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George C. Frazier

George Frazier, Major Professor

We have read this thesis
and recommend its acceptance:

Manion L. Hansen

Wayne J. Davis

Accepted for the Council:

C. W. Mink

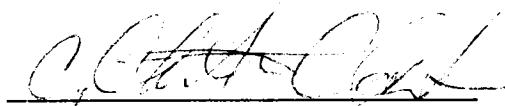
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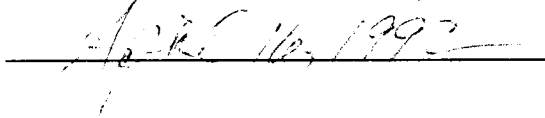
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REGENERATION OF AMMONIA FROM ASH PRODUCED IN A FLUE GAS
DESULFURIZATION PROCESS INVOLVING $\text{Ca}(\text{OH})_2/\text{NH}_3$ INJECTION

A Thesis

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ABSTRACT

A novel batch ammonia regeneration system was designed to recover ammonia from a flue gas desulfurization solid waste produced from a pilot plant technology in which a conventional spray dryer is incorporated with calcium hydroxide and ammonia injection to desulfurize high sulfur flue gas. The ammonia regeneration system is needed for this waste because 1) the ammonium products in the waste tend to be soluble, 2) an ammonia odor is given off by the ash, and 3) leaching tests on the waste show a tendency towards selenium leaching. These three characteristics would make the waste difficult to dispose unless an ammonia regeneration system is applied to the waste prior to disposal. This study developed an experimental ammonia regeneration reactor to use on the waste.

In the reactor, ammonia is dissolved from the solid waste into an aqueous phase which is then air stripped to recover the ammonia gas. Various parameters affecting this dissolution/stripping process (i.e. pH, temperature, solids loading, and gassing flow rate) are investigated through experimentation using the laboratory scale reactor. The ammonia regeneration process is also modeled using material balance equations for each of the three phases: solid ash, aqueous, and gaseous, in which the ammonia is found during experimentation.

The overall results of the experimentation demonstrated that the reactor system can regenerate up to 95% ammonia in no

more than 45 minutes with a pH of 11, a temperature as low as 45°C, a solids loading of 100 g/L, and with easily obtained air flow rates of approximately 33 liters/liter-min. The mass transfer model predicts similar ammonia regeneration results and is found to be in relatively good agreement for 12 out of 14 of the experiments modeled. The model is based on the existence of two forms of ammonia in the solid. These two forms include a strongly bound ammonia, believed to be ammonium sulfite, and a weakly bound ammonia, believed to be adsorbed ammonia. The mass transfer model with the best correlation to the experimental data included four stages of the ammonia regeneration process: 1) the conversion of strongly bound ammonia to weakly bound ammonia by a first order reaction, 2) the dissolution of the weakly bound ammonia into the aqueous phase, 3) the stripping of the ammonia from the aqueous phase, and 4) the removal of ammonia in the gas phase from the reactor.

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1. INTRODUCTION

With increasing population growth in the world, new demands for energy are continuously increasing. Twentieth century society demands the use of economical, highly efficient sources to produce energy [1]. Within the last few decades however, Congress has mandated that electricity production meet another criteria: environmental soundness. The major choices available for production of electricity are nuclear, natural gas, petroleum, and coal. The most abundant of these energy resources is coal. Therefore, it is expected that coal use will remain a predominant source for a long time. Coal use, however, is not environmentally sound without pollution controls added to the coal burning process. The major by-products formed from coal combustion include air-borne particulates, sulfur dioxide, carbon dioxide and nitrogen oxides. The particulates are controlled by electrostatic precipitators or fabric filter systems. However, the gaseous products must be handled by implementing many elaborate control systems. Control of the major corrosive effluent, sulfur dioxide or SO_2 , from coal burning utilities is regulated by the Environmental Protection Agency (EPA). These regulations are designed to curb the formation of corrosive acid rain, which can be produced in the upper atmosphere by the presence of high concentrations of sulfur dioxide.

1.1 Development of the Flue Gas Desulfurization System

Removal of sulfur dioxide from the exit gases, or flue gases, is called flue gas desulfurization (FGD). Many types of flue gas desulfurization systems have been developed, but all typically involve the use of a metallic alkaline scrubbing solution which reacts with the SO_2 . These solutions most often contain lime, limestone, sodium hydroxide, or magnesium oxide [2]. The waste formed from the SO_2 -alkali reaction can sometimes be recovered but most often is a throw away product that must be disposed of in a landfill or sludge pond.

The most widely used flue gas desulfurization systems involve the use of lime or limestone scrubbing solutions [2]. These solutions are typically sprayed into a large process reactor counter-current to the flue gas flow. The sulfur dioxide reacts with the calcium to form calcium sulfite (CaSO_3) or calcium sulfate (CaSO_4). The form of the product is determined mainly by the amount of excess oxygen in the gas stream [3].

The two major types of FGD systems include wet scrubbing and dry scrubbing or spray drying. Wet scrubber flue gas desulfurization systems remove sulfur dioxide efficiently and are relatively cheap because of low cost of the lime caustics typically used. Most wet scrubbing systems are utilized under ambient temperatures [4]. The waste stream is a sludge typically containing calcium sulfite. This sludge is very difficult to

dewater and initial disposal occurs in settling ponds. However, the sulfite solution does not easily settle or harden. Final disposal therefore must include some type of material addition to the sludge to promote solidification before removal to a landfill. Wet scrubbing process problems include formation of large scale deposits on equipment as well as equipment erosion [5]. In order to overcome these problems with wet FGD processes, spray dryers are implemented.

Spray dryers have been used in production of many diverse products such as detergents, paint pigments and instant coffees [5]. The technique of the spray dryer FGD process is similar to the wet scrubber in that a caustic slurry comes in contact with the flue gas in a counter-current flow. The major difference in the two processes is gas stream temperature. In the dry scrubber, the flue gas is not cooled up stream of the scrubber. The higher temperature of the SO_2 -calcium reaction in the spray dryer allows for formation of a dry product. This resulting calcium-sulfur product can be collected from the gas stream in the existing particulate collection system. This waste can be landfilled along with the other particulates, mostly fly ash, produced from coal combustion. This dry FGD system is as effective as the wet scrubber system and does not have the scaling problems associated with the wet, ambient temperature scrubber [5]. The major drawback to the spray dryer is a low SO_2

removal efficiency when a coal containing a high sulfur concentration is burned.

When a high sulfur coal is burned, a high ratio of calcium-to-sulfur in the spray chamber is needed. This ratio can only be achieved with a more concentrated slurry. Wet scrubbers can achieve this ratio but at a cost of faster scale build-up rates. For dry scrubbing, the pumpability and atomization of calcium slurries is limited to a maximum of 30-35% solids [6]. Also, a limited amount of water can be sprayed into the dryer without reducing the system temperature and forming a wet product. These two system constraints have limited the application of the dry FGD scrubber to only low sulfur coal situations.

Because of these spray dryer limitations, a supplementary FGD method was needed for wider use of the dry desulfurization system. Many system additives and/or recycle schemes were tested as possibilities in an effort to increase the SO_2 efficiency. However, no method is considered to be efficient enough for widespread use [6]. Some studies were performed using gaseous ammonia as the singular reactant with SO_2 . These studies showed that ammonia injection could be used for high sulfur coal FGD with near 100% removal efficiency [7, 8]. The presence of water is required to promote the product formation of ammonium sulfite. The limiting factor for this system seemed to be a plume which formed above the stack when the ammonia was used in

excess [6]. Therefore, the need to run the system in an ammonia starved mode, in order to prevent plume formation, would limit the total system efficiency.

Spray dryer efficiency with calcium hydroxide as the single sorbent gave 60% removal of SO_2 for high sulfur coal in pilot tests [6]. Therefore, the process of ammonia injection combined with the spray dryer technology was developed for high sulfur coal applications [9]. This system was tested in the pilot plant at the University of Tennessee. A description of the Tennessee system can be found elsewhere [6]. The results showed that the system was 90%+ efficient in removing the sulfur. The dry product that resulted consisted mainly of fly ash, calcium sulfite (CaSO_3), and ammonium sulfite ($(\text{NH}_4)_2\text{SO}_3$). A large-scale demonstration of this system was performed by Babcock and Wilcox during August of 1990 [10]. This study showed the effectiveness of the calcium/ammonia desulfurization process on a large scale. Ammonia was injected into a power plant flue gas stream following a calcium sorbent desulfurization process. Utilization of the sorbent increased from 55% to 85% with no deterioration of the electrostatic precipitator (ESP) performance. However, some concern was expressed about the waste from this combined ammonia/calcium FGD system.

The waste from this process has shown some physical characteristics which may prohibit its disposal in a nonhazardous waste landfill. First, the ammonium products in the waste are

relatively soluble. This solubility could cause problems in landfills by increasing the total level of dissolved solids in landfill runoff. Second, an ammonia odor, suspected to be adsorbed ammonia, is given off by the dry ash, which if landfilled, may violate EPA ammonia emissions regulations. Third, the ash exhibits an increased potential for selenium leachability [6]. Currently, EPA regulations exempt FGD wastes from disposal in hazardous landfills [11]. However, if the waste exhibits characteristics that cause concern, it could be considered a nonexempt or characteristic waste.¹ Power plants would then incur increased waste disposal costs because the waste would have to be sent to a hazardous waste treatment facility. One solution to this problem is treatment of the FGD waste prior to disposal.

Treatment of the FGD waste for ammonia recovery would remove the ammonium products causing the waste to be nonexempt. If designed properly, a waste treatment scheme would recover the ammonia as a gas for reinjection into the FGD system thereby improving the process economics also.

¹ A characteristic waste is a solid waste that exhibits one of the four characteristics of a hazardous waste. The characteristics are ignitability, reactivity, corrosivity, and failure of the Toxicity Characteristic Leaching Procedure (TCLP). This TCLP test measures the leachability of listed hazardous metals from the waste. Selenium is one of the listed metals.

1.2 Objective

The objective of this investigation is 1) to determine the feasibility of air stripping ammonia from highly alkaline, aqueous slurries of ammoniated fly ash in a laboratory scale stripping reactor and 2) to interpret the experimental results in terms of a simple process model based on material balance principles. Such a model, if successful, can be used as the basis of a preliminary design of a commercial-scale fly ash regeneration system. The preliminary design can be used for economic evaluation studies.

1.3 Methodology

An aqueous ammonia regeneration system for the FGD waste of the batch type was investigated in this study. The system involved slurrying the ammonia ash in water. The slurry pH and temperature are increased to the range of about 9.5 to 11.0 and 30 to 45°C, respectively. Under these conditions, the ammonia is released from the solid particulate matter to the liquid phase. Air stripping of the resulting liquor desorbs the ammonia into the gas phase. In a full scale system, the air/ammonia mixture can, in principle, be recycled to the spray dryer in the flue gas desulfurization system. The remaining ash slurry may be dewatered readily prior to disposal. Thus, ammonia recycle is potentially incorporated into the total FGD system.

A series of laboratory experiments were designed in order to investigate separately the effects of temperature, pH, air flow rate, and solid-to-liquid ratio on the ammonia stripping rate in a

pecially designed, sparged batch regeneration reactor. One liter of water and 50 to 100 grams of dry weight of ammoniated fly ash were used in each experiment. The fly ash was previously ammoniated in the pilot plant FGD process and stored dry in a sealed container until used in this investigation. The average ammonia content of the fly ash was 0.0002 moles NH_3 /gram of ammonia-free ash. Air bubbled through the ash/water slurry stripped the dissolved ammonia from the solution. In the laboratory, the ammonia was absorbed into a boric acid solution. All of these experiments were used to generate data for the development and test of a mass transfer model for this ammonia regeneration process using the FGD waste. This model was developed from the material balances of the three phases (solid, liquid and gas) in which the ammonia occurs during the regeneration process. A Fortran computer program was written in order to solve the differential equations developed in the material balances. The final model of this laboratory regeneration system can be used as a preliminary design for further ammonia regeneration studies on a pilot scale.

2. BACKGROUND

Development of a flue gas desulfurization system for application in high sulfur coal situations includes an examination and evaluation of many alternatives. One option is the use of a spray dryer system with calcium hydroxide and ammonia injection. This system was shown to remove 90% of the sulfur dioxide present in high sulfur flue gases [9]. The system advantages include (1) above 90% FGD efficiency for an influent SO_2 concentration of 3000 ppm, (2) near 100% sorbent utilization, and (3) a dry residual waste. As with any new FGD system, the question of waste management options arises. Similar wastes have been utilized for (1) nutrients in soils, (2) a feed stream for liquid ammonia plants, and (3) feed for sulfuric acid plants [12, 13]. Treatment and direct disposal are options as well. However, if onsite recovery plants for the ammonia and sulfuric acid products are not available, transportation of the waste will be involved. Transportation to the recovery site may be more expensive than the profit made from the waste sale. Also, the low concentration (approx. 5%) of ammonium products in the waste inhibit utilization as feed for ammonia plants [14]. Therefore, the only economical options may be treatment and/or disposal. Transportation costs are also incurred if onsite disposal is not available. However, if the FGD waste has properties of a characteristic waste, the disposal at a hazardous landfill site would be very expensive. Therefore, one of the most

viable options for the waste is treatment onsite. Onsite treatment of the FGD waste for ammonia recovery improves the flue gas desulfurization system economics as well as providing an inert waste that will be unregulated and easily landfilled.

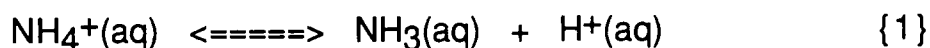
A variety of ammonia recovery systems are available for ammoniacal wastes. Besides flue gas desulfurization systems, many other systems develop wastes and wastewaters with high ammonia concentrations, i.e. petrochemical, semiconductor, pulp and paper, and textile manufacturing as well as livestock handling industries. Varied methods are used in each of these industries for ammonia removal. Some of the methods include selective ion exchange, bio-nitrification-denitrification, breakpoint chlorination, tray and packed bed steam stripping towers, absorption systems, and air stripping systems. Flue gas desulfurization systems that recover ammonia from its wastes have previously used only the various stripping and absorption methods. Advantages and disadvantages of each of these systems for use with the ammonia/calcium injection FGD waste are presented in Section 2.1.

2.1. Ammonia Recovery Systems

2.1.1. Stripping Processes

Stripping systems incorporate a mass transfer operation for ammonia removal. These systems utilize steam or air to strip the ammonia. Some physical parameters of the stripper system, which can be used for optimization, are temperature, pH, liquor viscosity, and stripping gas flow. Ammonia is in equilibrium

with the ammonium ion in aqueous systems. The ammonia (NH_3)-ammonium ion (NH_4^+) system is influenced by temperature and pH. Figure 1 shows the equilibrium system as a function of temperature and pH. This equilibrium, given in equation 1, shifts to the right, i.e. toward the non-ionized ammonia when



the pH is greater than 10 and temperatures are over 30°C [15]. The ammonia stripping efficiency is also dependent on the viscosity of the system and the air and/or steam flow rate. Typically, a higher viscosity will require a high stripping gas rate through the ammonia removal system. Optimization of these ammonia stripping systems will be discussed below.

2.1.1.1. Tray and Packed Stripping Towers. Sour waters from petroleum refineries are liquid wastes containing mixtures of hydrogen sulfide and ammonia. The use of tray or packed bed towers is typical for removal of these components from sour waters, although tray towers are more common [16]. Hydrogen sulfide is reduced to sulfur and removed from the top of the tower with ammonia being concentrated in the bottoms. The tray towers utilize caustic addition on the lower trays to promote ammonia removal [17]. The caustic raises the pH of the stripping liquor. This caustic addition must be carefully monitored because it will neutralize and fix any hydrogen sulfide

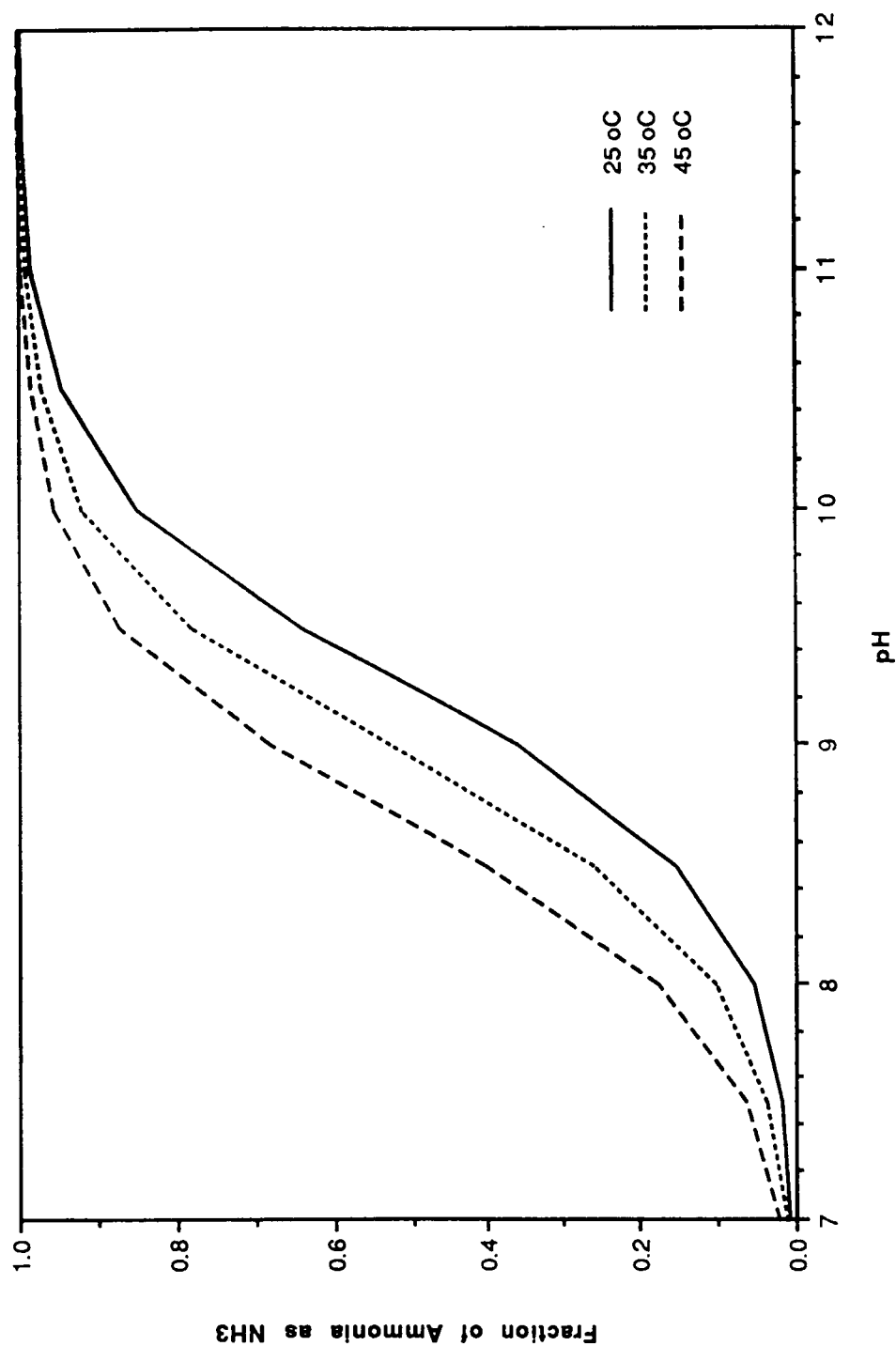


Figure 1. Fraction of Ammonia Present as NH_3 in an Aqueous System (Source: Ammonia, 1965, World Health Organization)

present in the lower trays, which reduces sulfur removal efficiency [16]. Steam is used to maintain the proper temperature for ammonia stripping. Many computer models were found that could be used to determine the stripper efficiencies of ammonia and sulfur from the tray tower system for sour water applications [16, 18]. Ammonia removal up to 99% can be achieved with this system but is expensive to operate and maintain. Increasing the number of columns to two or more increases the ease in which the ammonia can be removed [13]. However, use of multiple columns increases the costs and complexity of operating the process.

One FGD system, that removes sulfur dioxide from industrial flue gases with ammonia scrubbing, uses steam stripping for ammonia recovery. This system was developed by Foster Wheeler and Weirtam UGINE Kuhlmann (a French engineering firm). Sulfur dioxide removal efficiencies of 95% were achieved for the FGD system [19]. The flue gas is reacted in a scrubber with a spray of ammonia and water vapor. The resulting liquor is reacted with a lime slurry. Ammonia is released into solution and then the ammoniacal solution is steam stripped. This process recovers nearly 100% of the ammonia. The ammonia is then recycled and reinjected into the FGD system.

These steam stripping systems give high ammonia recoveries but show the need for a high temperature in the ammonia reclamation system. Optimization of the ammonia recovery system, however, should take into account the

economics associated with operation of a moderate to high temperature process.

2.1.1.2. Air Stripping Systems. Types of air strippers include batch, continuous, and spray towers. Batch and continuous systems usually employ a tank reactor in which air and/or steam is bubbled into the ammonia rich wastewater. In a dual system examined by Srinath [15], the steam raises the temperature of the system to promote ammonia release, while the air is used to strip ammonia from the solution. However, air bubbles in the stripping tanks become saturated with ammonia after the first few millimeters of ascent through the liquid. Therefore, to increase the stripping efficiency of the system, the air-to-liquid ratio must be increased. This ratio is increased by one of three ways: (1) by higher bubbling rates, (2) by creating smaller bubbles, or (3) by increasing the bubble production area. The choice of which method is used depends on the system under study. The use of steam for temperature control of the reactor is logical, but it increases the quantity of water droplets entrained in the exiting air stream. Because of ammonia's high solubility in water, nearly 50% of the ammonia stripped from the tank is removed via the entrained water droplets [20]. This entrained water must be taken into account when the water material balance is calculated. Removal efficiencies of 96% or better can be attained using this ammonia recovery system [20].

Another method of ammonia removal from wastewaters involves air stripping via spray towers. This process was

demonstrated at the wastewater treatment plant in South Lake Tahoe, California [21]. A cross flow of air through a packed bed cooling tower was utilized and experimental results indicated that 95% removal was achieved from wastewater streams. Problems encountered by this system include a very high air-to-water ratio requirement and bad cold weather performance [22, 23]. In the winter, if the atmospheric temperature decreases below 32°F, low ammonia removal efficiencies are observed due to the increased ammonia solubility in water at the lower air temperatures [21].

2.1.2. Absorption Systems.

Ammonia recovery by absorption is the opposite of stripping and is typically used when removing ammonia from a gas stream. An absorption solution, usually water, flows countercurrent to the gas stream carrying the ammonia gas. The high solubility of ammonia in water allows for ammonia absorption and removal from the gas stream. The ammonia-water solution can then be sprayed directly back into the flue gas desulfurization system for reuse. The absorption system can be a tray, packed bed, or spray tower. Ammonia recovery by absorption after an FGD process is discussed by Frank, et.al. [12]. Frank's E-Beam FGD system involves injection of a stream of electrons into a flue gas stream to convert the sulfur and nitric oxides to an acid mist [12]. Then, injection of ammonia saturated water stabilizes the mist which then dries to a powder. The ammonia products are in the form of ammonium sulfates and nitrites [24]. Recovery of the ammonia

gas involves slurring the by-product with water, and heating the slurry to approximately 90-110°C. The slurry is then scrubbed with a water solution to absorb the ammonia. This ammonia-water solution is then recycled for injection into the E-Beam FGD process. Approximately 60% ammonia recovery can be expected from this process [12].

A different process described by Rice and Busa, involves ammonia separation from acid gases by absorption with monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) [13]. A phosphate solution is reacted with the gas stream to form diammonium phosphates. The resulting liquor is steam stripped to recover nearly 100% of the phosphate reactant. Ammonia from the stripper is released as a gas and is then sent to a fractionator and recovered as a liquid [13].

Another process was examined by Shale, et.al., which utilizes ammonia injection for FGD [25]. In this process, ammonia and water (or steam) are injected directly into the flue gas stream. The gas mixture is then cooled to allow sublimation of the resulting ammonium product, ammonium sulfite. Regeneration of ammonia occurs via a vaporizer and reaction with zinc oxide. The zinc oxide reacts to form zinc sulfate and the ammonia is released as a gas for system reinjection. However, the use of the zinc oxide created problems caused by the precipitation of the insoluble sulfates in the solution. These problems included (1) increased scaling on the regeneration system equipment and (2) deterioration of heat transfer in the

system. Further studies by Shale reported the regeneration of ammonia by a two step process [8]. First, the ammonium sulfite reacts with sodium hydroxide, NaOH, a soluble base, to liberate the ammonia gas. Then, the NaOH solution is recovered by reaction with lime, Ca(OH)_2 , in a batch system leaving calcium sulfates as the waste product. This two step system reduces the scaling on the regeneration equipment while producing an inert calcium sulfate, CaSO_4 , product.

