CHAPTER 1:

INTRODUCTION

1.1 Why Nitrogen Oxides?

Experts have recognized nitrogen oxides as some of the most harmful and most difficult to control of the man-made pollutants. Part of the difficulty of dealing with nitrogen oxides resides in the complexity of the chemistry that the components participate in. The term "nitrogen oxides (NOx)" encompasses an entire class of compounds that possess different chemical and physical properties. To complicate matters further, most can spontaneously react to change their identity, becoming a different member of the NOx family.

Nitrogen oxides have many characteristics similar to other man-made gaseous pollutants. They often arise as by-products from other processes, damage the environment, and can be harmful to the health of humans. Until recently, companies producing and emitting such compounds have largely gotten away with these negative impacts to the environment and humans. Despite the similarities between nitrogen oxides and other gaseous pollutants, nitrogen oxides, as a class, provide us with special challenges, as well as opportunities, that require further research and understanding. The field of environmental engineering is still new and we do not yet have all the information on some specific subjects within the field, such as NOx control.

With government agencies and regulations now providing companies with ever-increasing economic "incentives" to reduce waste emissions, work must be done on the specific problems to keep all waste products "below reg." With these regulations becoming more and more stringent, simple rules of thumb for reducing waste, though still needed, will not complete the task. We need in-depth research in order to find solutions to these numerous problems related to NOx emissions.

1.2 Why Computer Modeling?

The complexity we refer to requires special techniques to solve the practical problems that arise when engineers attempt to tackle NOx emissions. The mathematical models proposed by researchers are informative, but they give few useful suggestions to engineers in the field. We set as a goal of this thesis to give practical suggestions that will reduce NOx emission problems without causing new ones. The use of an advanced commercial software tool for process simulation, ASPEN (Advanced System for Process Engineering) Plus, allows us to test many design options and process variables quickly. We first determine the important variables that exhibit a strong effect on the processes under consideration. We then optimize the processes by adjusting these variables or by retrofitting equipment.

We believe this to be the first in-depth study of NOx absorption combined with selective catalytic reduction in the literature. This thesis exposes the many possibilities and limitations associated with combining these two very different processes. We hope that the processing suggestions we develop here assist those currently struggling with similar processes as well as aid those considering design of new units to handle a NOx control problem.

1.3 An Overview of This Thesis

Chapter two of this thesis explores the literature for current information relating to NOx control and removal. First, we outline the main sources of NOx and the hazards associated with releasing NOx to the environment. The remainder of the chapter focuses on technology available to control NOx emissions from stationary sources. The term "stationary sources" refers primarily to power plants utilizing combustion and chemical plants. A short overview of the most popular techniques in use at these facilities follows, complete with process flow diagrams to aid the reader.

Next, we sharpen our focus to two of the most promising forms of NOx control, those being selective catalytic reduction (SCR) and absorption into aqueous media (NOx absorption). We find these two processes most intriguing because they offer highly effective, compatible, and complimentary NOx removal. Sections 2.3 and 2.4 present to the reader the most current research in the literature for these two processes. Chapter two closes with a discussion of the computer-modeling approach we use in the following chapters to simulate these key processes.

Chapter three introduces the reader to the case-study process found at the Radford Facility and Army Ammunition Plant (RFAAP) in their so-called NOx abatement plant. The process at RFAAP utilizes both gas absorption and SCR in series to reduce NOx in an effluent gas stream. Chapter three further explores the individual processes and associated equipment that RFAAP operates for NOx abatement. We close chapter three with an introduction of the primary evolution of the steady-state ASPEN Plus computer model for simulating the two processes at RFAAP. The first model assumes simple stoichiometric conversion reaction to model the chemistry. The end of chapter three contains conclusions that we can draw from even this simple model as well as explanations of shortcomings of the model that we rectify in following chapters.

Chapter four contains the most detailed information from the literature on the mechanisms involved in the two key processes. We use this in-depth study to develop equilibrium-reaction models for NOx absorption and SCR. For NOx absorption, we begin with the most complex and complete mechanism available. In chapter four, we pare down the mechanism to a manageable system of reactions. We accomplish this for the reader by systematically applying assumptions that eliminate superfluous aspects of the mechanism. In this way, the reader understands the logic we use to arrive at a pertinent and useful model of the systems under study. For SCR, we use the most popularly accepted reaction set and simulate it under the assumption of thermodynamic equilibrium.

In chapter four, we present the results of the ASPEN Plus simulations that use the mechanisms under the aforementioned assumptions. As in chapter three, we close chapter four with a discussion of the information provided by the simulations and the shortcomings of the equilibrium-reaction approach to modeling the processes.

Chapter five outlines the third iteration of our hypothesized model for the NOx absorption and SCR processes at RFAAP. This model continues the use of the equilibrium assumption for NOx absorption as in chapter four. However, the model incorporates kinetic rate equations from the literature for the reactions encountered in SCR. Again, we close chapter five with discussion of the results and the advantages and disadvantages of the chosen model.

Chapter six departs from the format of the three previous chapters by utilizing the same model introduced in chapter five. In chapter six, we expand on the model to cover equipment retrofit and possible process optimization techniques for improving NOx removal. We summarize the process economics of the major opportunities explored with ASPEN Plus. We also include brief explanations of opportunities theorized in the literature that we could not successfully simulate with ASPEN Plus.

Chapter seven completes this thesis with the major conclusions and recommendations concerning both of the NOx removal processes, their industrial applications, as well as the computer simulation thereof. To the reader, we offer all the insight we gained after extensive work on the above subjects. The appendix contains duplicate figures and tables, computer output, a glossary of terms, and the complete reference list.

1.4 Nomenclature

ASPEN	Advanced System for Process Engineering
NOx	nitrogen oxide compounds
RFAAP	Radford Facility and Army Ammunition Plant
SCR	selective catalytic reduction