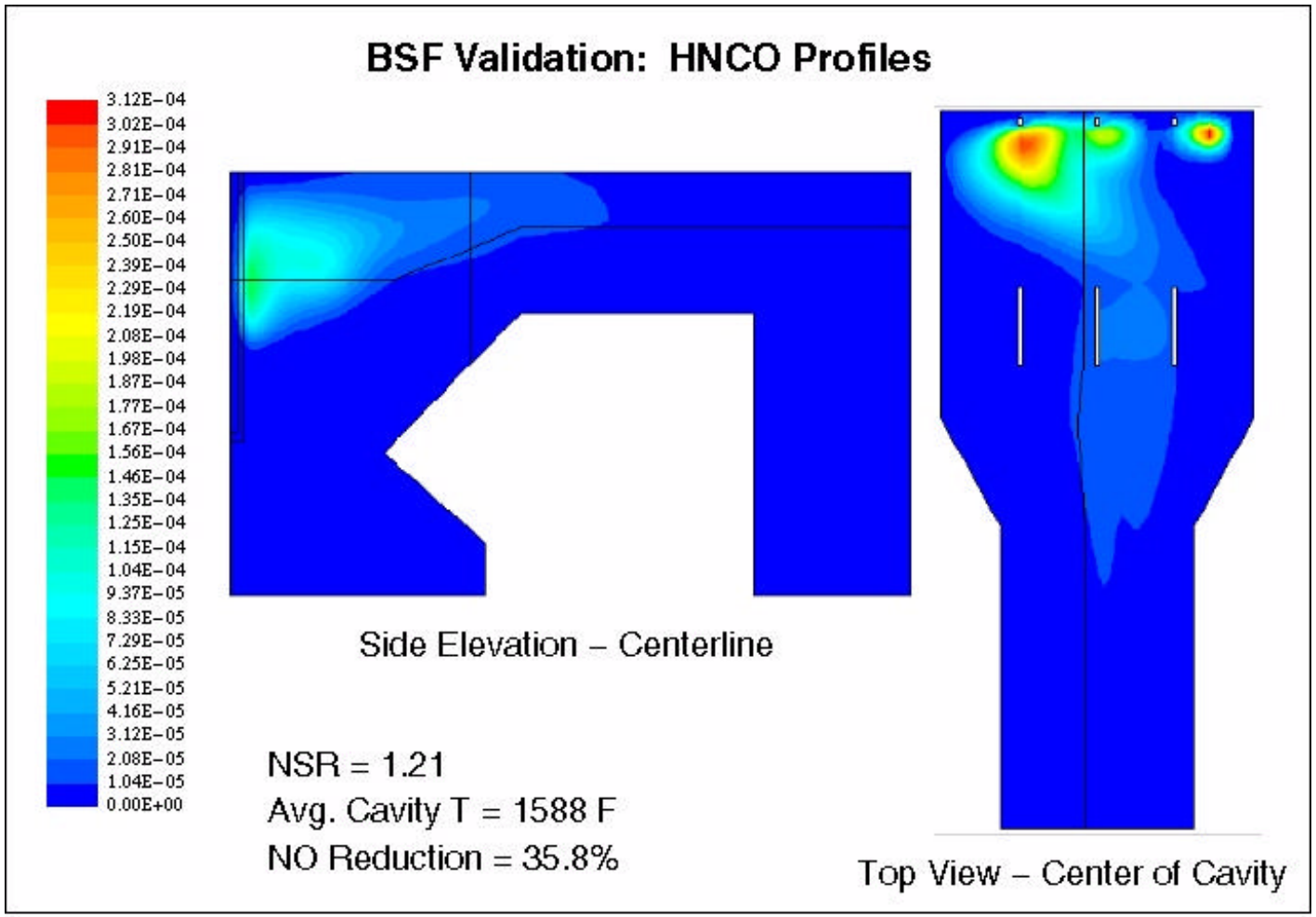
Side Elevation – Centerline
NSR = 1.21
Avg. Cavity T = 1588 F
NO Reduction = 35.8%
Top View – Center of Cavity

FIGURE 4


BSF Validation: HNCO Profiles
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2.71E-04
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2.29E-04
2.19E-04
2.08E-04
1.98E-04
1.87E-04
1.77E-04
1.67E-04
1.56E-04
1.46E-04
1.35E-04
1.25E-04
1.15E-04
1.04E-04
9.37E-05
8.33E-05
7.29E-05
6.25E-05
5.21E-05
4.16E-05
3.12E-05
2.08E-05
1.04E-05
0.00E+00
Side Elevation – Centerline
NSR = 1.21
Avg. Cavity T = 1588 F
NO Reduction = 35.8%
Top View – Center of Cavity

FIGURE 5

Parametric Study Matrix

Case #	NSR	Temperature (^oF)	Inlet NO (ppm)	Inlet O_2 (% by mole)
1	0.70	1588	162	2.5
2	1.21	1588	162	2.5
3	1.70	1588	162	2.5
4	1.21	1668	162	2.5
5	1.21	1892	162	2.5
6	1.21	2340	162	2.5
7	1.21	1668	162	4.2
8	1.21	1668	300	2.5

FIGURE 6

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