2.2. Development of the Ammonia Regeneration Process for the FGD Waste

The $\text{Ca(OH)}_2/\text{NH}_3$ desulfurization process combines two sulfur dioxide removal technologies. This combined technology was developed at the University of Tennessee (Knoxville) pilot plant station. A process schematic of their spray dryer/baghouse system is given in Figure 2 [9]. This system includes Ca(OH)_2 slurry injection into a spray dryer and gaseous ammonia injection into the flue gas stream. The spray dryer is used as the FGD scrubber. The flue gas flows through the spray dryer at approximately 300°F. The calcium hydroxide in the slurry droplets react with the sulfur dioxide in the gas stream, allowing rapid formation of calcium sulfite in the scrubbing chamber. Simultaneously, the relatively high gas temperature evaporates the water in the slurry droplets, so that when operated under proper conditions, a dry powdery fly ash is produced before the gas stream enters the baghouse. The dry product is removed from the flue gas stream in the power plant dust removal equipment

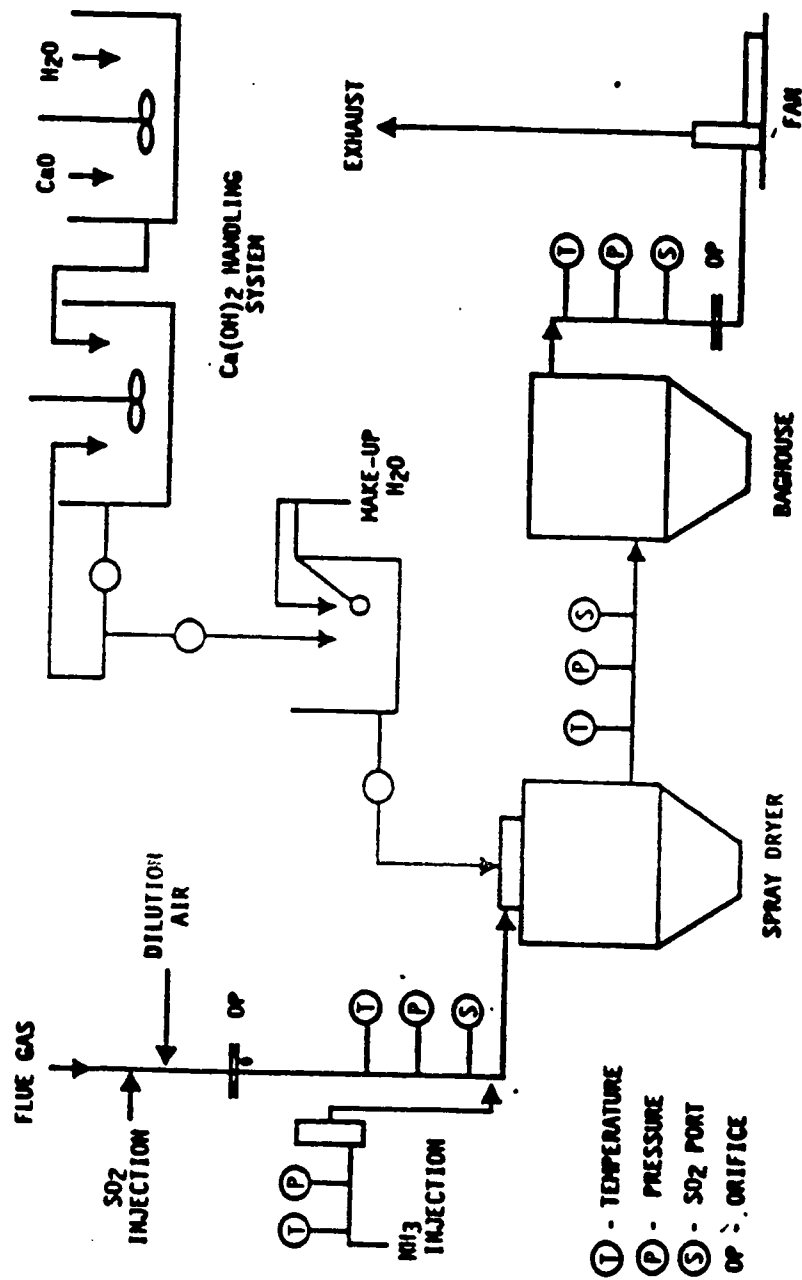


Figure 2. Schematic Diagram of Spray Dryer/Fabric Filter Pilot Plant (Source: Pakrasi, A. et al. "A Combined $\text{Ca}(\text{OH})_2/\text{NH}_3$ Flue Gas Desulfurization Process for High Sulfur Coal: Results of a Pilot Plant Study". Journal of Air and Waste Management Association, 1990. Vol 40. Issue 7.pg 987-992.)

(i.e. electrostatic precipitator or fabric filter) before exiting the stack.

Conventional scrubbing using a spray dryer with only lime slurry injection can remove up to 88% of the sulfur dioxide from the flue gas [6]. However, without recycle, this system has low utilization of the sorbent. To achieve high sorbent utilization a near 1-to-1 calcium-to-sulfur ratio is used. The efficiency of SO₂ removal, then however, is reduced to 55-60%. Because it is desirable to have both high utilization of sorbent and high SO₂ removal, a better system needed to be found. To compete with current wet FGD systems and to meet the EPA regulations, the desulfurization efficiency must be 90% or better for all types of coals. When conventional spray drying is applied to a high sulfur coal flue gas, the efficiency of SO₂ removal, as well as sorbent utilization, decreases significantly [6].

Many desulfurization studies have been conducted demonstrating the rapid reaction of gaseous ammonia with sulfur dioxide [7, 26]. These studies determined that ammonium sulfite is the major product. Pilot plant studies were conducted using only ammonia as the desulfurizing agent. These tests indicated that ammonia reacts completely with sulfur dioxide to form ammonium sulfite, (NH₄)₂SO₃ [6]. Desulfurization efficiencies of 30-40% were recorded. Removal efficiencies could have been higher, but a white plume (suspected to be ammonium sulfite) escaped from the stack. Because the spray dryer system needed

help for high sulfur gases, integration with ammonia injection seemed logical for efficient desulfurization.

In the pilot plant facility, the integration of the two systems was easily accomplished. The only requirement was the addition of an ammonia gas line to the spray dryer equipment. Logically, the ammonia could be injected either before or after passing through the spray dryer. Similar FGD efficiencies were seen at either injection point in the pilot tests. Therefore, the best injection site was dictated by the influence it had on the waste's physical properties.

In the spray dryer system, the lime slurry is atomized yielding small droplets which absorb the SO_2 . After the water in the droplet evaporates, a dried calcium sulfate particle remains [27]. Ammonia injection prior to the spray dryer may result in competing reactions between the calcium sulfate and ammonium sulfate formation [28]. The SO_2/NH_3 reactions occur very rapidly but this gas-gas reaction needs some type of particle on which to sublime these reaction products. In the spray dryer, the available particles are the calcium sulfate particles and the fly ash particles. If the calcium sulfate forms simultaneously with the ammonium products, the ammonium reaction products can become entrapped in the larger calcium sulfate particles. If the ammonia is trapped, regeneration would be difficult. Preliminary regeneration tests were used to determine if this entrapment was seen.

In 1988, Keener used a laboratory system that regenerated a maximum of 56% of the ammonia from a wet regeneration process [28]. In his process, $\text{Ca}(\text{OH})_2$ was added to the reactor to increase the pH and drive the ammonia out of the liquid phase. Keener explained the inefficient ammonia degassing as a deficiency of stripping gas into the basic solution. Another possibility was the waste type because the waste used in the tests was produced during ammonia injection before the spray dryer. However, these tests did not conclusively confirm this ammonia entrapment.

In the winter of 1990, the $\text{Ca}(\text{OH})_2/\text{NH}_3$ FGD system was tested in the University of Tennessee's pilot plant. Davis, et.al. gives a full description of the pilot plant system [9]. Because previous tests determined that the ammonia injection site did not affect the desulfurization efficiency, the system used ammonia injection after the spray dryer. The waste produced was used in further ammonia regeneration studies. Laboratory tests were performed by Yang and Keener, at the University of Cincinnati, to determine its ammonia regeneration potential [14, 29]. A separate reactor and stripper column apparatus was used to recover up to 90% of the ammonia from the ash. These laboratory tests served as a model for building a pilot plant ammonia regeneration system.

The pilot ammonia regeneration system was built at the site of the University of Tennessee's pilot spray dryer system. The pilot regeneration system was tested using ash from the University of Tennessee's FGD pilot plant system. This

regeneration system is shown in Figure 3. For the design of the pilot system, the residence time needed was estimated from the laboratory tests to be 90 min. In order to design a system with this residence time, three reactors in series were used. The reactors, which were 50 gallon drums, were each heated with external wrap-around heaters. Strippers, placed on top of each reactor, were used to deammoniate the ash mixture, but were not heated. The reactors were mixed with internal propeller type mixers. The first reactor served as the initial mixer of the ash solution. Ash addition, water addition, and $\text{Ca}(\text{OH})_2$ slurry addition (for pH control) all occurred in the first reactor in the series. Once the ash solution was made, the slurry was pumped above the reactor to the stripper. Then, the deammoniated slurry fell back into the reactor and was remixed and sent to the second reactor. Since each reactor had a stripper, the ash was contacted with air for stripping three times before exiting the system. The deammoniated slurry was then pumped from the reactors to a holding tank. Waste solids were subsequently removed in a batch mode via a vacuum press. The liquor removed from the solids was sent back to the first reactor as makeup water. Ammonia was stripped from the ash slurry by air under vacuum. Unfortunately, many technical difficulties were seen during the testing. These problems included large heat losses, slurry pumps clogging, poor slurry suspension, and large air leaks. The heat losses were due to operation during cold weather. No testing could be performed long enough to reach a steady state without these difficulties

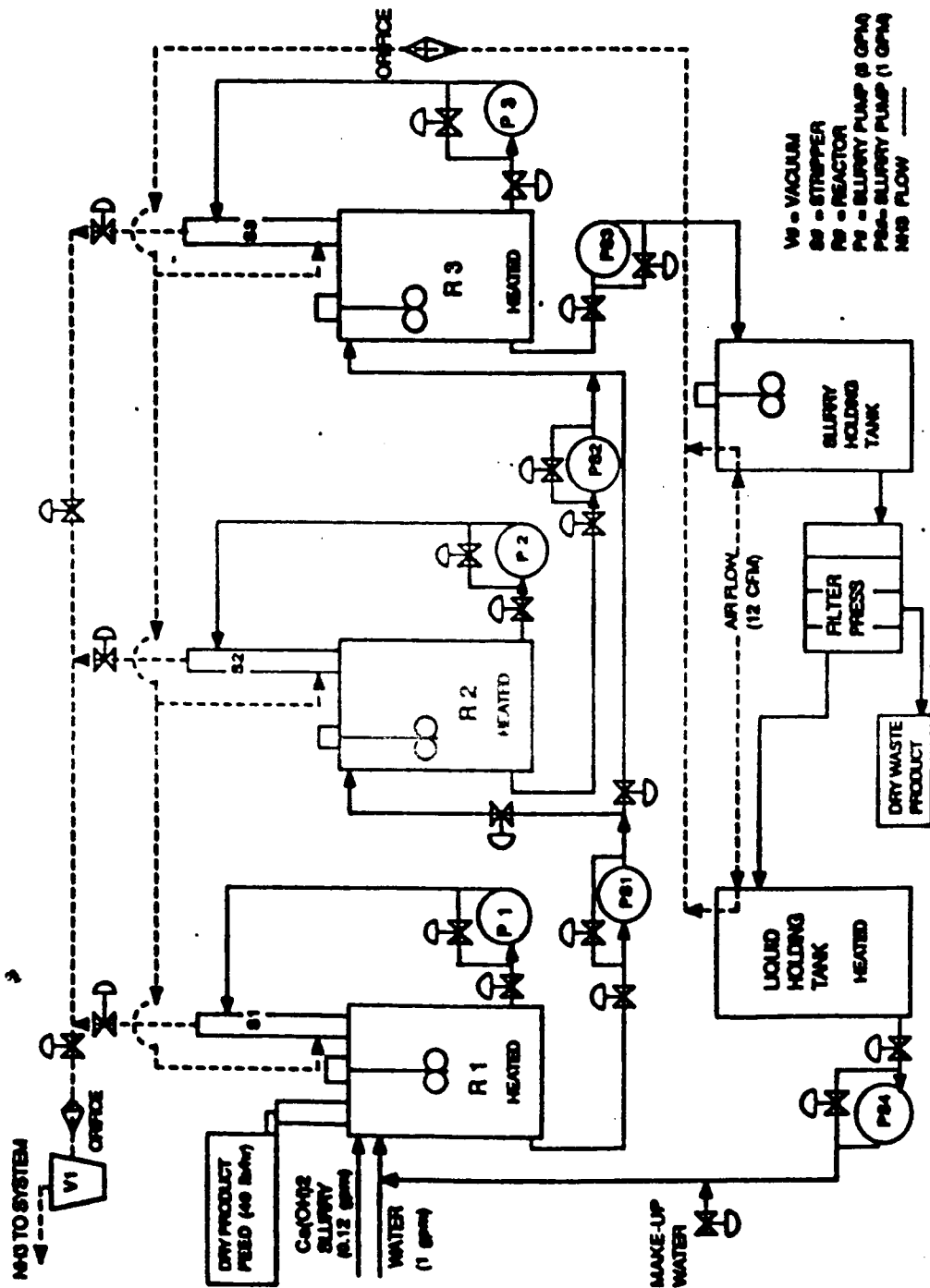


Figure 3. Pilot-Scale Design for an Ammonia Regeneration System

interfering. Therefore, the laboratory work was begun again in an attempt to define a better stripper system.

Yang and Keener's [14, 29] laboratory work was thoroughly reviewed in order to provide insight into the new system that should be tested. An overview of their study is given below.

Yang and Keener developed a continuous regeneration system in which the ammonia was degassed from an ash/water mixture by air stripping. The ammonia loss rate was measured over time by an ammonia gas analyzer. The design for this continuous system was developed from a batch study. The batch study used a simple, mixed reactor into which was placed the ash/water mixture. The pH and ammonia concentration were measured in the reactor with electrodes. The gas exiting the reactor was captured in an ammonia gas analyzer to determine the ammonia release rate on a batch scale from this ash. The temperature of the batch system was varied to determine the dependence of the ammonia release rate on temperature, and the results showed that this release rate was highly dependent on temperature. This batch temperature versus ammonia release rate data predicted the apparent activation energy to be 11.2 Kcal/mol. The overall results of the batch study indicated that ammonia is released from the ash when placed in water at room temperature as well as at high temperature. However, unless the temperature of this aqueous ash mixture was raised to nearly 100°C, the ammonia release rate is relatively low. Therefore, in the continuous system the ammonia release rate was accelerated by use of an air

stripper. This batch study, however, did not investigate 1) the extent to which the ammonia could be recovered from the ash slurry, or 2) which values of the parameters of pH, temperature, and solids content were best suited to promotion of the highest ammonia recovery from the ash. Also, the rate limiting step of the overall process was not determined explicitly. Even without this information, the continuous system was designed from these batch test results.

The continuous system included a continuously mixed reactor operated at room temperature for ammonia dissolution and a separate, heated air/slurry stripper. One concern was the temperature differential between the reactor and stripper. Yang and Keener assumed that all the ammonia dissolution would occur in the reactor (held at room temperature) [14]. Since all samples had a pH of 13 or higher in this batch reactor, all the ammonia released into the liquid solution would be in the NH_3 form based on Figure 1. Even though all the ammonia is in the NH_3 form, the extent to which the ammonia is released from the ash is not discussed. If the ash does not release all the ammonia to the liquid phase at room temperature and the ammonia release from the ash is temperature dependent, when the ash slurry reaches the stripper, which is at a higher temperature than the reactor, more ammonia could be released in the stripper from the ash. Therefore, the ammonia release rate measured by the ammonia analyzer after the stripper could be from two sources:

- 1) ammonia in the slurry released in the reactor at room

temperature and 2) ammonia released into the slurry in the stripper due to the increased temperature in the stripper. This distinction was not made in Yang and Keener's study.

Overall mass transfer coefficients for the stripper, in terms of the liquid and gas phase coefficients K_x and K_y , were found from their data to be functions of the solids concentration, the temperature, and the gas-to-liquid ratio. The temperature dependence of the coefficients was described by an activation energy. This activation energy was found to vary with solids concentration and gas-to-liquid ratios also.

Yang and Keener postulated that the rate controlling step to the ammonia regeneration from this FGD waste was the ammonia mass transfer from the liquid phase to the gas phase. While the liquid-gas mass transfer could be the rate controlling step in this system, it is not clear that other possible rate controlling mass transfer operations were investigated in their study. High solids (approx. 200g/L), high temperature (55°C or greater), and high gas-to-liquid ratio (1000 vol/vol or greater) were found to be the best operating conditions for maximum ammonia release rate for their continuous system. High solids, however, can cause severe plugging problems as were seen in the pilot study and much care must be used in this area when scaling up the test results. Also, high system temperature will increase regeneration system costs. As the boiling point is approached, high water content will be produced in the regeneration gases, and must be taken into account when recycling the exit gases to the spray dryer system.

A toxicity test (TCLP) was performed on the sludge after ammonia recovery. The metals that had caused concern prior to ammonia regeneration, i.e. arsenic, chromium, and selenium, were determined in the final ash sludge product. The analytical results indicated the metal contents were below the EPA regulatory limits, and the sludge waste would not be considered a characteristic waste. However, the liquid waste was not analyzed and a potential water contamination problem may be seen from the liquid waste if it is not recycled back into the ammonia regeneration system.

Overall, Yang and Keener proved that ammonia could be recovered from this waste FGD ash. However, determination of the rate controlling step involved in recovering the ammonia was not fully investigated. With these conclusions and questions in mind, a new system was designed for the laboratory study reported on here. A reactor/bubbler system was utilized that incorporated stripping and dissolution of the ammonia in one reactor. The new apparatus was used to determine reaction rate parameters as well as stripping rate parameters. Observation of the two mechanisms occurred both separately and together in order to examine the parameters controlling the NH_3 regeneration. The development of a preliminary ammonia regeneration design model was, then, devised for use in scale-up with the FGD process.

3. EXPERIMENTAL DESIGN AND RESULTS

A wet treatment process is of interest for the ammonia regeneration system because ammonium sulfites are highly soluble in water [30]. Air stripping of the aqueous ammonium solutions is desirable for the ammonia recovery system so that direct injection back into the FGD process can be utilized for recycle. This ammonia recycle scheme accomplishes two goals: (1) it improves FGD economics, and (2) it removes the ammonium products from the waste that cause concern over waste handling [28]. In the experimental reactor, the ammonium products are dissolved into an aqueous solution. Air sparging of the reactor aids in stripping the ammonia from the liquid. Various parameters affecting the dissolution/stripping processes in the reactor, such as temperature, pH, solids content of the solution, and gas-to-liquid ratios (gassing rate per unit liquid volume), can be investigated in this experimental setup. A theoretical regeneration model is developed from these experimental results. Important factors in the model include (1) the mass transfer of ammonia from the solid phase to liquid phase and then from the liquid to the gas phase, (2) the determination of the ammonia removal efficiency by the reactor, and (3) the operational time required to achieve this efficiency at different temperatures and air flow rates.

3.1. Process Description.

The regeneration of ammonia from the combined ammonia/calcium injection FGD waste was accomplished in the experimental reactor shown in Figure 4. Air enters the reactor from a small air pump. The Commander air pump has a 5 gal storage tank and was rated to produce 25 cfm @ 100 psi. A 0-100 psi rated pressure gauge measures the air pressure from the pump and a 20-140 scfh rated flow meter measures the gas flow into the reactor. The flow meter was calibrated by an American 3-liter wet test meter. This calibration data can be found in Appendix B. A regulator and water trap are also placed inline before the flow meter.

A reactor experiment begins by first placing the reactor, with air lines previously connected, into a temperature bath to help adjust the system to a constant temperature. The temperature bath is a PVC plastic tub with a mechanical mixer immersed in the water. The temperature is heated by an immersion heater. An Athena temperature controller with a thermocouple regulates the bath temperature. Air flow into the reactor then begins at the desired flow rate by adjusting the pressure on the regulator and the flow on the flow meter. Then, the operator pours 1000 ml of distilled water into the reactor and allows the water and reactor system to equilibrate to the desired temperature. For the high temperature experiments, an immersible heater is placed inside the reactor in the liquid solution to help maintain a constant specified temperature. This

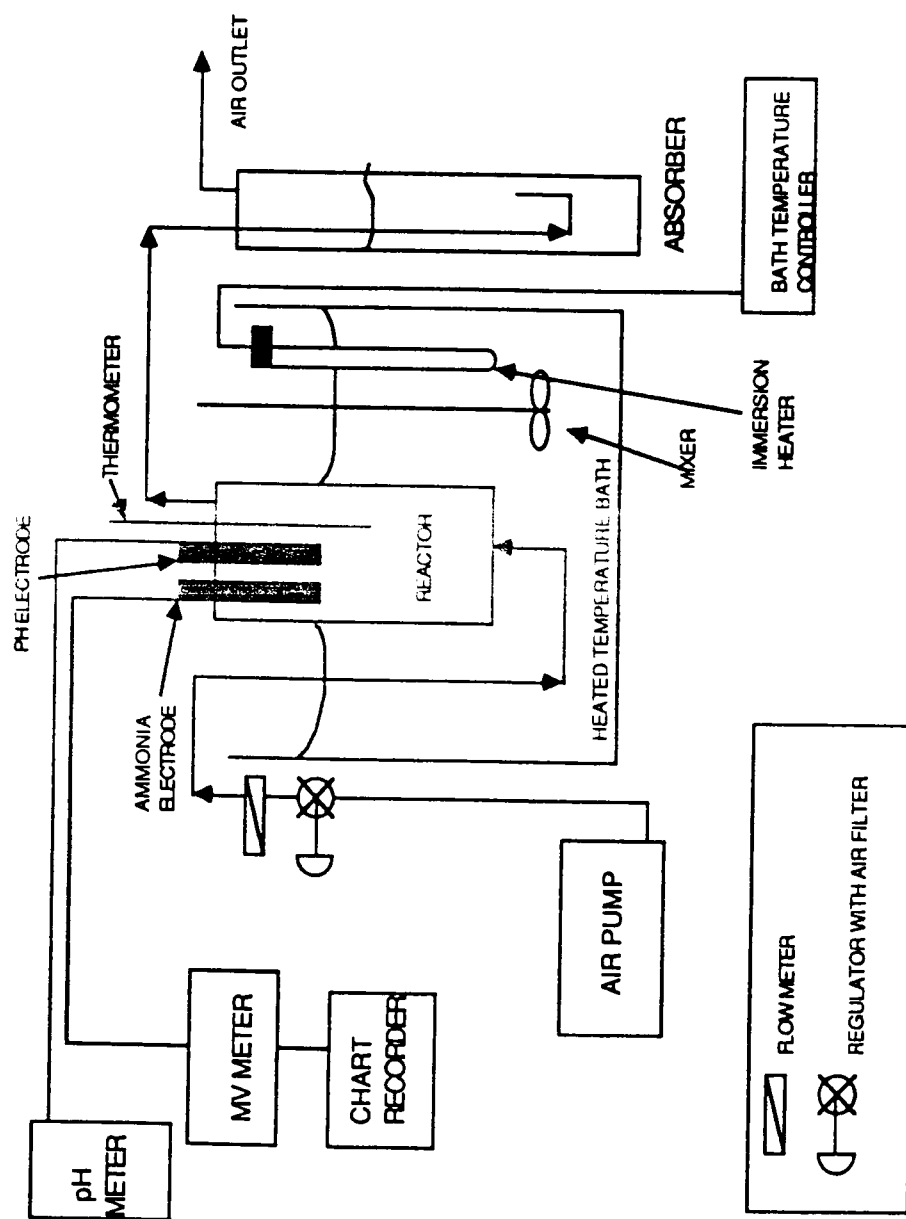


Figure 4. Ammonia Regeneration System Design

heater output is controlled by a rheostat. After a steady temperature is reached in the reactor as shown by the thermometer reading over time, the operator pours the ash into the top of the reactor. The amount of ash input corresponds to the desired solids loading for the test. As soon as the ash begins to fall into the reactor, the timer is started. The ammonia gas concentration in the liquid is measured in the reactor by an ammonia ion selective electrode. This electrode was an Orion Model 95-12. The electronic signal of the electrode was measured by a Beckman Model 3500 digital pH meter and then sent to a chart recorder. This electrode was calibrated daily by NH_4Cl standards. A sample calibration curve and data can be found in Appendix B. The NH_4Cl standards are in the range of 0.1 to 0.001 M solutions. The standard solutions placed in 100 ml beakers stay in a temperature bath until a steady experimental temperature is reached. The calibration curve is plotted on semi-log paper and a correlation gives the relationship between the ammonia concentration and millivolt readings. The calibration is also noted on the chart paper to obtain a relationship between the millivolt readings and the chart paper reading. A sample chart paper reading is given in Appendix B. During the test, the chart paper records the NH_3 electrode response continuously, while the operator records periodic readings of the millivolt values shown on the meter to double check the recorded chart paper value.

The temperature and pH are also monitored in the reactor. A mercury thermometer measures the temperature in Celcius. A

TRW Model No. 34100-787 pH probe measures the pH in the reactor. A Beckman Model 3400 pH meter receives the pH probe output. The pH probe is calibrated daily by use of standard pH solutions of 4, 7, and 10. During an experiment, addition of a 1 M $\text{Ca}(\text{OH})_2$ slurry in small amounts (approximately 1 ml) keeps the pH constant to the desired level within ± 0.2 pH values.

The gas leaving the reactor is bubbled into an absorption solution of boric acid through a sparger. This method of ammonia collection is similar to EPA Method 350.2 for standard water and wastewater solutions. A copy of this method is given in Appendix A. Boric acid reacts with ammonia by the equation



After the reaction, the acid solution is back-titrated with 0.02 N H_2SO_4 solution and a methyl red/methylene blue mixed indicator. This method determines the total amount of ammonia absorbed during the reaction. The sparger is a stainless steel tube which is U-shaped at the bottom. In the bottom of the U-shaped portion of the tube, small holes are drilled to allow air to escape. The sparger was placed in a tall 2000 ml Nalgene graduated cylinder. The level of acid in the graduated cylinder was varied from 800 - 1000 ml as needed to collect the ammonia in the gas. The top of the graduated cylinder is sealed with a cap held in place by O-ring seals. A stainless tube in the cap allows the air to escape to the atmosphere.

3.2. Details of the Stripping Reactor

Details of the stripping reactor design are shown in Figure 5. The cylindrical reactor has a length of 15 in., and an inside diameter of 5-7/8 in. Air flows into the reactor through a 1/4 in. I.D. air hose and tubing connector. The air is then expanded into a 2.5 in. cylindrical section of 5/8 in. height. Then the air flows through a 1.5 in. diameter sparger. The sparger was initially made of a coarse, porous glass, fritted disk. During the second half of experimentation, however, this fritted disk broke due to a pressure build-up in the reactor. The disk was replaced with a plastic one in which 94, 1/16 in. I.D. holes had been punched in a random order. A diagram showing this sparger is given as an inset on Figure 5. The reactor mixing did not seem affected by the change in sparger type.

In order to reduce the amount of dead space in the bottom of the reactor and to promote uniform mixing, a solid, cylindrical piece of PVC plastic, with an inverted cone section machined out of it, is placed in the bottom of the reactor. The height of the cone is 4.7 in., and the angle is approximately 20.4° extending downward from side of the reactor to the sparger. The reactor system is built out of plexiglass so that mixing in the reactor can be observed. The cone shaped section, however, is made of a non-transparent plastic, so that mixing could not be observed in the bottom 4.7 in. of the reactor. The ash particles are easily suspended in the reactor by the combination of air sparging and

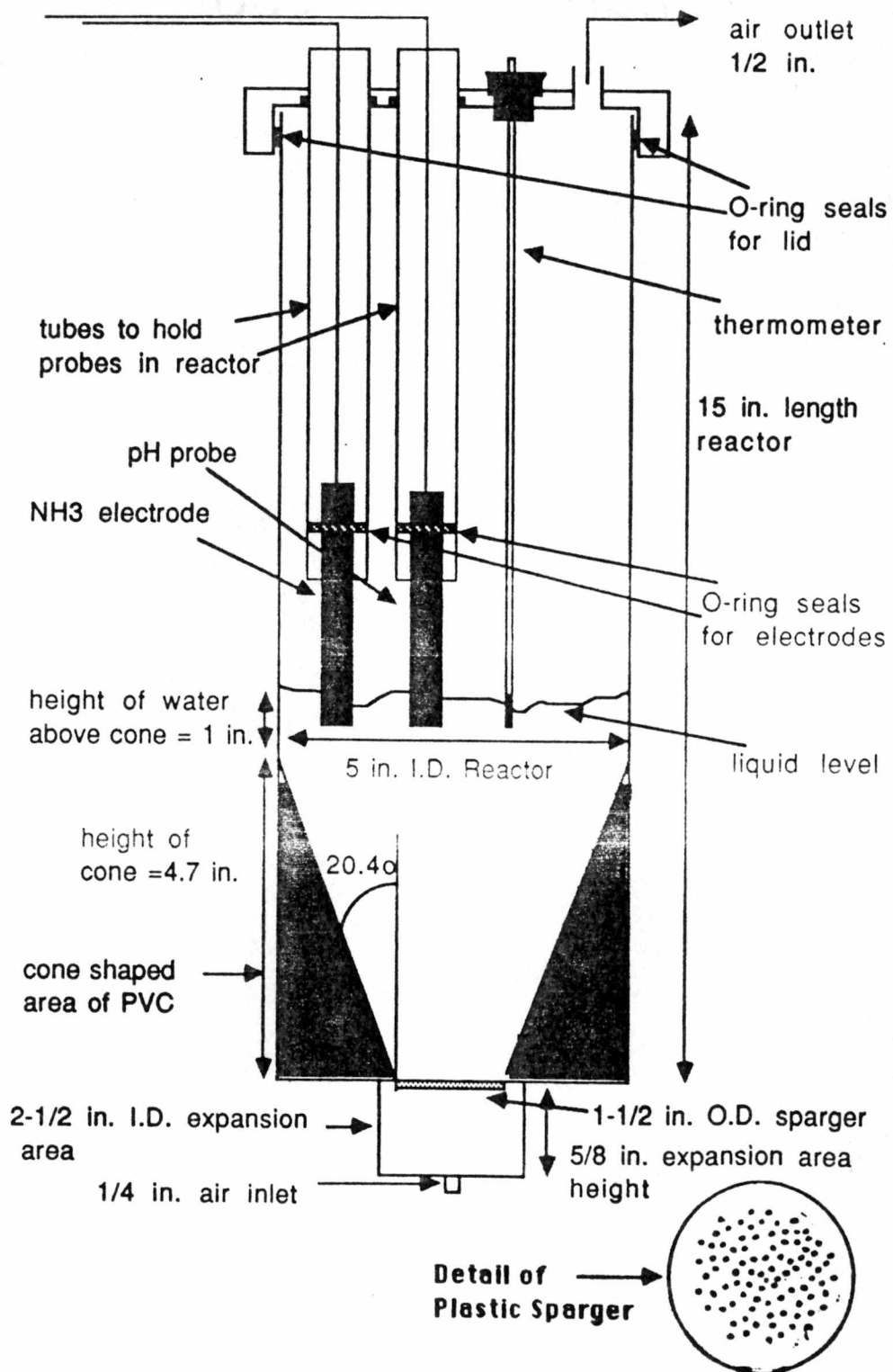


Figure 5. Schematic Drawing of the Ammonia Regeneration Reactor

reactor design because the ash particles are small (i.e. < 50 microns) [6].

The reactor top is made of PVC plastic and removable. O-ring seals, as well as a flange sealed with nuts and bolts, keep the top air tight. The ammonia and pH electrodes are placed in the reactor through holes in the PVC top. Transparent plastic tubes hold the electrodes in the top of the reactor and extend into the solution. O-ring seals hold the tubes securely in place while retaining an air tight seal. The electrodes are held in place in the tubes by O-rings also. The tubes are long so the height of the electrodes in the reactor could be adjusted as needed. A thermometer, sealed in a stopper and inserted through another hole in the top, extends into the liquid and measures the internal reactor temperature. The gas outlet at the top of the reactor is a 3/4 in. tube connection. A 1 in. O.D. plastic tube connects the gas outlet on the reactor and to the sparger inlet.

When 1000 ml of distilled water is placed in the reactor, the water level extends approximately 1 in. above the solid plastic cone in the bottom of the reactor at low air flow. Very good mixing is observed in the reactor when the air flow is 40 scfh or higher. A lower air flow could have been used with successful mixing but the flow meter was not very accurate below this level.

3.3. Experimental Design

The experiments were designed to determine the possible rate controlling mechanisms of the ammonia regeneration system.

Three major mechanisms are believed to be involved in this ammonia regeneration process:

- (1) dissolution of the solid ammonium sulfite contained in the fly ash,
 - (2) mass transfer of the ammonia from the solid-to-liquid phase
- and, (3) the mass transfer of the ammonia from the liquid-to-gas phase.

In this simplest model design, the mass transfer operations are believed to follow the 2-film theory in which an equilibrium is reached at the phase interface [31]. Therefore, a 2-phase equilibrium relationship may be needed to determine the mass transfer rate between the solid-liquid phases as well as for the liquid-gas phases. A third equilibrium which may have impact on this system is the reaction between the ammonium ion and non-ionized ammonia in the liquid phase. This equilibrium is expected to be such that reaction {1} is far to the right (highly in favor of dissolved gaseous ammonia) in the pH and temperature ranges of this investigation, according to the data provided by Figure 1. This assumption will be verified by the experimental results.

Two types of experiments were conducted. One experimental set tried to define the solid-liquid equilibrium relationship. The second set of experiments investigated the operation and performance of the reactor system with the ammoniated ash. For the mass transfer rate between the solid and liquid phases, no previous work has been performed with the

exception of Keener and Yang. Therefore, their work can be used as a guide for estimating the experimental boundaries. The solid-liquid equilibrium is believed to be dependent on the temperature, solids concentration, and pH of the solution formed by mixing the solids in water. Therefore, the experiments will examine these parameter effects. The second mass transfer operation is ammonia transfer from the liquid to the gas phase. This transfer rate is found by recording the ammonia concentration in the liquid phase over time. The ammonia liquid-gas equilibrium relationship has been thoroughly reported on in the literature [32-35]. These data are necessary for estimating the driving force for the liquid-to-gas mass transfer rate. The reactor experiments are conducted at specified values of temperature, solids concentration, pH, and gas flow rate in the reactor. Yang's results were used as a guide in determining the ranges of each parameter for the tests performed. His tests involved changes in temperature from 25 to 65°C, a solids content of 25 to 198 g/L, a stripper gas-to-liquid ratio of 100 to 1000, and a pH of 13 or greater [14]. During the current study, the parameters of pH, temperature, solids content, and gas flow rate were varied over the ranges given in Table 1. The data generated from these experiments served as a basis for the formulation of an ammonia regeneration model.

When comparing the experimental ranges of Yang's study and the current study, some differences can be seen which need explanation. In Yang's experiments, the pH of his system was only

Table 1. Experimental Parameter Ranges

Type of Experiment	pH	Temperature, °C	Solids Content, g/liter	Nominal Gas Flow Rate, scfh L/L-min	
Solid-Liquid Equilibrium	9-11	26-46	20-100		
Ammonia Regeneration	10-11	30-45	50-100	40-80	19-38

measured and not controlled [14]. When the ash Yang used was placed in water, the pH was always 13 or greater [14]. Therefore, according to Figure 1 and the equilibrium of equation {1}, for Yang's experiments all the ammonia was initially in the non-ionized form (NH_3) because of this high pH, and therefore the pH was not controlled in his system. For the tests performed in this study, however, the ash pH was only 8.5-9 when placed in water. This lower pH is thought to be due to free ammonia loss from the ash prior to its use in this study. In order to assure the ammonia was predominantly in the non-ionized form for the experiments, the pH had to be adjusted to 10 or higher.

The system temperature range used was lower for this study than for the Yang study. For the current study, the maximum system temperature was 45°C because of the manufacturer's recommendations on the use of the ammonia electrode. The ammonia electrode manual by Orion states that the electrode should not be used in systems over 50°C [36]. A

copy of this manual can be found in Appendix A. Therefore, the reaction temperature was kept at 45°C or less in order to keep from damaging the ammonia electrode.

3.3.1 Solid-Liquid Equilibrium Experiments.

The first set of experiments examined the solid-liquid equilibrium system. The transfer of ammonia from the solid to the liquid phase involved the dissolution of the ammonium sulfites and free ammonia from the ash into water. The components in the ash, other than the ammonium compounds, were considered as inerts. These components include the fly ash, CaSO_4 , and CaSO_3 solids. Most of these components are insoluble, and therefore will have little impact on the ammonium sulfite dissolution. Experiments to determine the solid-liquid equilibrium curve involved tracking the ammonia concentration of the liquid in an aqueous ash solution over time. This solution is placed in a tightly closed container (See Figure 6). To avoid ammonia loss to the gas phase, the air space above the liquid was minimized. The flask was placed in a temperature bath to assure constant temperature.

A solid-liquid equilibrium experiment is begun by placing one liter of distilled water in a 1000 ml Erlenmeyer flask. The water is allowed to come to temperature equilibrium with the bath temperature. The liquid in the flask was constantly stirred by a magnetic stirrer. The ash is then added to the flask. The pH of the solution is measured by a pH probe. If the pH is not at the desired level, a solution of 1M Ca(OH)_2 is added in small

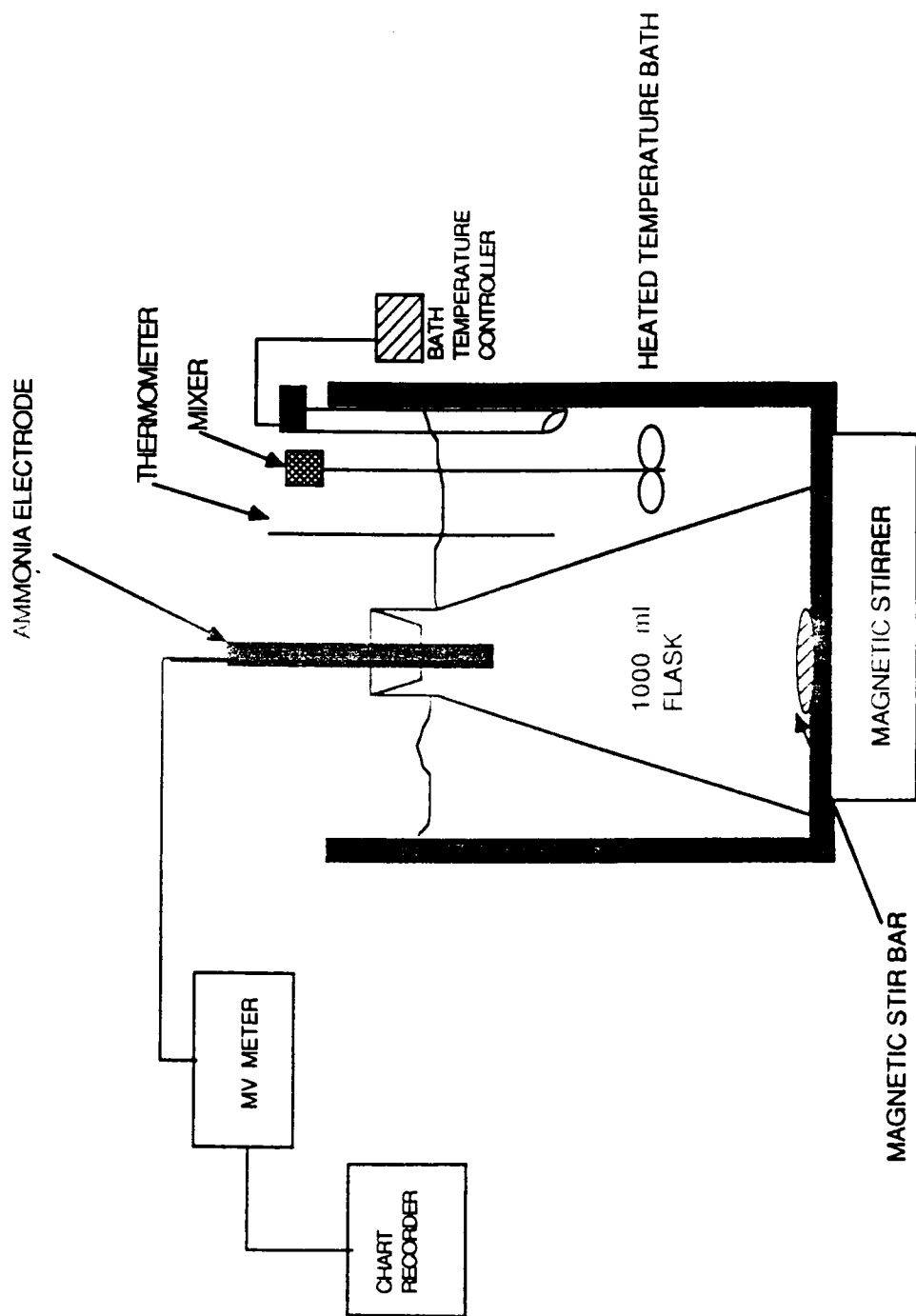


Figure 6. Solid-Liquid Equilibrium Experimental System

increments until the desired pH is reached. A stopper containing the ammonia electrode is then placed in the flask. Then the ammonia electrode is placed in the solution and the millivolt reading is recorded through a pH meter to a chart recorder. The ammonia electrode monitored the release of ammonia from the solids into the liquid over time. After a constant reading is shown on the electrode meter (indicating equilibrium), an aliquot of the solution is removed and quickly filtered. This aliquot is analyzed for ammonia concentration by EPA Method 350.2 using a distillation and titration procedure used for wastewater analysis [37]. This method measures the amount of non-ionized ammonia, NH_3 , found in the solution removed from the flask at equilibrium. The EPA method is also used to analyze for the concentration of ammonia initially in the solid. Ten grams of the ash are slurried in 500 ml of distilled water. This solution is used as the wastewater sample for the EPA method analysis. The ammonia concentration from this slurry analysis is converted to the initial concentration of ammonia in the solid on an ammonia-free basis, i.e. C_{Aso} . The material balance on the ammonia then becomes

$$\begin{array}{lcl} \text{Equilibrium mass of} & = & \text{Initial mass of} - \text{Equilibrium mass} \\ \text{ammonia in the} & & \text{ammonia in solids} & \text{of ammonia} \\ \text{solids} & & & \text{in the liquid} \end{array}$$

Mathematically, this equation is

$$C_{\text{A(eq)s}} * W_s = C_{\text{Aso}} * W_s - C_{\text{A(eq)L}} * V_L \quad \{3\}$$

and calculates the equilibrium solid ammonia concentration.

These equilibrium experiments involved varying the temperature,

solids concentration, and pH over the ranges in Table 1. Examples of these data are plotted and provided in Appendix B.

3.3.2. Reactor Experiments.

After the solid-liquid equilibrium experiments were completed the reactor experiments were performed. These experiments used the reactor previously described (See Figure 5) and were conducted over the temperature, solids concentration, pH, and air flow ranges given in Table 1. The results of these experiments are discussed in Section 3.4.

3.3.3. Other Experiments.

In examining the mass transfer operations of the ammonia regeneration system, it was anticipated that a few other experiments needed to be performed so that the parameters of the mass transfer equation could be well defined. These experiments involved measuring the volume increase in the reactor due to ash addition, and estimating the volume of gas in the reactor. An experiment was also done to estimate the overall mass transfer resistance in the gas phase, i.e. the K_La value. These experiments and calculations are explained below.

3.3.3.1. Solid Volume in the Reactor. The experiment to determine the volume increase due to ash addition was performed using a graduated cylinder. A volume of 500 ml of distilled water was placed in a 1000 ml cylinder. Then, 50 grams of dry ash were added to the cylinder. The mixture was stirred slightly to insure proper wetting of all the particles. The volume increase due to the ash addition was recorded as 30 ml.

3.3.3.2. **Estimation of the Gas Hold Up Volume.** For this experiment, the reactor was set-up as described in Section 3.2. for an ammonia regeneration study. The reactor was held at room temperature of 20°C. A volume of 1000 ml of distilled water was placed in the reactor. Then 100 grams of ash was added. The air flow in the system was then cut back so that the minimum flow needed to suspend the liquid in the reactor was seen. The level of the liquid in the reactor was marked. Then, the air flow was increased to the levels used in the experiments, i.e. 40 scfh and 80 scfh. At each air flow level, the average height of the liquid in the reactor was marked. The measured difference between the two marks for each air flow was recorded. This height difference was 0.5 inches for the 40 scfh air flow and 1 inch for the 80 scfh air flow. The gas volume in the reactor was then calculated from these values for each flow rate by multiplying by the cross-sectional area of the reactor. This gas volume must be corrected for the temperature differential between this room temperature experiment and the actual temperature of the reactor experiment. The gas volume measurement test was also repeated for the reactor without ash addition. The height difference for this test was 0.4 inches for 40 scfh and 0.7 inches for 80 scfh, which indicates that the presence of the ash affects the gas hold-up.

3.3.3.3. **Estimation of $K_L a$ for Liquid-to-Gas Mass Transfer.** These experiments are designed to determine the resistance to ammonia degassing in the reactor system. The

reactor was set-up as in Section 3.2 for an ammoniated ash experiment. The ash used, however, was deammoniated before the experiment and ammonium chloride was used as the ammonia source. Four tests were performed in this experiment set, one at each air flow level of 40 and 80 scfh. Then, for each air flow, two experiments were done at the temperatures of 30 and 45°C. The pH of the reactor system was kept at 11 ± 0.2 . The reactor system with 950 ml of distilled water was allowed to come to a steady state temperature. The remaining 50 ml of liquid needed was added later as a concentrated (0.4 M) NH_4Cl solution to make the initial ammonia concentration of the solution at 0.02 M. This concentration is the level typically found when 100 grams of ash is used in the reactor. The ash was dried at 103°C overnight before the first test. Then, 100 g of the ash was added to the 950 ml of distilled water. It was thought that the heating process would deammoniate the ash, but when the ash was placed in the reactor, a nearly 0.01 M ammonia concentration was registered by the ammonia electrode in the reactor solution. Therefore the ash had to be deammoniated by stripping in the reactor. When a constant ammonia reading was registered by the chart recorder, the NH_4Cl solution was added through a tube held under the reactor liquid level. The ammonia concentration in the liquid in the reactor was tracked by the chart recorder. For the second test, the ash was allowed to dry overnight in a 145°C oven. This heating, however, still did not deammoniate the ash. Since the ammonia stripping of the ash was very time consuming, the

third and fourth tests used the ash from the second test after all the ammonia stripping was achieved and a stable reading was shown on the chart recorder. The ammonia loss from the reactor (moles/liter) was graphed versus reactor time (min). The graphs of these four experiments are given in Figure 7. From this figure, a break in the data is seen after the first 10 minutes of the reaction. This break can be explained by imperfect mixing of the liquid phase in the reactor after the NH_4Cl solution is added. The ammonia electrode reads the initial concentration of the ammonia in solution as that of the concentrated 0.04 M NH_4Cl initially added to the water before the dilution of mixing takes place. These data indicate a lack of perfect mixing in the liquid solution, at least initially.

The K_La values were calculated using a computer program similar to the mass transfer model developed in Section 4. This model used the experimental gas hold up values to estimate the K_La from only the liquid and gas mole balances. A copy of this program is found in Appendix C. In this program, the gas hold up is also considered as an unknown. The program converges on the optimal values for the H_g and K_La using the experimental H_g values as starting points for the convergence. The values output from the program are summarized in Table 2.

As can be seen from this table, the gas hold up for the experimental and model predicted values were similar for the low temperature systems. However, for the high temperature system, there is quite a bit of difference between the two H_g values,

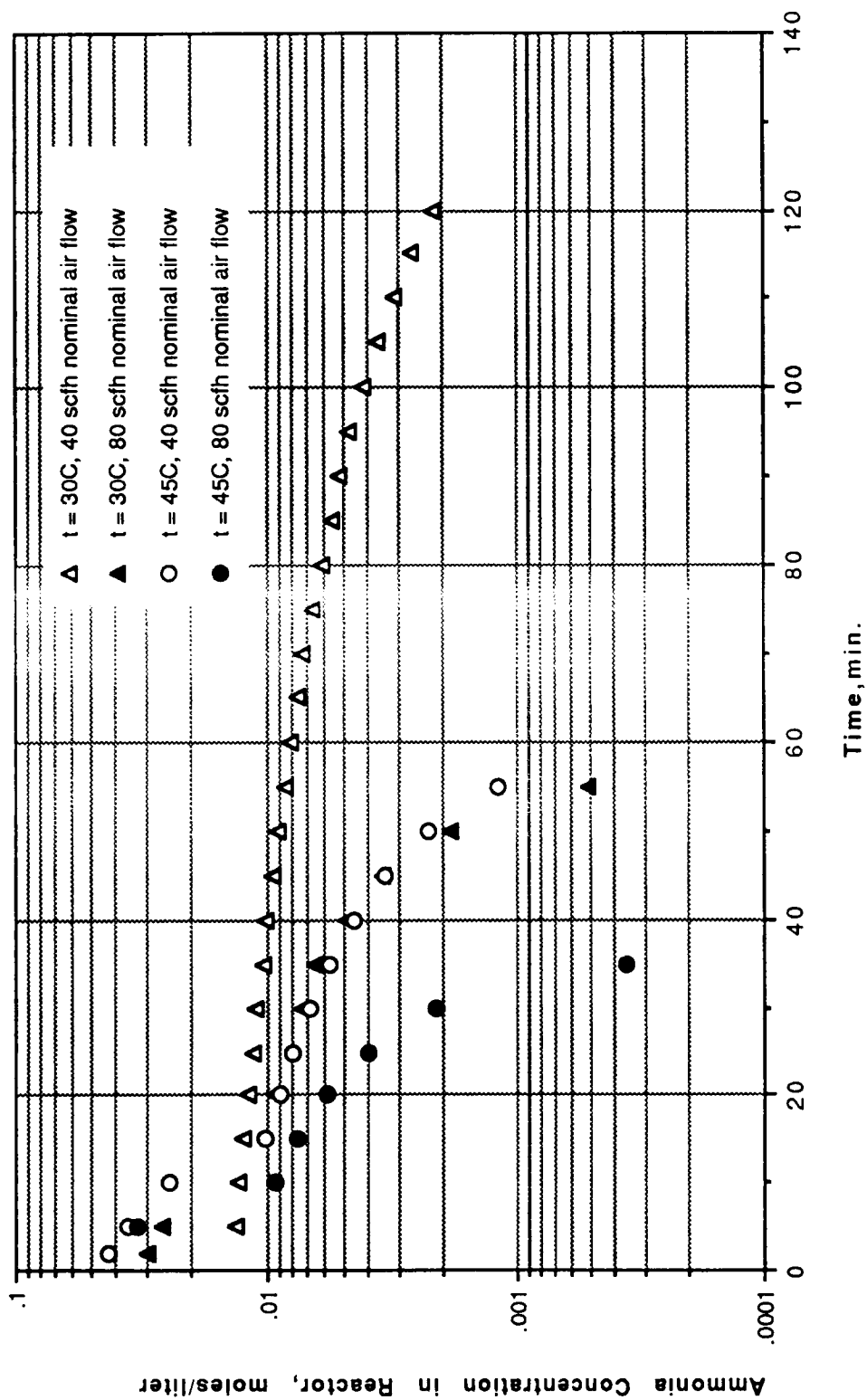


Figure 7. Experimental Results for the Determination of the K_{La} Values for the Reactor System

approximately 100%. This difference can be explained by the difficulty in measuring the Hg experimentally, since an average height of the liquid level is gotten while the reactor system is bubbling vigorously.

Table 2. Estimated $K_L a$ Values for the Reactor System, With Ammonia Provided in the Form of NH_4Cl

Experiment Date	No.	Temp. °C	Nominal Air Flow Rate, scfh	Gas Hold Up		$K_L a$ cm/min
				Exper.	Model	
2/27/92	1	30	40	0.1596	0.1593	0.01559
2/28/92	1	30	80	0.2753	0.2203	1.939
2/28/92	2	45	40	0.1662	0.3508	0.5449
2/28/92	3	45	80	0.2850	0.5855	20.49

3.4. Results

3.4.1 Solid-Liquid Equilibrium Experiments.

The results of the solid-liquid equilibrium experiments are given in Table 3. These experiments were plotted on an x-y scale with the concentration of ammonia in the liquid (moles/liter solution) versus the concentration of ammonia in solid (moles ammonia/gram of ammonia-free ash). An example plot is shown in Figure 8. This plot gives all the data for the experiments with pH = 11, and the temperature = 30°C at different solids concentrations. This graph shows the measurement data from

Table 3. Solid-Liquid Equilibrium Data

<u>Experiment</u>		<u>Temp,</u>		<u>Solids</u> <u>added,</u>	<u>Method</u>	<u>Equilibrium Values</u>	
<u>Date</u>	<u>No.</u>	<u>°C</u>	<u>pH</u>			<u>in liquid,</u> <u>moles/</u> <u>liter</u> <u>solution</u>	<u>in solid,</u> <u>moles NH3/</u> <u>g NH3-</u> <u>free ash</u>
6/12/91	1	26	10	40	electrode	0.016	-0.000113
10/14/91	1	29	10.1	50	titration	0.0093	0.000037
		29	10.1	50	electrode	0.0191	-0.000160
11/8/91	1	29	10	50	titration	0.0101	0.000016
		29	10	50	electrode	0.014	-0.000064
4/24/91	2	26	10	80	electrode	0.0245	-0.000097
10/4/91	1	29	10	80	titration	0.0121	0.000077
		29	10	80	electrode	0.029	-0.000134
10/10/91	1	29.5	10.1	100	titration	0.0198	0.000028
		29.5	10.1	100	electrode	0.0233	-0.000008
11/7/91	2	29	10	100	titration	0.022	0.000015
		29	10	100	electrode	0.026	-0.000025
5/16/91	1	27	11	40	electrode	0.024	-0.000133
10/15/91	1	29	11	50	titration	0.0079	0.000065
10/16/91	1	30	11	50	titration	0.0098	0.000028
		30	11	50	electrode	0.0186	-0.000151
11/5/91	2	30	11	50	titration	0.0089	0.000041
		30	11	50	electrode	0.0172	-0.000127
11/6/91	2	30	11	50	titration	0.0089	0.000042
		30	11	50	electrode	0.0129	-0.000037
10/29/91	2	30	11	100	titration	0.0159	0.000066
10/30/91	1	30	11	100	titration	0.023	-0.000005
		30	11	100	electrode	0.0171	0.000054
11/5/91	1	30	11	100	titration	0.0219	-0.000001
		30	11	100	electrode	0.0232	-0.000014
4/23/91	2	25	11.5	40	electrode	0.0156	-0.000182
5/18/91	1	36	10.1	40	electrode	0.0143	0.000182
5/20/91	1	37	10	80	electrode	0.0215	0.000187
10/22/91	1	39	10.5	75	titration	0.0155	0.000015
		39	10.5	75	electrode	0.0172	-0.000009

Table 3. (Continued)

<u>Experiment</u>		<u>Temp,</u>		<u>Solids</u> <u>added,</u>	<u>Method</u>	<u>Equilibrium Values</u>	
<u>Date</u>	<u>No.</u>	<u>°C</u>	<u>pH</u>			<u>in liquid,</u> <u>moles/</u> <u>liter</u> <u>solution</u>	<u>in solid,</u> <u>moles NH3/</u> <u>g NH3-</u> <u>free ash</u>
10/28/91	2	37	10.5	75	titration	0.0166	0.000004
		37	10.5	75	electrode	0.0241	-0.000097
11/4/91	2	39	10.6	75	titration	0.0163	0.000005
		39	10.6	75	electrode	0.0181	-0.000019
6/20/91	1	45	10.05	20	electrode	0.003	0.000099
6/20/91	2	45	10.2	20	electrode	0.0073	-0.000117
6/21/91	1	45	10.25	20	electrode	0.0022	0.000170
6/19/91	2	46	10.05	40	electrode	0.0075	0.000108
6/21/91	2	45	10	40	electrode	0.0086	0.000065
6/22/91	1	45	10	40	electrode	0.0095	0.000044
10/28/91	1	46	10	50	titration	0.009	0.000045
		46	10	50	electrode	0.0111	0.000004
11/7/91	1	46	10	50	titration	0.0114	0.000007
		46	10	50	electrode	0.0009	0.000218
6/23/91	1	45	9.95	80	electrode	0.0166	0.000073
6/23/91	2	45	10	80	electrode	0.0215	0.000011
10/7/91	1	46	10.4	80	titration	0.0165	0.000024
		46	10.4	80	electrode	0.0156	0.000035
10/9/91	1	45	9.95	100	titration	0.0179	0.000046
		45	9.95	100	electrode	0.0179	0.000046
10/21/91	1	45	10	100	titration	0.0218	0.000003
		45	10	100	electrode	0.0222	0.000000
10/29/91	1	46	11	50	titration	0.0094	0.000037
		46	11	50	electrode	0.0151	-0.000077
11/6/91	1	45	11	50	titration	0.0104	0.000013
		46	11	50	electrode	0.0093	0.000035
10/8/91	1	44.5	11	100	titration	0.0142	0.000079
		44.5	11	100	electrode	0.0235	-0.000014
11/4/91	1	45	11	100	titration	0.0206	0.000016
		45	11	100	electrode	0.0154	0.000068

experiments by two methods: 1) when a 25 ml aliquot was removed from the mixing flask at the time of equilibrium, filtered, and analyzed with the EPA distillation/titration method and 2) the ammonia electrode measured liquid concentration at the time of equilibrium. The difference between these two types of measurements can clearly be seen on the graph. Both values were calculated from the mass balance in which the initial concentration of ammonia in the ash is measured by the EPA titration method. The solid equilibrium titration values were typically positive and the solid equilibrium electrode values were typically negative. From examination of this data, it can be suggested that the titration experiments typically show an ammonia loss due to the distillation and sampling procedure.

In order to determine the accuracy of these methods, the EPA titration test and the NH_3 electrode were used to find the ammonia concentration in NH_4Cl solutions of known concentration. In these tests, NH_4Cl standards were distilled as in the EPA method into boric acid. The boric acid solution was then titrated with 0.02 M H_2SO_4 to find the ammonia concentration. Then, more NH_4Cl standards were distilled and the resulting solution of boric acid/ NH_3 was pH adjusted to $\text{pH} > 11$ and then measured by the NH_3 electrode. These accuracy test results are shown in Figure 9. This graph shows that both methods predict the ammonia concentration of the NH_4Cl standards correctly. Therefore, the problems with the data from the solid-liquid equilibrium test seem to occur from the sampling and

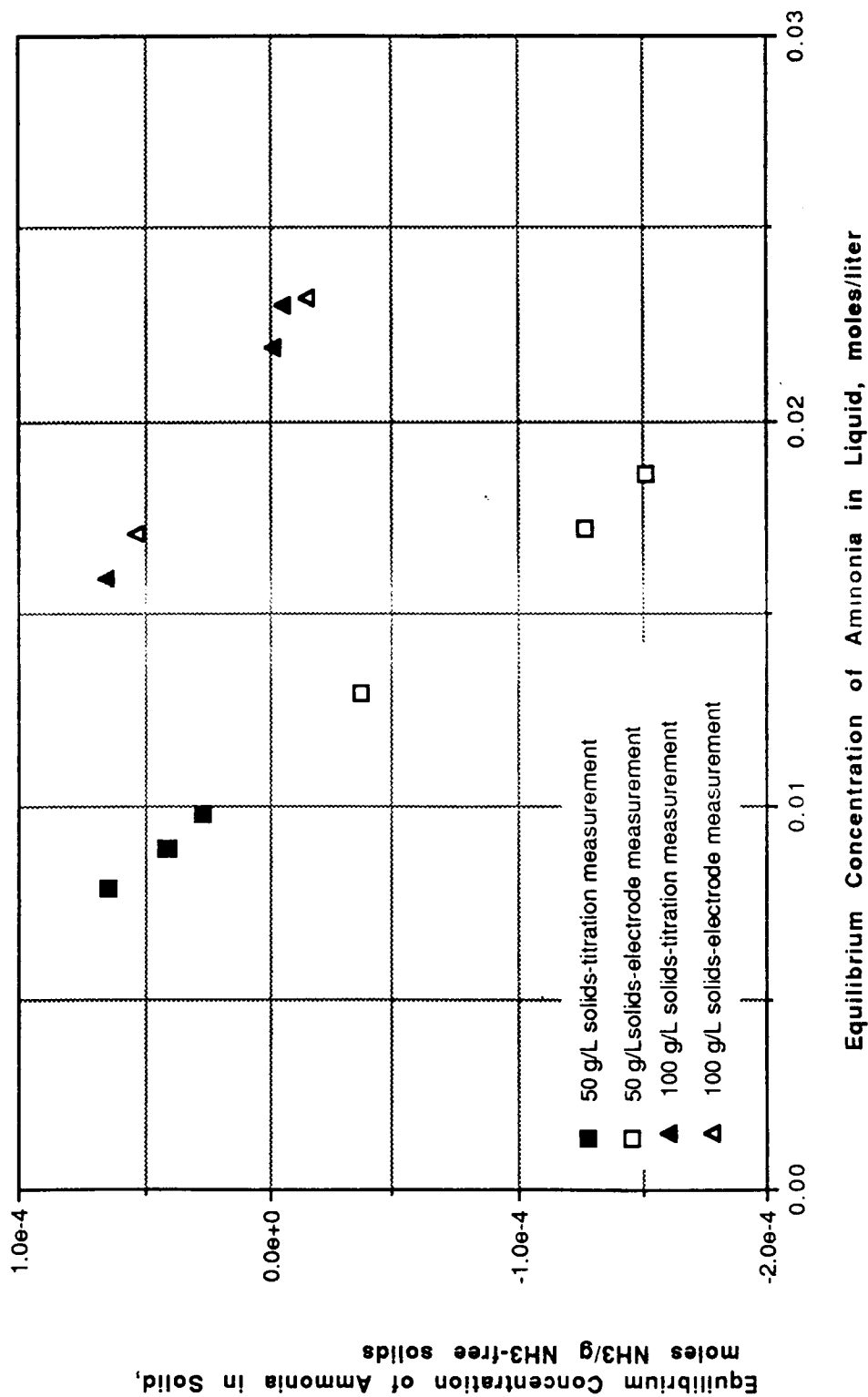


Figure 8. Solid/Liquid Equilibrium Data for Temperature = 30°C with pH = 11, (both electrode and titration measurements)

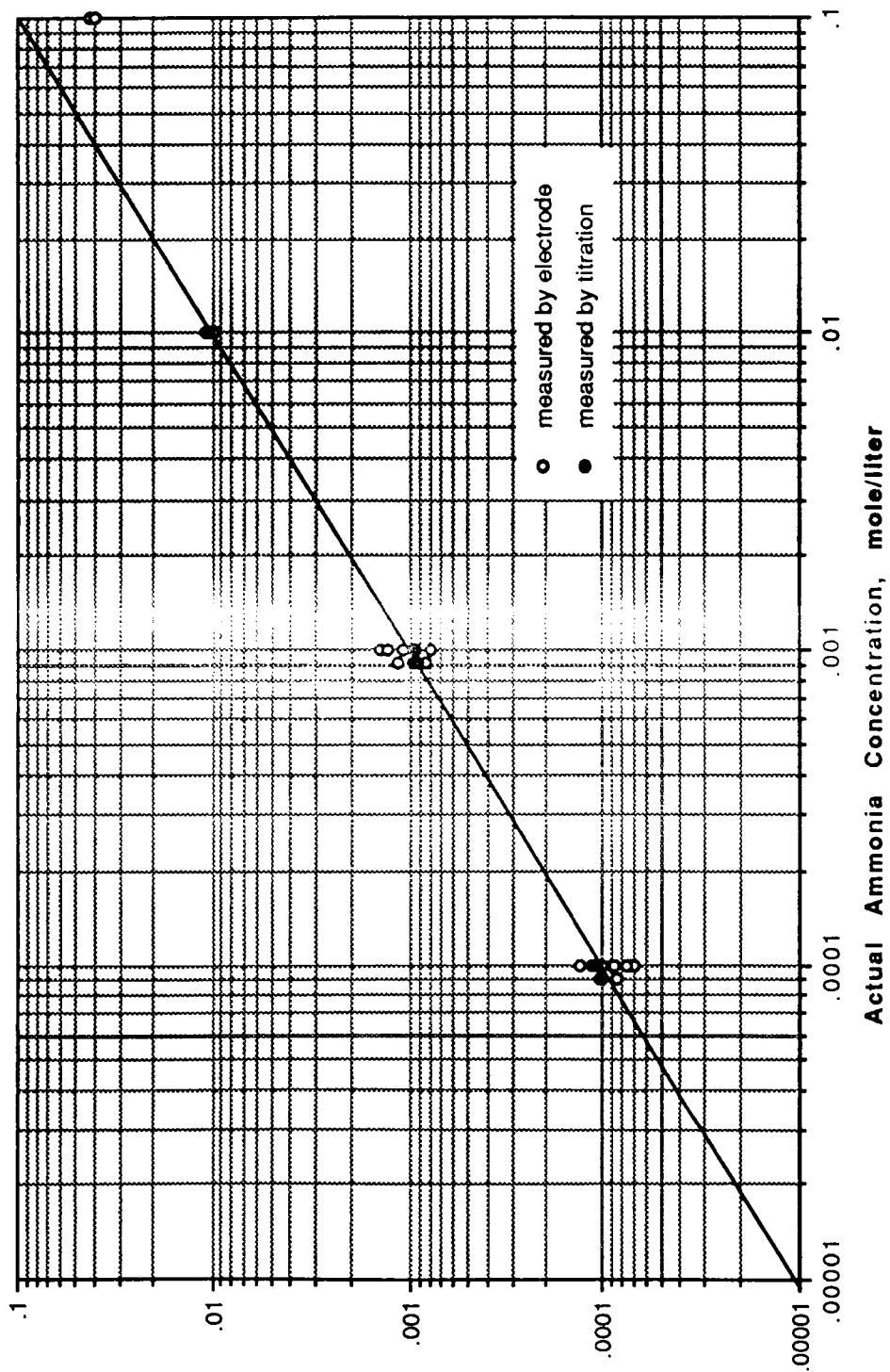


Figure 9. Comparison of Ammonia Concentration of NH_4Cl Standards Determined by Titration and by the NH_3 Electrode

filtering technique used prior to analysis of the final solid equilibrium value by the titration method. Also, the titration method used to find the initial concentration of ammonia in the solid is subject to minor ammonia losses. This ammonia loss is due to the ammonia degassing occurring from the ash constantly. This degassing is detected as an ammonia odor from the ash. With this initial solid ammonia concentration slightly less than the actual ammonia in the solid, the ammonia electrode values for the solid equilibrium, tend to be slightly negative. Therefore, these values cannot be used to predict an accurate model of the solid-liquid equilibrium system for the mass transfer rate model.

The data in Figure 8 show a high degree of scattering which points to low repeatability of these data. Therefore, none of these data lend themselves to use in predicting a simple solid-liquid equilibrium model. However, by looking at these solid-liquid equilibrium data some trends as to the effects of pH and temperature changes on the solid-liquid ammonia transfer can be seen.

Figure 10 gives data for solid-liquid experiments where the temperature was held constant at 30°C. The graph shows data for two pH levels (10 and 11) and two solids concentrations of 50 and 100 g/L. An average 38% less ammonia is found in the liquid at equilibrium for the low solids loading when the pH is increased. However, for the high solids loading, as the pH is increased, an average 45% more ammonia is found in the liquid at equilibrium. This higher ammonia concentration in the liquid at the higher pH

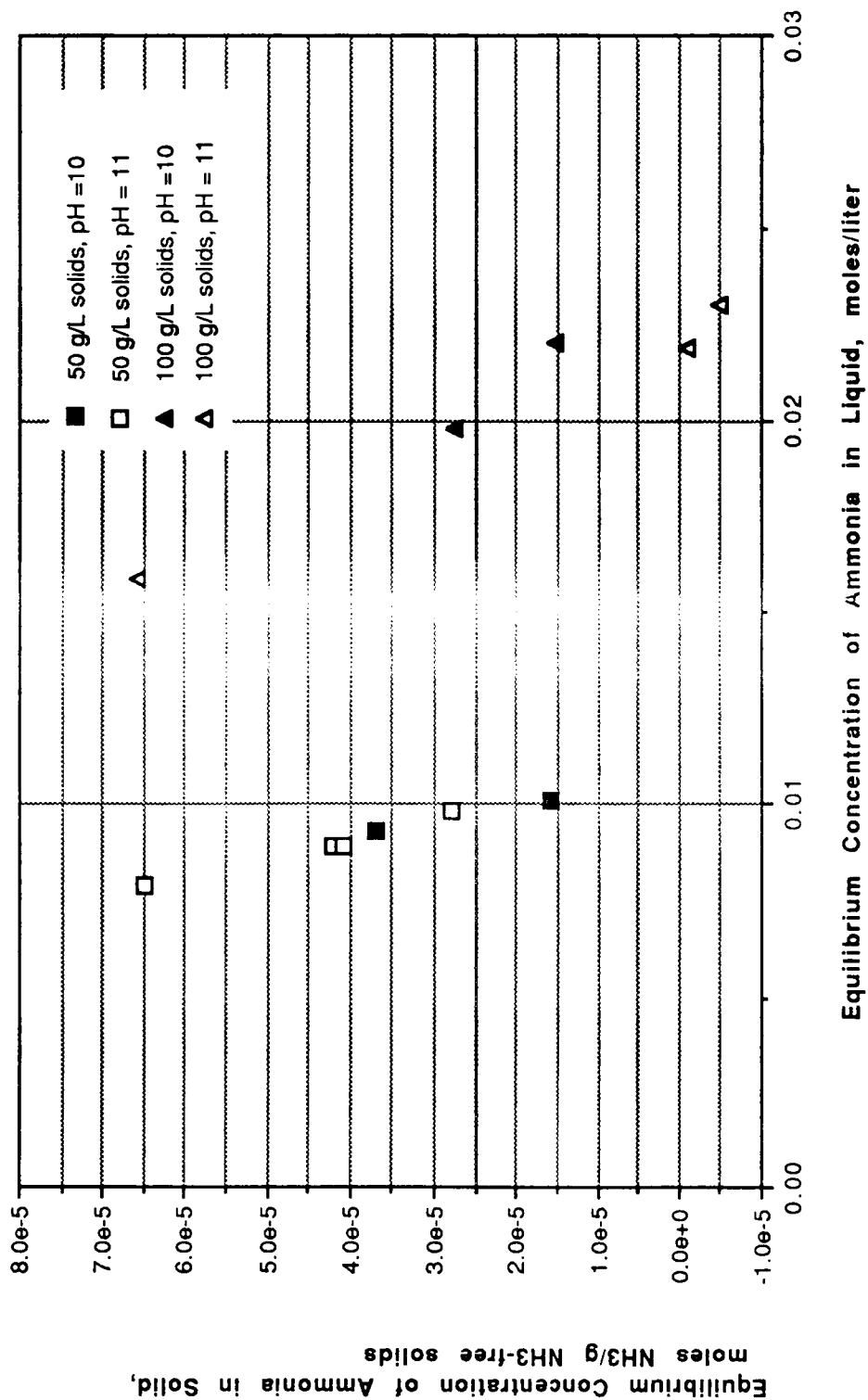


Figure 10. Solid/Liquid Equilibrium Data for Temperature = 30°C with pH = 10 & 11, (all data taken from titration measurements)

level and higher solids loading could be the result of the equilibrium shift shown in Figure 1. At a pH of 10 and 30°C, Figure 1 predicts the ammonia in solution to be approximately 85% in the NH_3 form while at pH of 11, there is approximately 97% ammonia in the NH_3 form. Since the ammonia electrode can only measure the non-ionized ammonia (NH_3) in solution, the concentration of ammonia measured by the electrode would be expected to be higher for a pH of 11 than for pH of 10. Therefore, what appears to be a shift of ammonia from the solid to liquid at equilibrium could actually be a shift of ammonia from NH_4^+ to NH_3 in solution. Since it cannot be known which shift is taking place, a pH of 11 or greater is recommended to promote the ammonia in solution to be in the NH_3 form. Since the non-ionized form is also the ammonia form which is transferred to the gas phase during stripping, the higher pH should promote better stripping of the liquid solution.

Figure 11 shows solid-liquid equilibrium experiments where the temperature was increased from 30°C to 45°C for both solids loadings and a pH of 11. With this temperature increase, an average 43% more ammonia is found in the liquid at equilibrium for the low solids loading and average 20% more in the liquid for the high solids loading. This trend indicates that a relatively high temperature will promote ammonia loss from the solid into the liquid at both solids loadings.

Therefore, overall, at the higher solids loading, a high pH and relatively high temperature would facilitate the dissolution

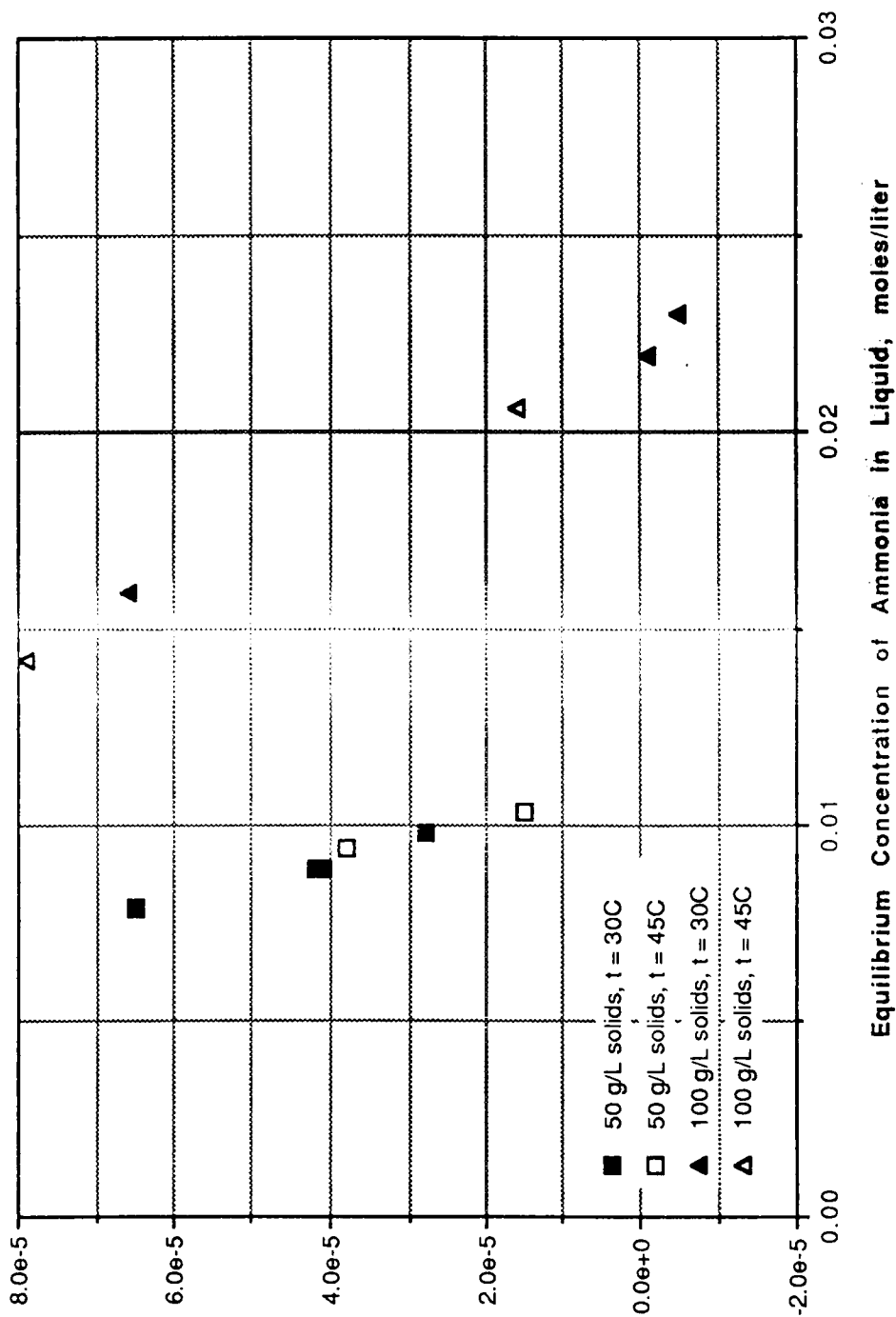


Figure 11. Solid/Liquid Equilibrium Data for Temperature = 45 & 30°C and pH = 11 (titration measurements only)

of ammonia from the solid into the liquid and thereby increase the tendency for a more efficient stripper. These results, however, are based on average values for the solid-liquid systems which contain a high percentage of data scatter, i.e. up to 65% scatter for some tests performed under the same conditions. Therefore, these trends are only estimates of what might be predicted by the solid-liquid system.

3.4.2 Reactor Experiments.

The experimental reactor tests were characterized by tracking the ammonia gain and loss from the liquid solution to the gas phase as measured by the ammonia electrode. Table 4 gives the parameters of each of the experiments and the initial concentration of ammonia found in the ash prior to each experiment by the EPA titration method. Figure 12 shows typical ammonia concentration versus time plots, for two solids loadings in the reactor, with a temperature of 30°C, pH of 11, and nominal air flow rate of 80 scfh. The initial concentration of ammonia in the ash ($C_{A_{SO}}$) was typically 0.0002 moles NH_3 /gram NH_3 -free solid as measured by the EPA distillation-titration method. In an ideal system, all of the ammonia in the solid would immediately be transferred to the liquid when the ash was placed in the water. Then the ideal initial concentration of ammonia in the liquid can be calculated as 0.02 moles/L for a 100 g/L solids loading and as 0.01 moles/L for a 50 g/L solids loading. As can be seen in the graph, this ideal initial liquid concentration was not reached, presumably because of the time required for transfer of ammonia

Table 4. Experimental Reactor Data and Initial Concentrations of Ammonia in the Ash

Experiment Date	Exp. No.	Temp C	Average pH	Nominal			Solids Loading, g/liter	Corrected Air Flow		Initial [NH3] in ash, moles NH3/g NH3 free ash	Est. Time for Removal to 0.001 mole/L, minutes (a)
				air scfh	flow, scfh	flow, scfh		L/L-min	gmol/min		
12/2/91	(b,c)	2	30	10	40	50	39.58	18.85	0.77	0.0002067	176
12/18/91		2	30	10	40	100	39.58	18.85	0.77	0.0002103	202
12/19/91		1	30	10	80	50	70.92	33.77	1.38	0.0002097	107
12/5/91	(b)	1	30	10	80	100	70.92	33.77	1.38	0.0002017	190
12/17/91		1	30	10	80	100	70.92	33.77	1.38	0.0002110	117
12/13/91		2	30	11	40	50	39.58	18.85	0.77	0.0002186	157
12/11/91		2	30	11	40	100	39.58	18.85	0.77	0.0002232	198
12/3/91	(b)	3	30	11	67.5	50	61.13	29.11	1.19	0.0002047	135
12/11/91		1	30	11	80	50	70.92	33.77	1.38	0.0002232	112
12/13/91		1	30	11	80	100	70.92	33.77	1.38	0.0002186	139
12/16/91	(c)	2	45	10	40	50	39.58	18.85	0.77	0.0002116	64
12/6/91	(b)	2	45	10	40	100	39.58	18.85	0.77	0.0002057	66
12/12/91	(c)	2	45	10	40	100	39.58	18.85	0.77	0.0002209	23
12/6/91	(b)	1	45	10	60	50	55.25	26.31	1.07	0.0002057	42
12/12/91		1	45	10	80	50	70.92	33.77	1.38	0.0002209	41
12/16/91	(c)	1	45	10	80	100	70.92	33.77	1.38	0.0002116	46
12/9/91	(b,c)	1	45	11	40	50	39.58	18.85	0.77	0.0002059	77
11/22/91	(b)	1	45	11	40	50	39.58	18.85	0.77	0.0002072	68
12/19/91	(c)	2	45	11	40	100	39.58	18.85	0.77	0.0002097	67
12/9/91	(b,c)	2	45	11	45	100	43.50	20.71	0.85	0.0002059	77
12/5/91	(b,c)	2	45	11	80	50	70.92	33.77	1.38	0.0002017	52
12/12/91		3	45	11	80	50	70.92	33.77	1.38	0.0002209	37
11/22/91	(b)	2	45	11	80	100	70.92	33.77	1.38	0.0002072	60

(a) i.e., 0.001 moles/L concentration in solution as measured by the ammonia electrode in the reactor

(b) These experiments used the fritted disk as the air sparger

(c) Experiments in which the electrode measured an initial ammonia concentration in solution above the predicted val

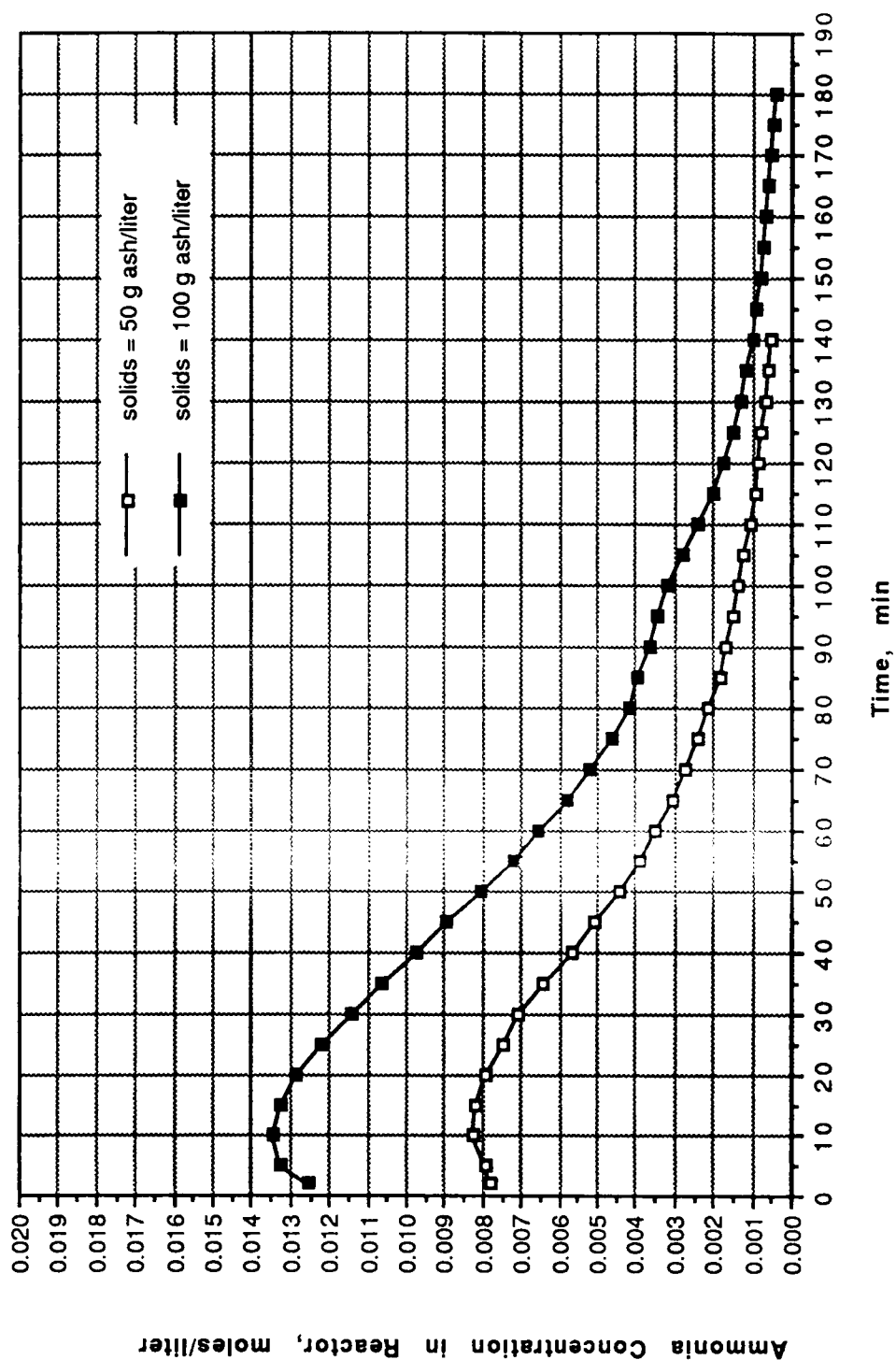


Figure 12. Reactor Data for Experiments under conditions: 30°C, pH = 11, 50 & 100 g/L solids, 80 scfh nominal air flow rate

from the solids to the liquid and because of ammonia loss from the liquid by degassing.

Figure 12 also shows a different time required to remove the ammonia to the same concentration level for both tests when the different solids loadings were used at this low temperature. The estimated time required to deplete the liquid ammonia concentration to a 0.001 mole/L level (as measured by the ammonia electrode) for all experiments is given in Table 4. This time data show, that at low temperatures, the solids loading may have more effect on the overall ammonia regeneration rate due to the ammonia transfer from the solid-to-liquid phase.

The effects of a change in the air flow rate are seen in Figure 13 for a temperature of 30°C, pH of 11, and solids loading of 100 g/L. Increasing the air flow from 40 to 80 scfh helped in removing the ammonia quicker from the liquid phase, in this case approximately 60 minutes faster. Similar decreases in the ammonia removal rate can be seen in the Table 4 data when the air flow rate is increased.

Effects of changing the temperature in the system from 30 to 45°C, for a pH of 11, nominal air flow rate of 40 scfh, and a solids loading of 100 g/L, can be seen in Figure 14. Operating the reactor at the higher temperature reduced the time needed to strip the ammonia from the reactor, in this case by approximately 2 hours. However, the temperature change did not seem to effect the height of the initial hump in the data or the time required to reach it. This "hump" is believed to correspond to the time during

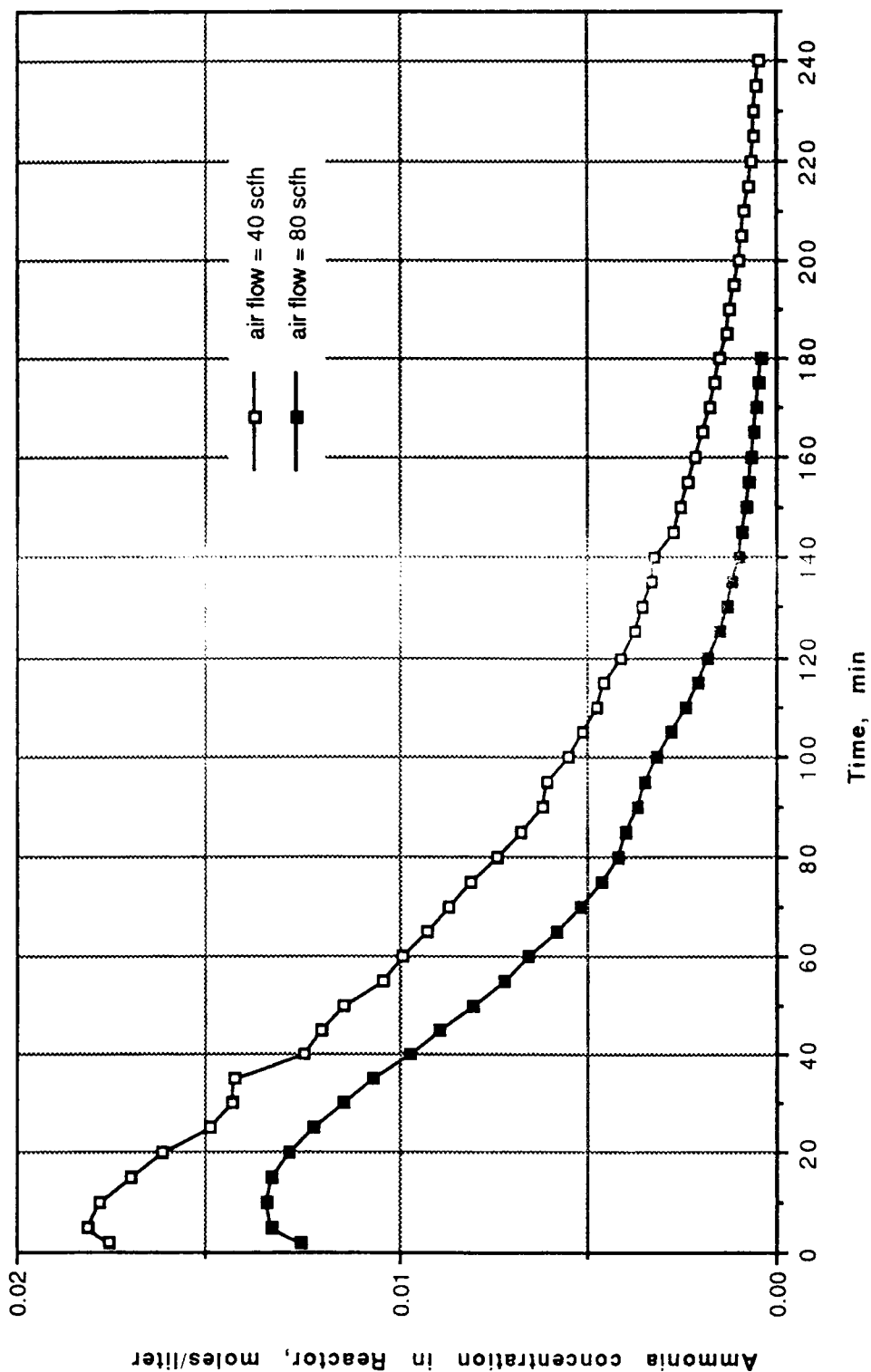


Figure 13. Reactor Data for Experiments under conditions: 30°C, pH = 11, 100 g/L solids, 40 & 80 scfh nominal air flow rate

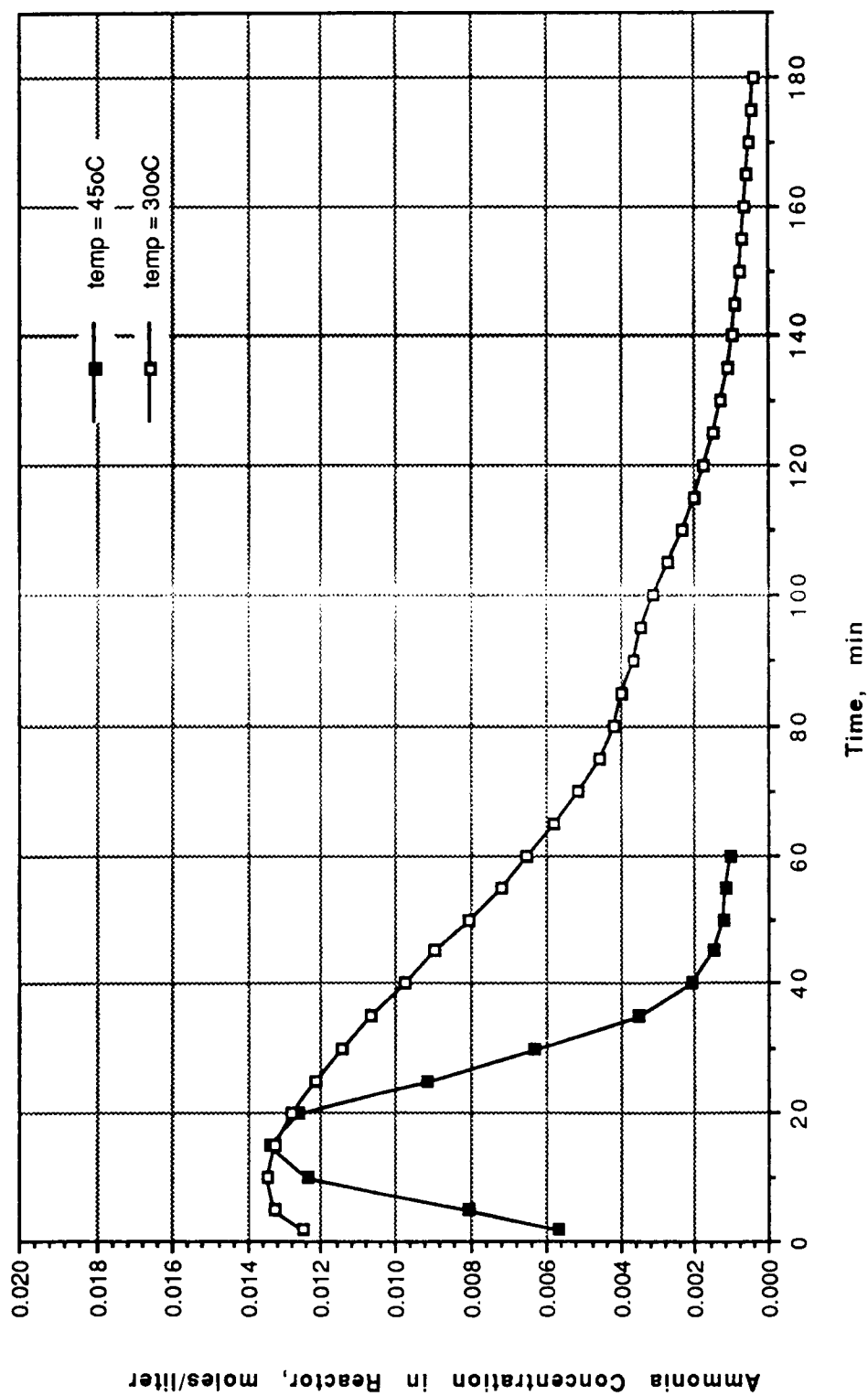


Figure 14. Reactor Data for Experiments under conditions: 30 & 45°C,
pH = 11, 100 g/L solids, 80 scfh nominal air flow rate

which the solid ash is still releasing the ammonia to the liquid. A much steeper slope is seen in the solid-liquid system for the higher temperature in trying to reach the hump, but both tests seem to reach the height of the hump within the same time frame.

The effect of the pH on the reactor system is seen in Figure 15. This graph shows data of experiments at 30°C, 100 g/L solids loading, and a nominal air flow of 40 scfh with pH levels of 10 and 11. The increase in pH seems to promote a faster release of the ammonia from the solid. This result was also predicted from the solid-liquid equilibrium experiments with the higher solids loading. However, this increase could be due to the increased amount of ammonia in the NH_3 form in solution at this low temperature and high pH, as given by the equilibrium shown in Figure 1.

The major effects of the solid dissolution of ammonia on the overall ammonia regeneration rate can be seen in Figure 16. This figure gives data for an experiment where the ammoniated ash was used and an experiment where non-ammoniated ash was used with a 0.02 M NH_4Cl solution providing the ammonia source for the reaction at 45°C, pH of 11, and nominal air flow of 80 scfh. This graph shows a nearly twice as fast stripping rate for ammonia from the NH_4Cl solution over the ammoniated ash system. This trend is to be expected due to the transfer of ammonia from the solid into the liquid solution when the ammonia is initially in the ash. Therefore, this ammonia transfer

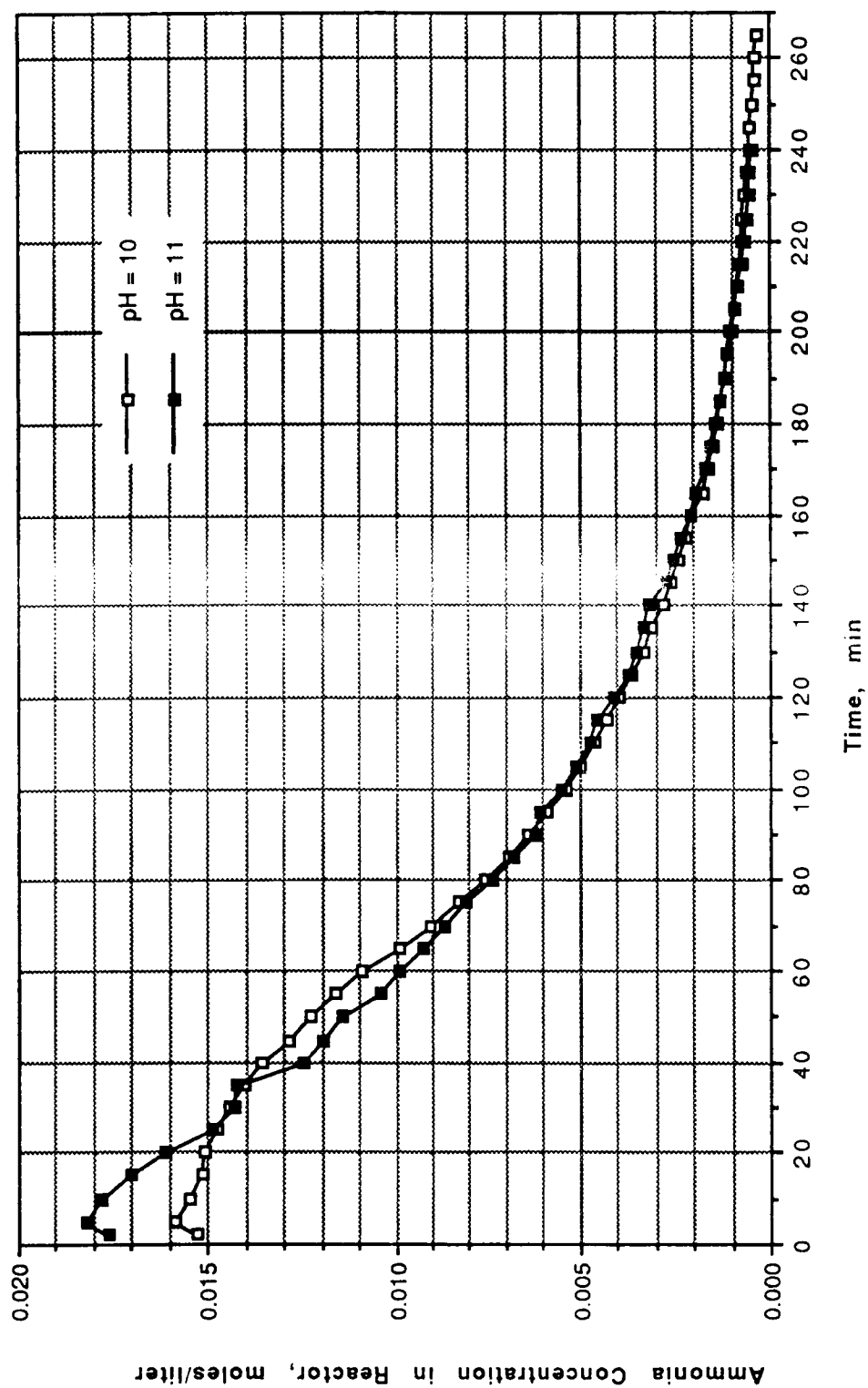


Figure 15. Reactor Data for Experiments under conditions: 30°C,
pH = 10 & 11, 100 g/L solids, 40 scfh nominal air flow rate

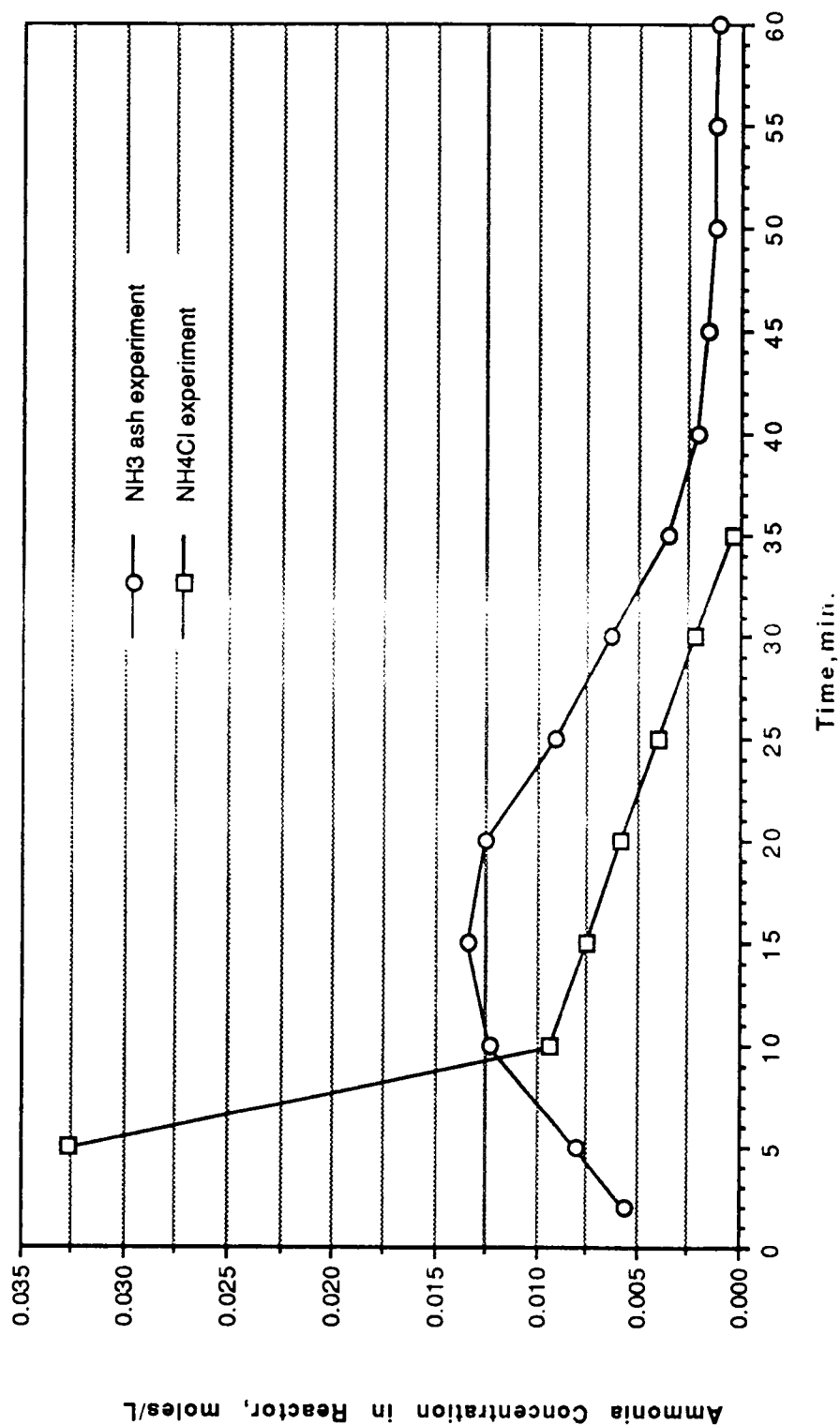


Figure 16. Comparison of Reactor Experiments with Ammoniated Ash and NH_4Cl solutions with Deammoniated Ash Present under conditions: 45°C , $\text{pH} = 11$, $0.02 \text{ M NH}_4\text{Cl}$, 30 scfh nominal air flow rate

from the solid to the liquid phase may be partially determining the rate of ammonia stripping from the reactor.

One anomaly, which was seen in the reactor tests, was a higher than expected measurement of the initial concentration of ammonia in the reactor by the ammonia electrode. This anomaly can be seen in Figure 17 for a reactor experiment at 45°C, pH of 11, 100 g/L solids, and 45 scfh nominal air flow rate. In this case, the initial concentration of ammonia in the ash was found to be 0.00020592 moles NH₃/g NH₃-free solid when measured by the EPA titration procedure. This initial concentration would correspond to a 0.0206 mole/L ideal ammonia concentration in solution if all the ammonia was released from the solid instantaneously. The peak of the data in Figure 17 shows approximately 0.029 moles/L ammonia in solution from the ammonia electrode measurement. The difference between the initial ammonia concentration in solution as measured by the electrode and the concentration value predicted by the EPA titration analysis cannot be explained easily. The EPA method, used to measure the ammonia in the ash initially, may have underestimated the actual concentration of ammonia similar to the problems seen in the solid-liquid equilibrium experiments. Another explanation could be imperfect mixing of the liquid phase seen similarly in the NH₄Cl experiments that determined the experimental K_La values. It is not known at this time the actual reason for this anomaly. The reactor data in which this anomaly was seen are found in Appendix B.

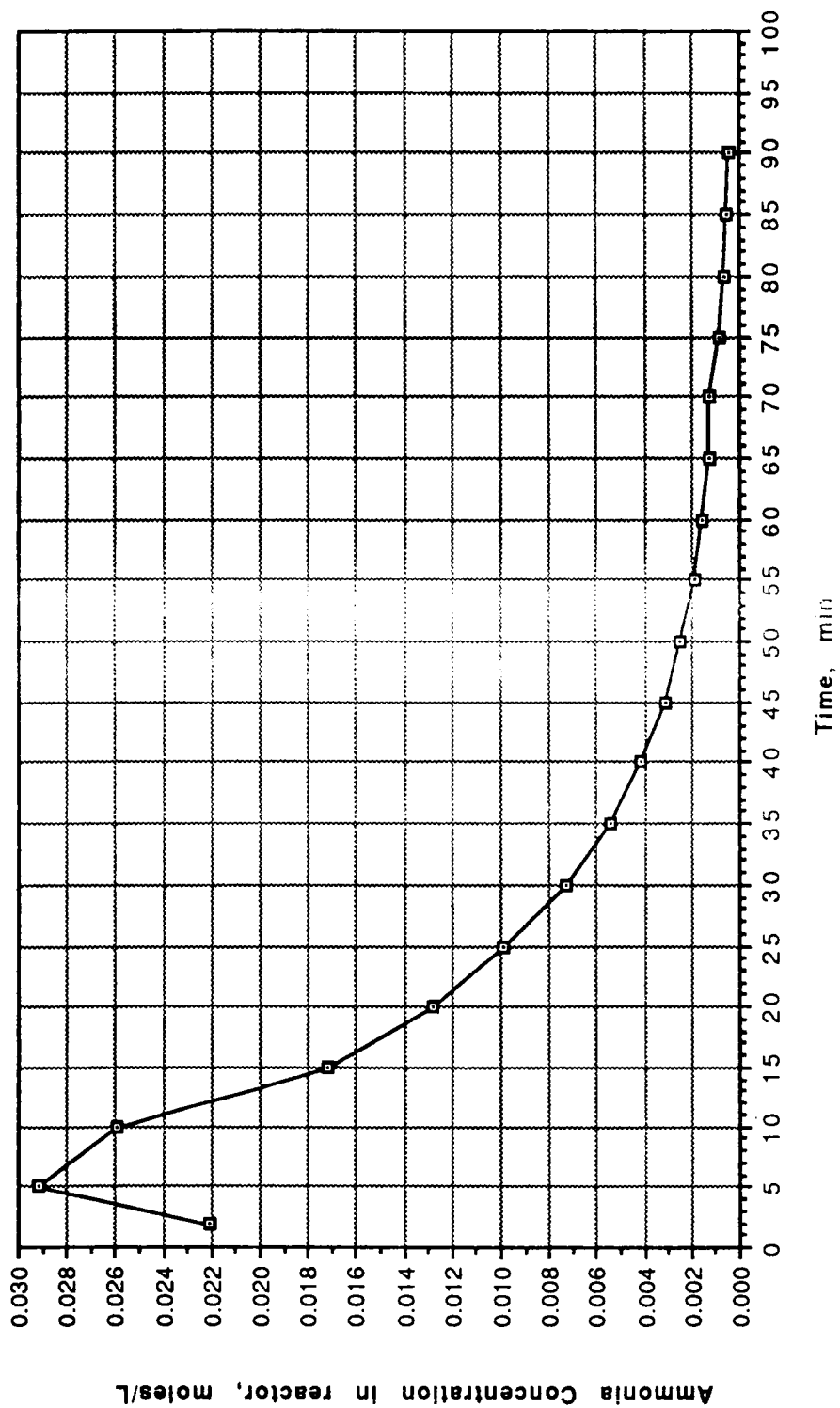


Figure 17. Anomaly Reactor Data under conditions: 45°C, pH = 11
 100 g/L solids, 45 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.00020592$ moles NH_3/g NH_3 -free solid

Overall, the results of these experimental reactor tests indicate that recovery of the ammonia from the waste ash can best be achieved with high pH, high temperature, and high gas flow rates. The maximum value of these parameters which can be used with cost effectiveness was not determined. The major qualitative conclusions drawn from these experimental tests are given below.

1) The ammonia regeneration time is increased as the solids loading, grams solids/liters of water, is increased. All other factors being constant, the solids loading has more effect on the ammonia regeneration time at the lower temperatures, indicating a slower solid-liquid mass transfer rate at this low temperature.

2) The ammonia concentration in the aqueous phase increases rapidly in the first 2 - 10 minutes after the solids are introduced into the reactor, although the maximum concentration achieved is always substantially below the calculated value corresponding to instantaneous, total release of the ammonia to the aqueous phase. This behavior, along with the fact that the raw ash possess the odor of ammonia, suggests that the total ammonia may be present in the solids in two forms: adsorbed ammonia, and as ammonium sulfite. This latter form was predicted from the pilot plant tests at the University of Tennessee during the initial study of the FGD process which produced the ash [6].

3) The ammonia stripping rate is increased as the nominal air flow rate is increased from 40 to 80 scfh, which suggests the process is controlled by the liquid-to-gas film coefficient, $K_L a$ at least at the lower sparging rate. This result is more pronounced at the lower temperature of 30°C than at 45°C.

4) Increasing the reactor temperature from 30°C to 45°C increases the ammonia stripping rate significantly, for a given sparging rate. This result may be explained by an improved value of the volumetric mass transfer coefficient, $K_L a$, at the higher temperature and by an increased value of the solid-to-liquid transfer coefficient, and by an increased ammonium sulfite dissolution rate.

5) Changing the pH of the slurry from 10 to 11 did not produce an appreciable change in the ammonia stripping rate for the reactor temperature of 30°C and a nominal air flow rate of 40 scfh. However, this pH change did increase the amount of ammonia initially measured in the aqueous phase, with this increase being contributed to the equilibrium shift between the NH_3 and NH_4^+ forms of ammonia.

6) When ammonia, provided in the form of NH_4Cl , is stripped from the aqueous slurries of ammonia-free ash, the stripping rate is substantially different than the case of the ammoniated ash stripping, all other factors (pH, temperature, and sparging rate) being the same. This result suggests that the ammonia dissolution and/or solids-liquid transfer rates are at

least partially determining the rate at which ammonia is stripped from the system.

From these results, the best plan is to operate the ammonia regeneration system with a pH $\Rightarrow$ 11, a temperature $\Rightarrow$ 45°C, and a gas flow $\Rightarrow$ 80 scfh. The cost effectiveness of using these values for the parameters should be examined more thoroughly by pilot-scale testing.

These experimental test results, however, must be considered very conservatively. This conservativeness comes from comparing the ammonia concentration in the ash used in these tests with the ammonia in the ash used in Yang's study. The ash used in Yang's study was manufactured and used in experiments within 6 months time. The current study encountered many delays and problems with determining the validity of the analysis techniques and with designing the reactor system. The ash used in this current study was not utilized in experimentation until 1-1/2 years after it was made. The ash lost nearly 72% ammonia to the atmosphere over this extended time in storage due presumably to an inadequate seal on the barrel containing the ash. Therefore, the predictions made by the current study must be examined with these facts in mind.

However, before any pilot testing is performed, these experiments should be modeled to better understand the processes involved in these mass transfer operations. This modeling was attempted with the help of a computer model described in Section 4.

4. INTERPRETATION OF RESULTS

The experimental ammonia regeneration results were interpreted in terms of the mass transfer of ammonia from the solid-to-liquid phase and then the liquid-to-gas phase. The overall mass transfer rate model consists of material balances on the ammonia in each of the solid, aqueous, and gaseous phases, along with a postulated distribution of the ammonia in the ash particles. Figure 18 gives a representation of this mass transfer process. The basic steps assumed to be involved in the ammonia dissolution/stripping process occurring in the reactor are detailed below.

- Step 1. Ash is wetted when placed in water, and the water instantaneously fills the pores and surrounds the particle, with flux N_w .
- Step 2. Water adsorbs onto the surfaces of the particle and displaces the weakly bound or adsorbed ammonia.
- Step 3. Dissolution of the strongly bound ammonia or ammonium sulfite begins in the presence of water. This transfer mechanism is presumed to be a first order dissolution-reaction process.
- Step 4. Ammonia is now present in the liquid in the pores of the particle and in the film surrounding the particle. This ammonia is then transferred to the bulk liquid phase, with flux N_{as} .

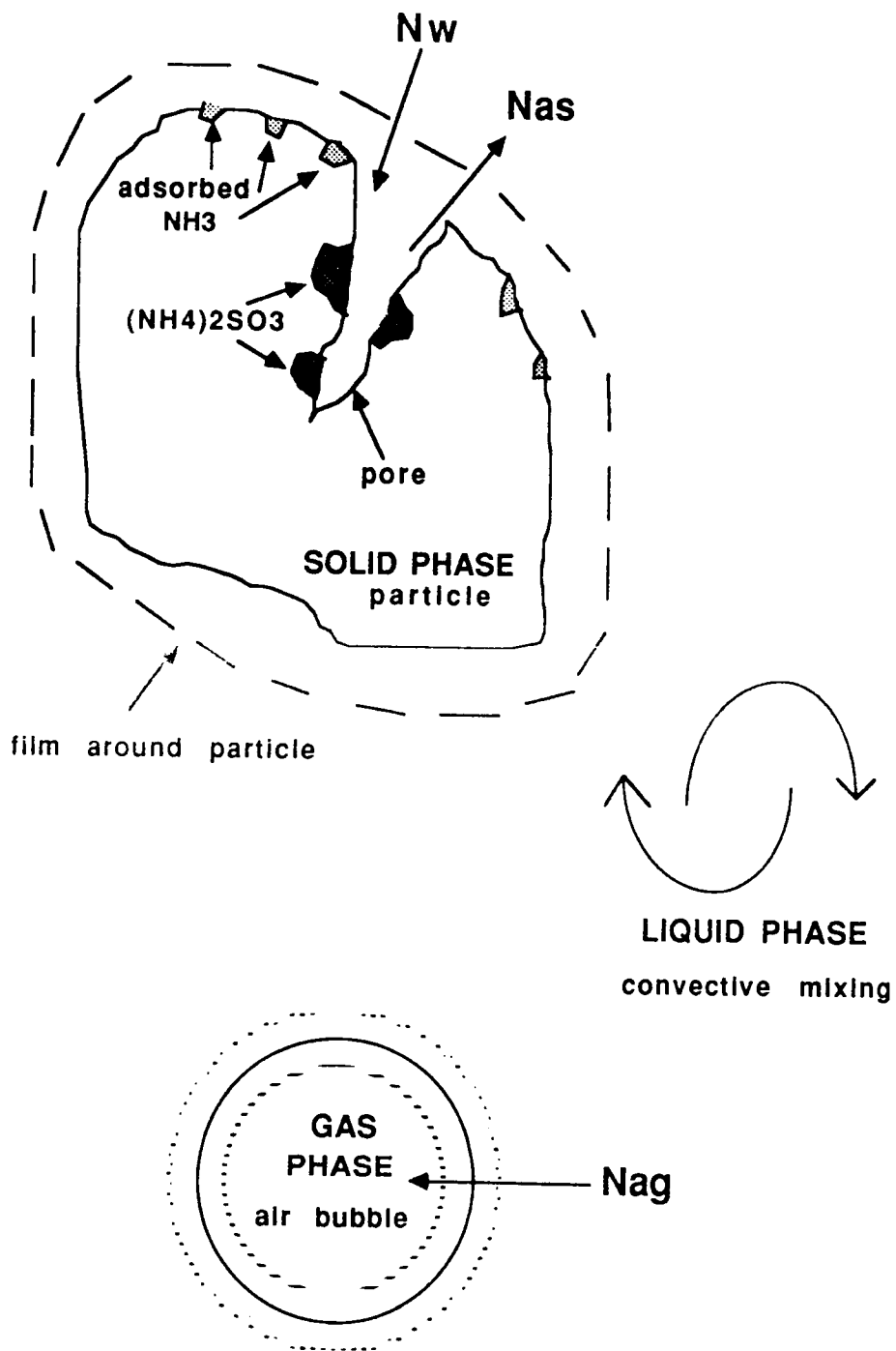


Figure 18. Representative Schematic of the Ammonia Mass Transfer in the Experimental Reactor

Step 5. Dispersion of ammonia in the liquid is by convective, turbulent mixing

Step 6. Dissolved ammonia in the liquid transfers to gas phase by way of the 2-film theory, with flux N_{Ag} .

One can now write a set of material balance equations for ammonia, based on this sequence of steps.

4.1 Solid Phase Mole Balance.

The mole balance of ammonia in the solid involves the transfer of the ammonia from the solid ash particles to the liquid phase. The basic form of the equation is given by:

Accumulation Rate = Transfer Rate of ammonia from the
of ammonia in the solid solid to the liquid phase.

Based on the experimental results, a theory was postulated to describe the ammonia distribution in the ash particles and a transfer process of the ammonia from the solid-to-liquid phase. The basis for this ammonia distribution and transfer is provided by the following set of assumptions.

1) The total ammonia in the solid phase is composed of a weakly-bound part (C'_{As}) and a strongly bound part (C''_{As}). The weakly bound part is presumed to be ammonia absorbed on the surface of the ash particles as NH_3 . The strongly bound part is considered to be principally the ammonium sulfite in the solid ash. The total ammonia in the solids is therefore given as

$$C_{As0} = C'_{As} + C''_{As} \quad \{4\}$$

2) When the ash is placed in the water, the adsorbed ammonia is essentially instantaneously displaced from the solid surface by water as it soaks into the particles, due to ammonia's high solubility in water [32]. The water is assumed to fill the pores within the particles immediately when the particles are immersed. The desorbed ammonia then exists in the aqueous solution within the pores of the particles. The initial concentration of the desorbed ammonia in the ash pores may be written as

$$C'_{Apo} = \frac{f \cdot W_S \cdot C_{Aso}}{(eps \cdot V_s)} \quad \{5\}$$

where:

C'_{Apo} = concentration of weakly bound ammonia initially in the water inside the pores of the ash particles, moles/cm³

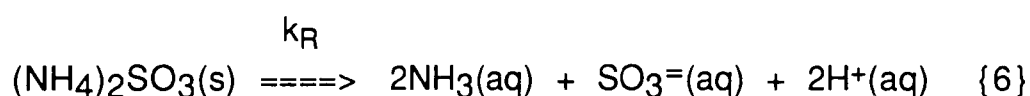
f = fraction of the total initial ammonia that is weakly bound

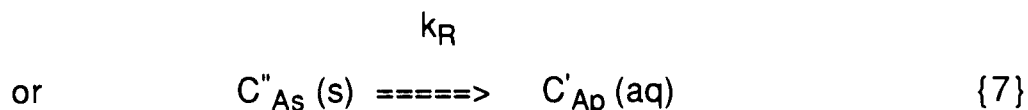
W_S = weight of solids on an ammonia-free basis, g

eps = effective void fraction within the solids

V_s = volume of the solids whose weight is W_S , cm³

3) When the water soaks into the pores of the solids, the strongly bound ammonia, or ammonium sulfite, undergoes a dissolution-reaction process which is considered to be overall first order.





The corresponding, initial concentration of the strongly bound ammonia in the water in the pores then becomes

$$C''_{Apo} = \frac{(1 - f) \cdot W_S \cdot C_{Aso}}{(\epsilon_s \cdot V_s)} \quad \{8\}$$

where:

C''_{Apo} = concentration of strongly bound ammonia initially in the water inside the pores of the ash particles, moles/cm³

The rate of reaction {7} is then taken to be

$$r''_{As} = -k_R \cdot C''_{As} \quad \{9\}$$

where:

k_R = Reaction rate constant for the first order conversion of the strongly bound ammonia to the weakly bound ammonia, cm³/min

4) The flux of ammonia from the particles into the surrounding liquid is defined by a concentration difference and the overall mass transfer coefficient given by equation {10} [31].

$$N_{As} = k_s(C_{Ap} - C_A) \quad \{10\}$$

where:

N_{As} = flux of ammonia from solid-to-liquid phase, moles/(cm²-min)

k_s = overall mass transfer coefficient between the particles and the surrounding liquid phase, cm/min

C_{Ap} = concentration of ammonia in the liquid occupying the pores, gmoles/cm³

C_A = bulk concentration of ammonia in the liquid phase, gmoles/cm³

In order to use such a simple mass transfer model, however, a low ammonia flux must be assumed for the process as well as no countercurrent diffusion. With these assumptions established, equation {10} is considered valid for this simple model.

Using this postulated model, the overall solid mole balance must be broken up into two equations: one for the strongly bound ammonia and one for the weakly bound ammonia. Referring to the assumptions 1 - 4 above, the mole balance equation for the strongly bound ammonia in the solid phase becomes

$$\frac{d}{dt} (C''_{As} \cdot W_S) = r''_{As} \cdot W_S \quad \{11\}$$

where:

r''_{As} = reaction rate for conversion of strongly bound ammonia to weakly bound ammonia, moles/cm³-min

t = time, minutes

If the total weight of ammonia-free solids, W_S , is assumed constant, then the leaching rate of these solids will be negligible. Combining equations {9} and {11}, and dividing by W_S the mole balance on the strongly bound ammonia becomes

$$\frac{d}{dt} (C''_{As}) = -k_s C''_{As} \quad \{12\}$$

Equation {12}, then, gives the transformation rate of the strongly bound ammonia, ammonium sulfite, to NH₃ in the aqueous phase.

The second mole balance involves the weakly bound ammonia. The weakly bound ammonia is accumulated in two ways: (1) by the transfer of the strongly bound ammonia into weakly bound ammonia (equation {12}), and (2) by the weakly bound ammonia being released into the liquid phase in the pores. Using assumptions 1, 2, 4, and equation {11}, the mole balance becomes

$$\frac{d}{dt} (C_{Ap} \cdot \epsilon_s \cdot V_S) = - W_S k_s a_s (C_{Ap} - C_A) - r''_{As} \cdot W_S \quad \{13\}$$

where:

a_s = specific external surface area of the solids, cm^2/g

Combining equations {9}, {13}, and dividing by $(\epsilon_s \cdot V_S)$, the mole balance on the weakly bound ammonia species becomes

$$\frac{d}{dt} (C_{Ap}) = - \frac{W_S k_s a_s}{(\epsilon_s \cdot V_S)} (C_{Ap} - C_A) - \frac{W_S k_s C''_{As}}{(\epsilon_s \cdot V_S)} \quad \{14\}$$

Therefore, the solid phase mole balance is defined by equations {12} and {14}.

4.2. Liquid Phase Mole Balance.

The mass balance on the liquid phase in the reactor system is given by the basic form below.

Accumulation Rate of ammonia in the liquid phase	= Transfer Rate of ammonia from the solid-to-liquid phase	- Loss Rate of ammonia to the gas phase
--	---	--

This equation in mathematical form is:

$$\frac{d}{dt} (C_A V_L) = W_S a_S N_{As} - V_t a N_{AG} \quad \{15\}$$

where:

V_L = liquid volume in reactor, cm^3

V_t = total volume (liquid + gas) in the reactor, cm^3

a = specific surface area of the gas-liquid interface, cm^2/cm^3

N_{As} = flux of ammonia from solid-to-liquid phase, $\text{moles}/(\text{cm}^2\text{-min})$

N_{AG} = flux of ammonia from liquid-to-gas phase, $\text{moles}/(\text{cm}^2\text{-min})$

The assumptions used to formulate this mole balance include the following.

- 1) The liquid phase is well mixed.
- 2) An isothermal operation occurs.
- 3) The pH is essentially constant.
- 4) The ammonia is present in the non-ionized form, which is approximately true for $\text{pH} \geq 10$.

5) The solubility of ammonia follows Henry's Law under the conditions of the experiment.

N_{As} is described as by equation {10} in the solid mole balance equation. The flux for the liquid-gas system, N_{AG} , is similar to equation {10} also, assuming the gas phase is well mixed. The differences include: 1) the mass transfer coefficient is based on the liquid-gas resistance and 2) the driving force is a liquid phase concentration difference. Equation {16} describes this relationship.

$$N_{AG} = K_L(C_A - C_A^*) \quad \{16\}$$

where:

K_L = overall mass transfer coefficient for the liquid-gas interface, cm/min

C_A^* = concentration of ammonia in the liquid phase in equilibrium with the gas phase, moles/cm³

In order to determine the C_A^* , the equilibrium relationship between the liquid and gas phase must be known. This relationship is typically defined by Henry's Law, given below, in systems where the liquid phase concentration is relatively low.

$$y_A = Hx_A^* \quad \{17\}$$

where:

y_A = mole fraction of ammonia in the gas phase

x_A^* = mole fraction of ammonia in the liquid phase in equilibrium with the gas phase

H = Henry's Law constant

Tabulated data for the Henry's constant can be found for many systems. For this system, a data table was found for ammonia at various pH and temperatures. Table 5 gives these data.

This data table does not extend totally into the range needed for our experiments, and therefore it was necessary to find the original literature source of the data to see if Henry's constant could be calculated for the high temperatures and pH used in this system. The original literature source, Click and Reed [34], gave an equation for the Henry's constant as a function of pH and temperature. This equation was programmed in Fortran and H was found over a range of ammonia concentrations. This

Table 5. Henry's Law Constant for Ammonia Gas in Water^a
(where H is in the mole fraction form: $y_A = Hx_A$)

pH	Temperature (°F)			
	40°	60°	80°	100°
6	0.000266	0.000754	0.00198	0.00486
7	0.00266	0.00753	0.0197	0.0480
8	0.0263	0.0734	0.186	0.428
9	0.238	0.586	1.20	2.05
10	1.20	1.94	2.65	3.31

^a Source: Thibodeaux, L.J., *Chemodynamics: Environmental Movement of Chemicals in Air, Water, and Soil*. 1979, New York: John Wiley and Sons.

Table 6. Comparison of the Calculated Henry's Constant with Thibodeaux's Values

Temperature °C	pH	Henry's Constant Values	
		Calculated	Thibodeaux
26.667	10	2.636	2.65
30.0	10	2.836	
30.0	11	3.149	
37.778	10	3.285	3.31
45.0	10	3.6687	
45.0	11	3.842	

program is found in Appendix D. The output values for the program are given in Table 6. Over the range of concentrations from 0.0005 to 0.5 moles/L, the H was found to be constant. The error seen between Thibodeaux's values and the calculated values is believed to be due to the temperature dependence of the specific gravity. The program calculated the H based on a specific gravity of water as 1.0.

If the Henry's law equation {17} is multiplied through by the total liquid concentration, C_L , it becomes

$$C_L \cdot y_A = H \cdot C_A^* \quad \{18\}$$

Assuming that C_L is constant and approximately equal to the concentration of the water in moles/cm³, equation {18} is valid. The definition of mole fraction for the gas phase is typically

$$y_A = C_A^g / C_g \quad \{19\}$$

where:

C_A^g = concentration of ammonia in the gas phase,
moles/cm³

C_g = total concentration of gas ($C_{g(\text{air})} + C_A^g$),
moles/cm³

Substituting this definition into equation {18} gives a simple relationship between C_A^* and C_A^g .

$$C_A^* = \frac{C_L}{H \cdot C_g} \cdot C_A^g \quad \{20\}$$

Since $[C_L/(H \cdot C_g)]$ is constant for a given experimental run, it is given the symbol b . Substituting this constant into equation {20}, and then using equation {20} in the flux equation {16}, the overall mole balance equation on the liquid phase can be reduced to equation {21}.

$$\frac{d(C_A \cdot V_L)}{dt} = W_S k_s a_s (C_{Ap} - C_A) - V_t K_L a (C_A - b \cdot C_g) \quad \{21\}$$

Since the liquid volume, V_L , is essentially constant during an experimental run, i.e. liquid carryover in the gas is negligible, this volume can be divided through the equation. Equation {21} then becomes

$$\frac{d(C_A)}{dt} = \frac{W_S k_s a_s}{V_L} (C_{Ap} - C_A) - \frac{V_t K_L a}{V_L} (C_A - b \cdot C_g). \quad \{22\}$$

The new term, W_S/V_L , is essentially constant for a given experiment and is called the solids loading. This term will be given the symbol S_L . The term V_t/V_L can be reduced by introduction of the term H_g , which is the gas loading. This H_g term is equal to

$$H_g = \frac{V_g}{V_t} = \frac{V_g}{V_g + V_L}. \quad \{23\}$$

Rearranging and substituting this term into equation {22}, the mole balance equation for the liquid phase finally becomes

$$\frac{d(C_A)}{dt} = S_L k_s a_s (C_{Ap} - C_A) - \frac{1}{(1 - Hg)} K_L a (C_A - b \cdot C_{gA}) \quad \{24\}$$

4.3. Gas Phase Mole Balance.

The loss rate of ammonia from the liquid phase to the gas phase can be defined in two ways, either as a plug flow or a fully mixed system. Both methods involve similar ammonia gain from the liquid phase, but differ in how the ammonia is lost from the reactor itself by the gas. The overall mole balance takes on the following form:

$$\begin{array}{lcl} \text{Accumulation Rate} & = & \text{Transfer Rate of ammonia} - \text{Loss Rate of} \\ \text{of ammonia in the} & & \text{from the liquid} \quad \text{Ammonia from} \\ \text{gas phase} & & \text{to the gas phase} \quad \text{the reactor by} \\ & & \text{the gas phase} \end{array}$$

The mathematical form is described below based on the following assumptions.

1) The gas phase is well-mixed, which is supported by literature statements for bubble columns having small L/D ratios [38]

2) The inlet air flow rate is held constant.

3) The mole fraction of ammonia in the gas phase is small relative to unity.

For the well mixed gas phase model, the mathematical form of the mole balance equation is:

$$\frac{d(C_{gA}^* V_g)}{dt} = V_L a N_{AG} - W_A. \quad \{25\}$$

where:

W_A = molar flow rate of ammonia leaving the reactor,
moles/min

V_g = volume of gas (bubbles) in reactor interacting with
liquid, cm^3

The molar flow rate of ammonia leaving the reactor, W_A , can be defined in terms of the mole fraction of ammonia in the gas phase, y_A . This relationship is shown in equation {26}.

$$W_A = y_A(W_{(\text{air})} + W_A) \quad \{26\}$$

where $W_{(\text{air})}$ = molar flow rate of air through the reactor,
gmol/min.

From assumption 3 above, $W_{(\text{air})} \gg W_A$. Using this assumption and substituting in the concentrations corresponding to y_A , equation {26} becomes

$$W_A = \frac{W_{(\text{air})} * C_{gA}}{C_g} \quad \{27\}$$

Combining equations {16}, {20}, and {27} into the mole balance equation {25}, the new balance equation becomes

$$\frac{d}{dt} (C_{gA} * V_g) = V_t K_L a (C_A - b * C_{gA}) - \frac{W_{(\text{air})}}{C_g} C_{gA} \quad \{28\}$$

Assuming that V_g is constant, and dividing it through equation {28}, we have a V_t/V_g term. The H_g term can also be used to redefine this V_t/V_g relationship. The H_g equation can also be used to substitute in for the $1/V_g$ term in the last part of equation {28}. Putting together equation {28} and the H_g

relationships, Equation {23}, the mole balance on the gas phase for the well mixed case becomes

$$\frac{d}{dt} (C_A^g) = \frac{1}{H_g} K_L a (C_A - b \cdot C_A^g) - \frac{(1 - H_g) W_{(air)} C_A^g}{H_g (V_L C_g)} \quad \{29\}$$

4.4. Summary of the Model Equations.

In summary, the rate of ammonia transfer from the solid to the gas phase is defined by four mole balances and one equilibrium system. Table 7 gives a summary of these equations.

TABLE 7. Summary of Material Balance Equations

Phase	Material Balance Equation
Solid (Strongly Bound)	$\frac{d}{dt} (C''_{As}) = - k_s C''_{As}$
Solid (Weakly Bound)	$\frac{d}{dt} (C_{Ap}) = - \frac{W_s k_s a_s (C_{Ap} - C_A)}{(\epsilon_s V_S)} - \frac{W_s k_s C''_{As}}{(\epsilon_s V_S)}$
Liquid	$\frac{d}{dt} (C_A) = S_L k_s a_s (C_{Ap} - C_A) - \frac{1}{(1 - H_g)} K_L a (C_A - b \cdot C_A^g)$
Gas	$\frac{d}{dt} (C_A^g) = \frac{1}{H_g} K_L a (C_A - b \cdot C_A^g) - \frac{(1 - H_g) W_{(air)} C_A^g}{H_g (V_L C_g)}$

The mole balances include two solid balances, one for each of the strongly and weakly bound species of ammonia in the ash given by equation {12} and {14}, respectively, the liquid balance given by equation {24}, and the gas balance given by equation {29} for the well-mixed case. The equilibrium system that describes the relationship between the equilibrium concentration of ammonia in the liquid phase, C_A^* , and the bulk concentration in the gas phase, C_{gA} , for the liquid-gas interface is given by equation {20} using literature values for the Henry's law constant. These 5 equations were used to model the mass transfer rate of the ammonia in the reactor. The unknown concentrations in this system of equations are C_A , C_{gA} , C_{Ap} , and C_{As}'' with the unknown parameters being K_{La} , k_{sa_s} , f , Hg , ϵ , and k_R .

A fortran computer program (program SIAM4.for, Appendix E) was written in order to solve the model equations, to test the model against the experimental regeneration data, and to develop the best estimates of the six unknown parameters. A flow sheet outlining the method used in the computer model to solve these equations and unknown parameters is given in Figure 19.

This program calls an Internal Mathematical and Statistical Library (IMSL) subroutine, "DIVPAG", to solve the set of first order differential equations representing the model, given an initial guess of the value of each of the six unknown parameters. A patterned search is then undertaken for the values of the parameters which provide the best fit to the experimental regeneration data, by parameter adjustment, and repeated calls to

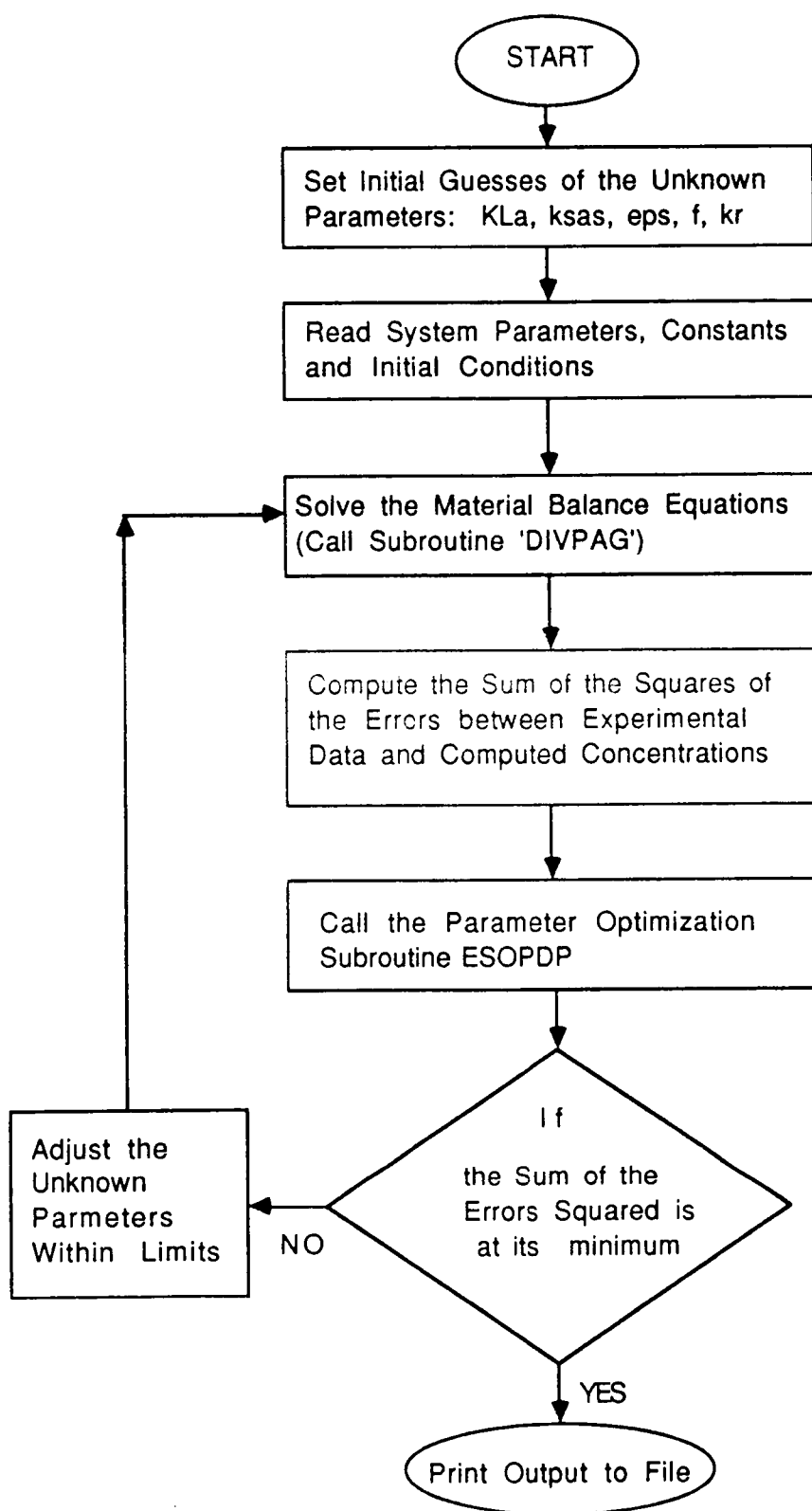


Figure 19. Flow Sheet for the Material Balance Computer Model

"DIVPAG'. The best fit to the experimental data is provided by that set of parameter values which gives the least value of the sum of the squares of the errors between the computed and experimental data points. Limits on the values of the unknown parameters are set in the input file and the program increments them within the given boundary range. The final predicted values are sent to an output file. The results of this model design are given in Section 4.5.

4.5. Test of the Model and Parameter Evaluations.

The mass transfer model predicts the concentration of ammonia in the liquid in the reactor system. These predicted results from the model were compared to the experimental concentration values measured by the ammonia electrode in the reactor. Figure 20 shows a typical plot of both sets of values for the conditions of 30°C, pH of 11, 100 g/L solids, and 40 scfh nominal air flow rate. Table 8 gives the data output file from the computer model for this experimental run. The other data graphs are found in Appendix B. All other output data files from the computer program are given in Appendix E.

Prior to testing the model described in Sections 4.1 - 4.4, other model systems were tested against the experimental data. For the solid mole balance, these other models included 1) a saturation type solid-liquid equilibrium system, and 2) a system where the strongly and weakly bound portions of the ammonia in the solid enter the liquid phase by separate reaction mechanisms.

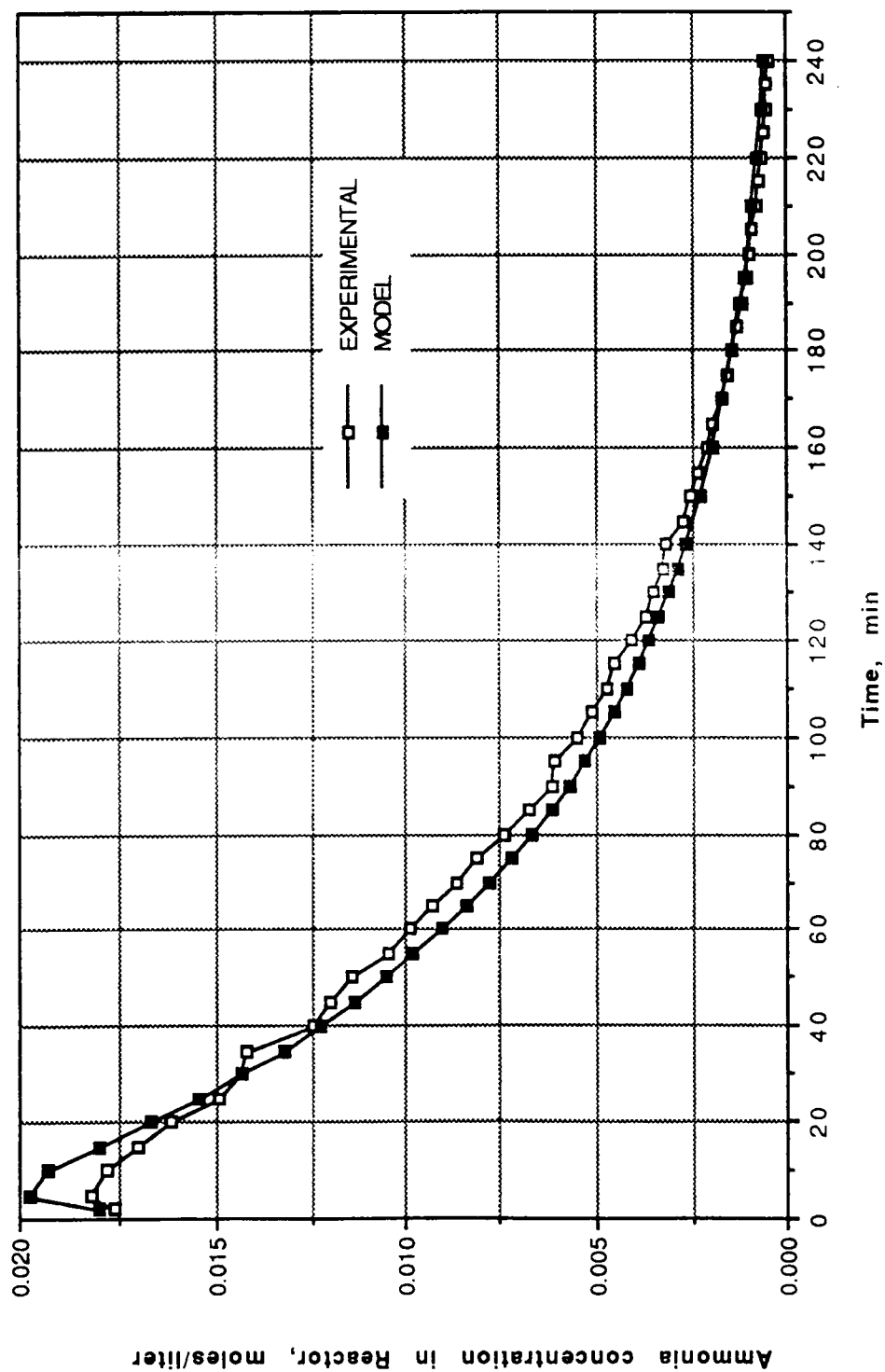


Figure 20. Reactor Experiment and Model Predicted Data for conditions:
 30°C, pH = 11, 100 g/L solids, 40 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.0002232$ moles NH_3/g NH_3 -free solid

Table 8. Computer Output Table for Experimental Conditions of 30°C, pH of 11,
100g/L solids, and 40 scfh nominal air flow rate

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION			FRACTIONAL			FRACTION	
						AMMONIA REMOVED	FROM SOLIDS	TO NH3(AQ)	CONVERSION OF (NH4)2SO3	YAG MOL	FRACTION	OF NH3 REMOVED	FROM SYSTEM
2	0.1759D-01	0.1798D-01	0.1020D-05	0.3755D-04	0.3857D-04	0.8272D+00	0.5415D+00	0.3792D-03	0.5415D+00	0.3792D-03	0.2171D-01		
5	0.1818D-01	0.1976D-01	0.3421D-06	0.1166D-04	0.1200D-04	0.9462D+00	0.8577D+00	0.4169D-03	0.8577D+00	0.4169D-03	0.6106D-01		
10	0.1782D-01	0.1928D-01	0.7819D-07	0.1659D-05	0.1738D-05	0.9922D+00	0.9787D+00	0.4069D-03	0.9787D+00	0.4069D-03	0.1285D+00		
15	0.1701D-01	0.1800D-01	0.3846D-07	0.2362D-06	0.2747D-06	0.9988D+00	0.9971D+00	0.3798D-03	0.9971D+00	0.3798D-03	0.1924D+00		
20	0.1614D-01	0.1669D-01	0.3080D-07	0.3364D-07	0.6444D-07	0.9997D+00	0.9996D+00	0.3522D-03	0.9996D+00	0.3522D-03	0.2519D+00		
25	0.1491D-01	0.1546D-01	0.2784D-07	0.4791D-08	0.3263D-07	0.9999D+00	0.9999D+00	0.3275D-03	0.9999D+00	0.3275D-03	0.3070D+00		
30	0.1433D-01	0.1433D-01	0.2567D-07	0.6835D-09	0.2635D-07	0.9999D+00	0.1000D+01	0.3005D-03	0.1000D+01	0.3005D-03	0.3580D+00		
35	0.1423D-01	0.1327D-01	0.2377D-07	0.9746D-10	0.2387D-07	0.9999D+00	0.1000D+01	0.2826D-03	0.1000D+01	0.2826D-03	0.4053D+00		
40	0.1247D-01	0.1229D-01	0.2203D-07	0.1386D-10	0.2204D-07	0.9999D+00	0.1000D+01	0.2594D-03	0.1000D+01	0.2594D-03	0.4491D+00		
45	0.1198D-01	0.1139D-01	0.2040D-07	0.1928D-11	0.2041D-07	0.9999D+00	0.1000D+01	0.2403D-03	0.1000D+01	0.2403D-03	0.4897D+00		
50	0.1144D-01	0.1055D-01	0.1890D-07	0.3547D-12	0.1890D-07	0.9999D+00	0.1000D+01	0.2226D-03	0.1000D+01	0.2226D-03	0.5273D+00		
55	0.1043D-01	0.9773D-02	0.1751D-07	0.2858D-12	0.1751D-07	0.9999D+00	0.1000D+01	0.2062D-03	0.1000D+01	0.2062D-03	0.5621D+00		
60	0.9890D-02	0.9053D-02	0.1622D-07	0.1241D-12	0.1622D-07	0.9999D+00	0.1000D+01	0.1910D-03	0.1000D+01	0.1910D-03	0.5943D+00		
65	0.9260D-02	0.8386D-02	0.1503D-07	0.3853 D-13	0.1503D-07	0.9999D+00	0.1000D+01	0.1770D-03	0.1000D+01	0.1770D-03	0.6242D+00		
70	0.8660D-02	0.7769D-02	0.1392D-07	0.2222D-12	0.1392D-07	0.9999D+00	0.1000D+01	0.1640D-03	0.1000D+01	0.1640D-03	0.6518D+00		
75	0.8110D-02	0.7198D-02	0.1290D-07	0.2379D-12	0.1290D-07	0.9999D+00	0.1000D+01	0.1519D-03	0.1000D+01	0.1519D-03	0.6775D+00		
80	0.7390D-02	0.6669D-02	0.1195D-07	0.1569D-12	0.1195D-07	0.9999D+00	0.1000D+01	0.1407D-03	0.1000D+01	0.1407D-03	0.7012D+00		
85	0.6780D-02	0.6179D-02	0.1107D-07	0.1550D-12	0.1107D-07	0.1000D+01	0.1000D+01	0.1304D-03	0.1000D+01	0.1304D-03	0.7231D+00		
90	0.6180D-02	0.5725D-02	0.1026D-07	0.9830D-13	0.1026D-07	0.1000D+01	0.1000D+01	0.1208D-03	0.1000D+01	0.1208D-03	0.7435D+00		
95	0.6100D-02	0.5305D-02	0.9504D-08	0.3403D-13	0.9504D-08	0.1000D+01	0.1000D+01	0.1119D-03	0.1000D+01	0.1119D-03	0.7623D+00		
100	0.5530D-02	0.4916D-02	0.8807D-08	0.1811D-14	0.8807D-08	0.1000D+01	0.1000D+01	0.1037D-03	0.1000D+01	0.1037D-03	0.7797D+00		
105	0.5100D-02	0.4554D-02	0.8160D-08	0.8870D-14	0.8160D-08	0.1000D+01	0.1000D+01	0.9612D-04	0.1000D+01	0.9612D-04	0.7959D+00		
110	0.4710D-02	0.4220D-02	0.7561D-08	0.1529D-13	0.7561D-08	0.1000D+01	0.1000D+01	0.8906D-04	0.1000D+01	0.8906D-04	0.8109D+00		
115	0.4530D-02	0.3911D-02	0.7007D-08	0.1852D-13	0.7007D-08	0.1000D+01	0.1000D+01	0.8253D-04	0.1000D+01	0.8253D-04	0.8248D+00		
120	0.4080D-02	0.3623D-02	0.6492D-08	0.1038D-13	0.6492D-08	0.1000D+01	0.1000D+01	0.7647D-04	0.1000D+01	0.7647D-04	0.8376D+00		

Table 8. (Continued)

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MQL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
125	0.3720D-02	0.3358D-02	0.6016D-08	0.5306D-14	0.6016D-08	0.1000D+01	0.1000D+01	0.7086D-04	0.8495D+00
130	0.3520D-02	0.3111D-02	0.5575D-08	0.4058D-15	0.5575D-08	0.1000D+01	0.1000D+01	0.6566D-04	0.8606D+00
135	0.3280D-02	0.2883D-02	0.5165D-08	-0.6602D-15	0.5165D-08	0.1000D+01	0.1000D+01	0.6083D-04	0.8708D+00
140	0.3190D-02	0.2671D-02	0.4786D-08	-0.7634D-14	0.4786D-08	0.1000D+01	0.1000D+01	0.5637D-04	0.8803D+00
150	0.2510D-02	0.2293D-02	0.4109D-08	-0.2343D-13	0.4109D-08	0.1000D+01	0.1000D+01	0.4839D-04	0.8972D+00
160	0.2090D-02	0.1968D-02	0.3525D-08	-0.3569D-13	0.3525D-08	0.1000D+01	0.1000D+01	0.4152D-04	0.9118D+00
170	0.1710D-02	0.1686D-02	0.3021D-08	-0.4690D-13	0.3021D-08	0.1000D+01	0.1000D+01	0.3559D-04	0.9244D+00
180	0.1440D-02	0.1445D-02	0.2589D-08	-0.3930D-13	0.2589D-08	0.1000D+01	0.1000D+01	0.3050D-04	0.9352D+00
190	0.1180D-02	0.1237D-02	0.2216D-08	-0.4341D-13	0.2216D-08	0.1000D+01	0.1000D+01	0.2610D-04	0.9446D+00
200	0.1090D-02	0.1059D-02	0.1898D-08	-0.5177D-13	0.1898D-08	0.1000D+01	0.1000D+01	0.2236D-04	0.9525D+00
210	0.8100D-03	0.9068D-03	0.1625D-08	-0.3606D-13	0.1625D-08	0.1000D+01	0.1000D+01	0.1914D-04	0.9594D+00
220	0.6500D-03	0.7768D-03	0.1392D-08	0.1369D-13	0.1392D-08	0.1000D+01	0.1000D+01	0.1639D-04	0.9652D+00
230	0.5500D-03	0.6655D-03	0.1192D-08	0.2009D-13	0.1192D-08	0.1000D+01	0.1000D+01	0.1405D-04	0.9702D+00
240	0.4800D-03	0.5706D-03	0.1022D-08	-0.4661D-13	0.1022D-08	0.1000D+01	0.1000D+01	0.1204D-04	0.9744D+00

Note: OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.02722	0.2983D-02	0.3899D+00	0.6330D+00	0.2050D-01

These other model systems, however, did not accurately predict the initial "hump" seen in the experimental data during the first 10-15 minutes of the reaction. Therefore, the best model fit of the data was found when the solid dissolution model included the strongly bound ammonia transferring to the weakly bound ammonia by a first order reaction. A plug flow gas phase model was also modeled initially, but it was found that the well-mixed gas phase model Equation {29}, fits the experimental data just as well and simpler. Therefore, the well-mixed gas phase model was chosen for this simple case regeneration system as predicted by the computer model.

Table 9. summarizes the results of the ammonia regeneration system as predicted by the computer model. This table gives the predicted time required to convert 90%, 95%, and 99% of the strongly bound ammonia, as $(\text{NH}_4)_2\text{SO}_3$, to the weakly bound ammonia, as adsorbed NH_3 . For the low temperature experiments, 90% of the ammonium sulfite could be converted within 35 min or less, 95% could be converted in 45 min or less, and 99% could be converted in 70 min or less. Two of the 8 experiments used in this modeling, however, showed data out of these ranges. These two sets of data, performed on 12/5/91 and 12/3/91, both gave much longer conversion times. These tests predicted that 90% of the ammonium sulfite was converted in 150 -160 min, 95% was converted in 177 - 190 min, and 99% was converted in 187 - 230 min. The main difference between these two tests and the other low temperature tests was the sparger

Table 9. Results of Ammonia Regeneration System Predicted by the Computer Model

Date	pH	oC	Experimental Values		Predicted Time Required to:									
					Convert (NH ₄) ₂ SO ₃ to NH ₃ (aq) by					Remove Total NH ₃ in solid phase by				
			Nominal Air Solids	Temp, Flow Rate, Loading,	90%,	95%,	99%,	90%,	95%,	99%,	90%,	95%,	99%,	min.
			scfh	g/L	min.	min.	min.	min.	min.	min.	min.	min.	min.	min.
12/18#2	10	30	40	100	34	45	70	16	26	161	210 (a)	250 (a)		
12/19#1	10	30	80	50	3	4	5	3	5	115	140 (a)	165 (a)		
12/17#1	10	30	80	100	18	24	40	7	14	80	110	180 (a)		
12/5#1 (b)	10	30	80	100	150	190	230 (a)	60	102	160	201 (a)	238 (a)		
12/11#2	11	30	40	100	7	9	15	4	6	155	200	280 (a)		
12/3#3 (b)	11	30	67.5	50	160 (a)	177 (a)	187 (a)	125	155 (a)	180 (a)	200 (a)	220 (a)		
12/11#1	11	30	80	50	21	26	45	12	17	110	141	175 (a)		
12/13#1	11	30	80	100	35	45	70	22	32	115	141	200 (a)		
12/6#2 (b)	10	45	40	100	1	2	3	1	2	51	70	105 (a)		
12/6#1 (b)	10	45	60	50	36	46	67 (a)	20	30	50	61	73(a)		
12/12#1	10	45	80	50	1	3	5	1	2	50 (a)	55 (a)	60 (a)		
11/22#1 (b)	11	45	40	50	6	8	11	6	8	60	79 (a)	95 (a)		
12/12#3	11	45	80	50	1	3	5	3	4	40	51	70 (a)		
11/22#2 (b)	11	45	80	100	6	8	11	4	8	34	45	60 (a)		

(a) Values calculated by extrapolation from the model predicted system
 (b) These experiments used the fritted disk as the air sparger

type. These two anomalous tests used the fritted disk sparger not the plastic disk with larger holes. However, the computer model was not adjusted for the different sparger type, and this 100+ minute difference for the conversion times of the ammonium sulfite predicted with the different spargers is not conclusive. Overall, these data predict that 99% of the ammonia can be converted from the ammonium sulfite to the adsorbed ammonia within 70 min or less when the plastic sparger is used. At the high temperature of 45°C, the data give 99% conversion of the ammonium sulfite within 11 min or less. This high temperature data also has one exception, the first experiment performed on 12/6/91, which predicts 99% conversion within 67 minutes. This anomalous data point also used the fritted disk as the sparger during the experiment.

Table 9 also gives the times predicted by the model for 90% and 95% total ammonia mass transfer from the solid phase to the liquid phase. For the 30°C experiments, the ammonia was 90% transferred to the liquid phase by 22 min, and 95% transferred by 32 min. Two experiments with the fritted disk sparger, however, also gave much longer times for ammonia transfer, i.e. 60 - 125 min for 90% transfer and 102 - 155 min for 95% transfer. The high temperature experiments gave 95% transfer of the total ammonia to the liquid phase within 8 min or less, with the exception of 12/6#1 experiment giving 95% transfer within 30 min.

The time required to remove all the ammonia from the reactor was also predicted by the model and these data are given in Table 9 for 90%, 95%, and 99% removal. For the low temperature experiments, the model predicted 180 min or less for 90% removal, 210 min or less for 95% removal and 280 min or less for 99% removal. All the data fell within these ranges with no preference seen for sparger type. For the 45°C experiments, the model predicted 60 min or less for 90% removal, 79 min or less for 95% removal, and 105 min or less for 99% removal. The 99% removal times however were extrapolated from the actual model output data as the experiments were not carried out to this length.

The total mass transfer model generally fit the experimental data well, except for a few cases, such as the run shown in Figure 21. In these cases, the experimental data seemed to have a delayed "hump". In most of the experiments, this initial peak in the data occurred within the first 10 - 15 minutes of the reaction time. The predicted model most often could predict this initial peak because of the use of weighting factors in the model. Sometimes, however, the peak did not occur until 25 - 30 minutes into the reaction (See Figure 21). When this delay of the peak occurred, the model did not predict the correct height and duration of the peak. Figure 21 shows an example graph of this phenomenon for the predicted data versus the experimental data under conditions of 45°C, pH of 11, 50 g/L solids, and 40 scfh

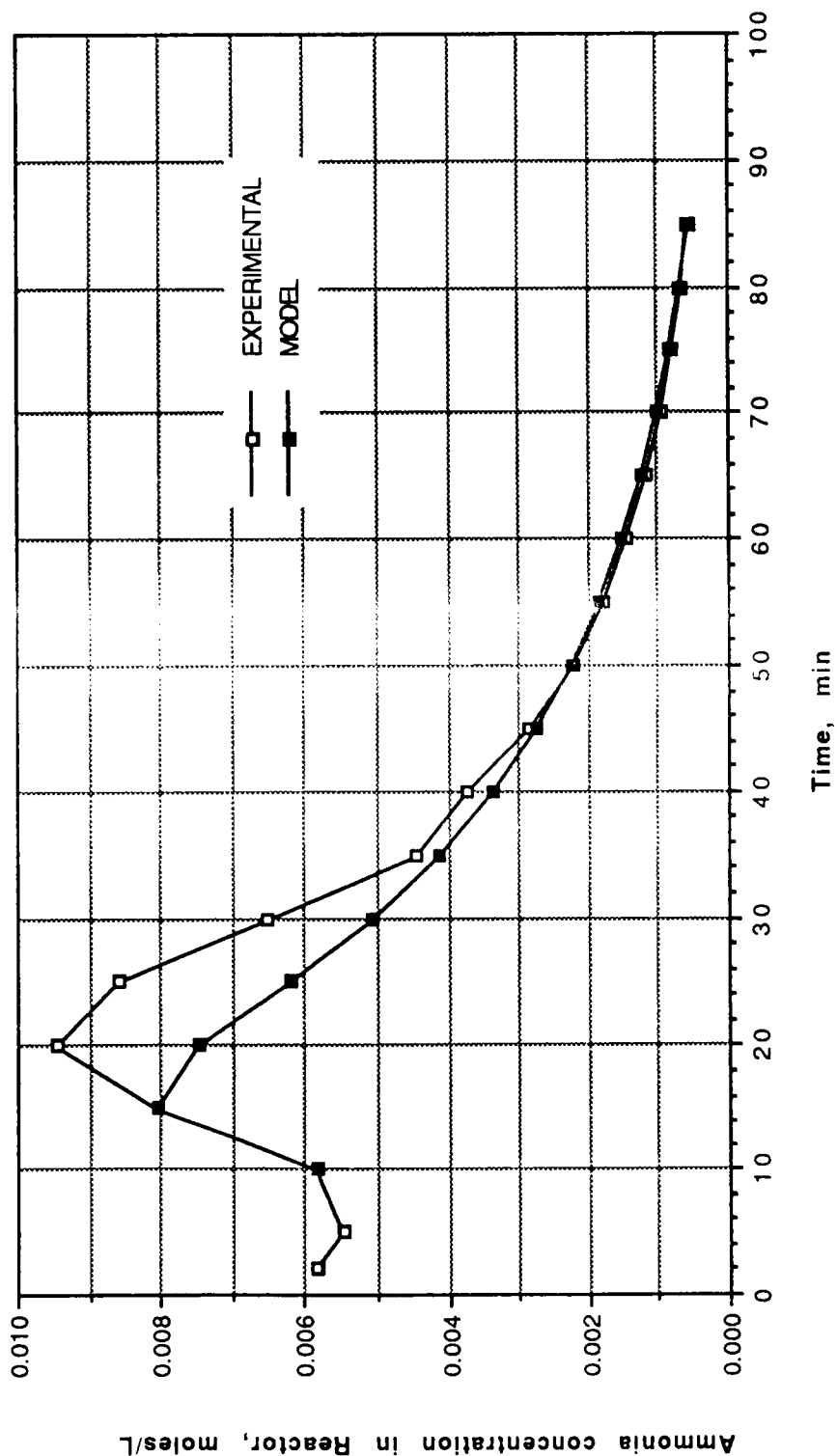


Figure 21. Reactor Experiment and Model Predicted Data for conditions:
 45°C, pH = 11, 50 g/L solids, 40 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.00020723$ moles NH_3/g NH_3 -free solid

nominal air flow rate. The predicted peak is much lower and occurs earlier than the experimental data in this graph.

The other two major drawbacks of the model include 1) the prediction of a faster release of ammonia from the liquid to the gas phase after the peak, and 2) the prediction of a slightly higher ammonia concentration in the liquid phase towards the very end of the experiment. Figure 22 shows these two trends for an experiment under conditions of 45°C, pH of 11, 50 g/L solids loading, and 80 scfh nominal air flow rate. These two trends may be the result of assuming perfect mixing in the gas and liquid phases in the reactor. These assumptions may not be true due to the reactor and/or sparger design.

The computer model searched for the optimal values for the unknown parameters in the mass transfer model for each experiment. These unknown parameters were (1) the solid-liquid mass transfer coefficient, $k_s a_s$, (2) the effective void fraction in the solid particles, ϵ_{ps} , (3) the reaction rate coefficient for the transfer of ammonia from the strongly bound species to the weakly bound species, k_R , (4) the fraction of total ammonia in the solids that is weakly bound, f , and (5) the gas-liquid mass transfer coefficient, $K_L a$. The gas hold up, H_g , was held fixed in the model. The predicted values listed in Table 2, and output from program SNH3.FOR (found in Appendix C), were used for the H_g values in the model. The optimal values for each of these unknown parameters as predicted by the mass transfer model are given in Table 10.

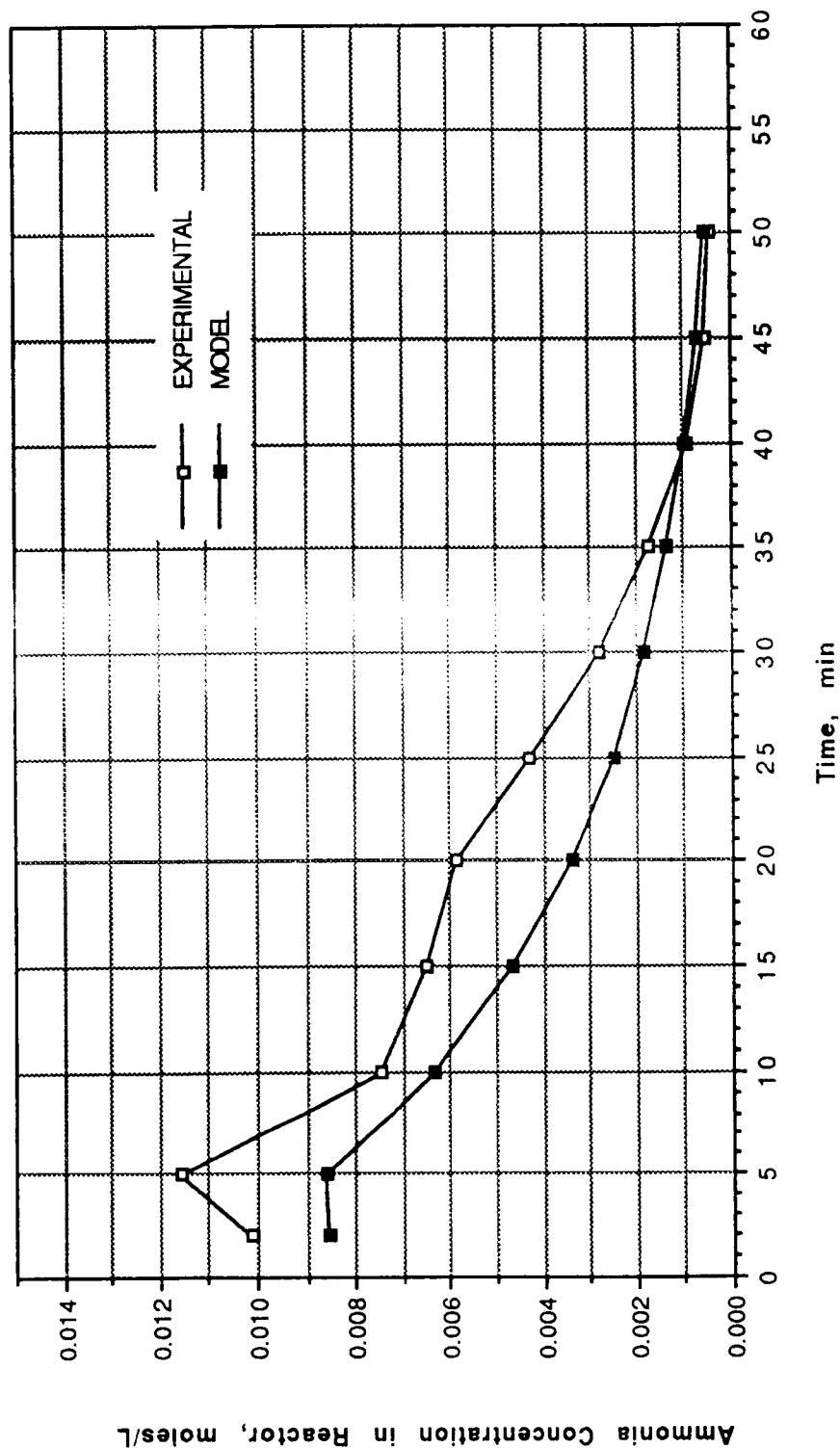


Figure 22. Reactor Experiment and Model Predicted Data for conditions:
 45°C, pH = 11, 50 g/L solids, 80 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.00022091$ moles NH_3/g NH_3 -free solid

Table 10. Optimal Values for the Unknown Parameters in the Mass Transfer Model as Determined by the Computer Model

Date	Experimental Values				Optimal Values of Model Parameters From SIAM4.FO				
	pH	Temperature, °C	Nominal Air Solids		KsAs (cm ³ /g-min)	EPS	Kr 1/min	F	KLa 1/min
			Flow Rate, scfh	Loading, g/L					
12/18#2	10	30	40	100	0.0052	0.0039	0.0704	0.7162	0.0209
12/19#1	10	30	80	50	0.0106	0.1050	1.0040	0.5316	0.0217
12/17#1	10	30	80	100	0.0095	0.0090	0.1295	0.7883	0.0230
12/5#1 *	10	30	80	100	0.0230	0.0032	0.0157	0.7516	0.0199
12/11#2	11	30	40	100	0.0272	0.0030	0.3899	0.6330	0.0205
12/3#3 *	11	30	67.5	50	0.0517	0.0006	0.0117	0.5794	0.0234
12/11#1	11	30	80	50	0.0061	0.0023	0.1142	0.6527	0.0241
12/13#1	11	30	80	100	0.0080	0.0072	0.0683	0.6089	0.0250
12/6#2 *	10	45	40	100	0.0217	0.0182	1.9820	0.8865	0.4503
12/6#1 *	10	45	60	50	0.0663	0.0066	0.0664	0.6274	0.3502
12/12#1	10	45	80	50	0.1316	0.0035	1.2290	0.8937	0.2485**
11/22#1 *	11	45	40	50	0.0107	0.0231	0.4293	0.5821	0.1221
12/12#3	11	45	80	50	0.0008	0.0148	2.5010	0.6581	0.0792
11/22#2 *	11	45	80	100	0.4009	0.0017	0.4307	0.2362	0.1603

* These experiments used the fritted disk as the air sparger

** This value had to be fixed to get this run to converge

Average values of the data in Table 10, are given in Table 11 as functions of temperature and pH. The predicted data in Table 10 did not show much correlation between solids loading or air flow rate with the different parameters. Table 11 shows some trends in the predicted parameters of the model with respect to pH and temperature. The solid-liquid mass transfer coefficient, $k_s a_s$, predicted by the model shows an increasing trend of the average values as the temperature and pH is increased from 30°C to 45°C and from 10 to 11, respectively. The $k_s a_s$ nearly doubles in value as the pH is increased from 10 to 11. Also, the average $k_s a_s$ increases by 83% as the temperature is increased from 30 to 45°C at both pH levels. The temperature dependence of this mass transfer coefficient is typical when the equilibrium-distribution curve between the two phases, solid and liquid, is dependent on temperature [39]. The dependence of $k_s a_s$ on pH is believed to stem from a pH dependence similar to the $\text{NH}_3/\text{NH}_4^+$ equilibrium pH dependence described in equation {1} and Figure 1. However, with the small number of experiments available, quantification of the dependency of $k_s a_s$ on the pH and temperature is difficult and can only be estimated.

The effective void fraction, ϵ_{ps} , average values seem to show quite a bit of scatter. This parameter should have been fairly constant for all the experiments, because the amount of voids in the particles is determined by the FGD process in which the particles are made. As the particles are being formed and dried in the spray dryer system, the particle voids are produced.

Table 11. Average Values of the Predicted Data for the Unknown Parameters in the Mass Transfer Model

VALUES		Number of Experiments Used in Average		
		4	4	3
Experimental				
pH		10	11	10
Temperature, oC		30	30	45
Average Optimal Model Parameters				
KsAs Mean, (cm ³ /g-min)		0.0121	0.0232	0.0732
Range		0.0051 - 0.023	0.006 - 0.052	0.02 - 0.13
EPS Mean		0.0303	0.0033	0.0094
Range		0.0032 - 0.1	0.0006 - 0.0072	0.0034 - 0.02
Kr Mean, 1/min		0.3049	0.1460	1.0925
Range		0.015 - 1.0	0.068 - 0.4	0.066 - 2.0
f Mean		0.6969	0.6185	0.8025
Range		0.53 - 0.75	0.57 - 0.65	0.62 - 0.90
KLA Mean, 1/min		0.0214	0.0232	0.4003
Range		0.019 - 0.023	0.020 - 0.045	0.35 - 0.45
				0.1205
				0.079 - 0.16

Therefore, the effective void fraction of each particle should not be influenced by the pH, temperature, solids loading or air flow when they are placed in the reactor system. The average values of this parameter predicted by the model are found in Table 11 to range from 0.003 to 0.03. These values given by the model are relatively low. This parameter, then, may be an estimate of the fraction of surface voids that contain ammonia not the total void fraction of the particles themselves. The scatter in this predicted value however leads one to believe this parameter should be experimentally determined.

The reaction rate coefficient, k_R , was also predicted by the computer model. From the average values of this parameter found in Table 11, k_R shows some dependence on temperature but little if any dependence on the pH. At 30°C, the average values for k_R are approximately 0.15 - 0.3 min⁻¹, and at 45°C the average value is approximate 1.1 min⁻¹. This increase in k_R with temperature is typical of a reaction rate coefficient. Usually, this temperature dependent data can be used to find an activation energy for the reaction using an Arrhenius equation, however, this data is too inconclusive to determine the activation energy with any kind of accuracy. Also, the process of converting the solid ammonium sulfite to dissolved gaseous ammonia is likely to involve more than one step, and it is not clear that the reaction step, or which reaction step, is rate controlling.

The fraction of weakly bound or absorbed ammonia in the solid ash, f , was also predicted by the model. Like the effective

void fraction, this f value should have been fairly constant for all the experiments. From the average values in Table 11, the fraction f was found to be approximately 0.61 - 0.7 for the 30°C experiments, which is fairly consistent. However, for the higher temperature experiments, the f increased to an average of 0.8 for the pH of 10 experiments and an average of 0.5 for the pH of 11 experiments. This change in the fraction of weakly bound ammonia in the solid with pH and temperature cannot be explained. The limited amount of experiments is not enough to quantify this value efficiently. The major result this data shows, then, is that the amount of weakly adsorbed ammonia in the ash is at least 50% of the total initial ammonia found in the solid.

The average values of the K_La predicted by the model were fairly consistent for the low temperature experiments at about 0.021 - 0.023 min⁻¹. The 45°C temperature experiments, however, showed more scatter, but overall increased to approximately 0.1 - 0.4 min⁻¹ average. The increase in the K_La with temperature can be associated with a correlation found in the literature for a similar system in which oxygen is absorbed in various aqueous solutions in a bubble column [38]. The K_La is correlated with parameters such as the viscosity, density, diffusion coefficient, and Henry's Law coefficient. Since these parameters have some dependence on temperature, when the temperature is increased, the correlation predicts a corresponding increase in the K_La value. Therefore, an

approximately 90% increase in the average K_La values with temperature over a 15°C range is not atypical.

4.6. Quantitative Conclusions.

The mass transfer model of the ammonia regeneration system predicts the ammonia concentration in the liquid phase. The model showed that the ammonia is most probably removed from the ash into the gas phase through the mechanisms presented in Sections 4.1-4.4. This model predicted 95% removal of the ammonia from the reactor through the air stripping within 45 minutes for a reaction under conditions of 45°C, pH of 11, 100g/L solids loading and 80 scfh nominal air flow rate. The model showed relatively good fit to the data even though 5 parameters in the material balance equations were unknowns. The major results based on the model are given below.

1) A solid dissolution model was determined for ammonia transfer into the liquid phase in which two types of ammonia are postulated to exist in the solid ash. One type of ammonia is strongly bound (ammonium sulfite) and is transformed into a weakly bound ammonia through a first order reaction mechanism. The weakly bound ammonia (adsorbed ammonia) is assumed to dissociate immediately when the ash is placed into the water.

2) A peak in the experimental data, which occurs in the first 10-15 minutes of the experiment, is predicted well by this mass transfer rate model, in 12 cases out of a total of 14 experimental runs modeled.

3) The model predicted the time required to convert the ammonium sulfite to the adsorbed ammonia, the time required for all the ammonia to transfer from the solid-to-liquid phase, and the time required for all the ammonia to be removed from the reactor. These data generally predict short, approximately 11 minutes or less, conversion times for the ammonium sulfite and the total ammonia transfer to the liquid phase at the high temperature (45°C). For 95% removal of ammonia from the reactor, the model predicted a required 79 min or less for all data at 45°C and 210 min for all the data at 30°C. Therefore, the higher temperature would be much preferred to perform the ammonia regeneration in as short a time as possible.

4) The model tends to predict a faster ammonia removal from the liquid to the gas phase in the reactor after the initial peak. The assumptions of perfect mixing in the gas and liquid phases may be incorrect and may be the cause of this error in the model predictions.

5) The unknown parameters in the model: $K_L a$, $k_s a_s$, f , ϵ_{ps} , and k_R , did not seem dependent on the solids loading or the air flow rate in the reactor.

6) The model did not predict a constant effective void fraction, ϵ_{ps} , in the solid particles. The range of possible values for the ϵ_{ps} is 0.001 - 0.023.

7) The model predicts at least 50% of the ammonia initially in the solid ash to be in the form of adsorbed, or weakly bound, ammonia.

8) The solid-liquid mass transfer coefficient, $k_s a_s$, is dependent on both temperature and pH. The $k_s a_s$ nearly doubled as the temperature increased from 30 to 45°C and increased by 83% as the pH is increased from 10 to 11.

9) The reaction rate coefficient for the strongly bound ammonia transfer to the weakly bound ammonia, k_R , is very dependent on temperature and increased approximately 80% with the temperature increase from 30 to 45°C.

10) The gas-liquid mass transfer coefficient, $K_L a$, is approximately constant for the lower temperature experiments but showed some scatter in the higher temperature experiments. A strong dependence of this parameter on the temperature is seen by the approximately 90% increase in $K_L a$ when the temperature is increased from 30 to 45°C.

5. SUMMARY AND CONCLUSIONS

A novel batch-type ammonia regeneration system was designed to recover ammonia from a flue gas desulfurization solid waste. The regeneration system involves ammonia dissolution from the solid into an aqueous phase which is air stripped to recover the ammonia as a gas. Various parameters affecting this dissolution/stripping process were investigated through experimentation in a laboratory scale reactor of one liter liquid capacity. These experimental parameters include temperature, pH, solids loading, and air flow rate. The ranges studied for these parameters are 1) temperatures of 30°C and 45°C, 2) a pH of 10 and 11, 3) solids loadings of 50 and 100 grams/liter, and 4) air flow rates of 18 and 33 liters/liter-min.

The ammonia regeneration process is modeled using material balance equations for each of the three phases: solid ash, liquid, and gas, in which the ammonia was found during experimentation. The model resulted in a set of four first order ordinary differential equations. The unknown parameters in the model are (1) the solid-liquid mass transfer coefficient, $k_s a_s$, (2) the effective void fraction in the solid particles, ϵ_{ps} , (3) the reaction rate coefficient for the transfer of ammonia from the strongly bound species to the weakly bound species, k_R , (4) the fraction of total ammonia in the solids that is weakly bound, f , and (5) the volumetric gas-liquid mass transfer coefficient, $K_L a$.

The computer model optimized on the best values of these unknown parameters for each experiment.

The overall results of the experimentation of this ammonia regeneration process demonstrated that the experimental apparatus could regenerate up to 95% ammonia in no more than 45 minutes with a pH of 11, a temperature as low as 45°C, a solids loading of 100 g/L, and with easily obtained air flow rates of approximately 33 liters/liter-min, which produces a relatively low pressure drop through the system. The modeling results predicted similar ammonia regeneration results and were found to be in relatively good agreement for 12 out of 14 of the experiments modeled.

From the experimental data, the ammonia was observed to release relatively slowly into the liquid phase causing a delayed peak in the ammonia concentration measured in the liquid phase. This peak generally occurred in the first 10 to 15 minutes of the experiment. From the experimental observations of the shape of this peak, an ammonia dissolution model was postulated to explain this slow release into the liquid. The ammonia was assumed to be held in the solid in two forms. One part of the ammonia was weakly bound, presumed to be adsorbed ammonia, and the second part was strongly bound and assumed to be the ammonium sulfite. The mass transfer model considered the adsorbed ammonia released instantaneously into the liquid within the solid pores, while the strongly bound ammonia was first transferred by a first order reaction into the weakly bound

ammonia before release into the liquid. The model was made into a fortran program which was used to predict the concentrations of ammonia in each of the two solid phases as well as the liquid and gas phases. The model also predicted the mass transfer parameters not found by experimentation by a least squares fit to the experimental data. These predicted parameters were correlated with the experimental parameters of temperature, pH, gas flow and solids loading to determine which mass transfer parameters controlled the regeneration process during the experiment.

Based on these experimental and model results, the following conclusions can be made about this system.

1) Based on the equilibrium system of ammonia in aqueous solutions, a $\text{pH} \geq 11$ is needed to insure that the ammonia is completely in the non-ionized, or NH_3 , form in the liquid phase. This form is necessary for the experimental system because the NH_3 ammonia is the only ammonia form that can be desorbed into the stripping air of the reactor.

2) The model tended to predict a faster ammonia removal from the liquid to the gas phase in the reactor after the initial peak. The incorrect assumptions of perfect mixing in the gas and liquid phases seemed to cause this error in the model predictions.

3) The model parameters $K_L a$, and $k_s a_s$ did not seem strongly dependent on the solids loading or the air flow rate in the reactor. However, the experimental results showed that an increase in the air flow rate from 40 to 80 scfh reduced the

ammonia regeneration time by approximately 60 minutes in some cases. These results suggest that the stripping process may not be rate controlling, but that the solids dissolution and ammonia transfer to the liquid phase processes may be the controlling steps.

4) At low temperature, a high solids loading takes longer to regenerate the ammonia to 95% removal than at the low solids loading. However, at the higher temperature, the solids loading doesn't seem to have a strong effect on the regeneration rate. The predicted model parameters, though, did not reflect any significant change with a change in solids loading at the low or high temperature.

5) The model requires the knowledge of the effective void fraction within the solids. As this value is not available, it was considered as an unknown parameter for each experimental run. The values were found to range from 0.001 - 0.023, which suggests the particles are relatively impervious to water. It was expected that the ash samples used in the experiments, all from the same source, would have the same effective void fraction. It is not clear why the values, as obtained here, exhibit such a wide range.

6) The model predicted at least 50% of the ammonia initially in the solid ash to be in the form of adsorbed, or weakly bound, ammonia. The experimental results reflected this to be true because the peak in the liquid concentration data was

significantly below the level expected if all the ammonia were instantaneously desorbed into the liquid.

7) The solid-liquid mass transfer coefficient, $k_s a_s$, nearly doubled as the temperature increased from 30 to 45°C and increased by 83% as the pH rose from 10 to 11. The experimental data reflected this change by a much steeper slope before and after the peak in the data at the higher temperature.

8) The reaction rate coefficient for the strongly bound ammonia transfer to the weakly bound ammonia, k_R , increased approximately 80% with the temperature increase from 30 to 45°C. The temperature effects on the peak in the data could also be caused by this parameter increasing with temperature.

9) The gas-liquid mass transfer coefficient, $K_L a$, predicted by the model, is constant for the lower temperature experiments but showed some scatter in the higher temperature experiments. A strong dependence of this parameter on the temperature is seen by the approximately 90% increase in $K_L a$ when the temperature is increased from 30 to 45°C. The model seemed to predict a higher $K_L a$ than the experimental results needed and the predicted ammonia concentration in the liquid was seen to decrease much quicker than the experimental values.

6. FUTURE WORK

Based on the experimental and model results, future work, which is needed to better understand the mechanisms of the ammonia regeneration system, should include the following tasks.

- 1) Independent determination of the effective void fraction in the solids.
- 2) An alternative method should be found to measure the initial ammonia concentration in the solid ash. This method's results can then be compared with the EPA distillation/titration procedure.
- 3) Independent determination of the gas holdup fraction.
- 4) Examination of the reactor system and parameters over a wider range than presented in this paper.

7. TABLE OF NOTATION

- a = Specific surface area of the gas-liquid interface, cm^2/cm^3
- a_s = Specific external surface area of the solids, cm^2/g
- b = $[C_L/(H \cdot C_g)]$
- C_A = Bulk concentration of ammonia in the liquid phase, $\text{gmoles}/\text{cm}^3$
- C_A^* = Concentration of ammonia in the liquid phase in equilibrium with the gas phase, moles/cm^3
- $C_{A(\text{eq})L}$ = Equilibrium concentration of ammonia in the liquid, moles/cm^3
- C_{Ap} = concentration of ammonia in the liquid occupying the pores, moles/cm^3
- C'_{Apo} = Concentration of weakly bound ammonia initially in the water inside the pores of the ash particles, moles/cm^3
- C''_{Apo} = Concentration of strongly bound ammonia initially in the water inside the pores of the ash particles, moles/cm^3
- $C_{A(\text{eq})s}$ = Equilibrium concentration of ammonia in the solid, $\text{moles NH}_3/\text{grams-NH}_3$ free ammonia
- C'_{As} = Ammonia concentration in the solid found as weakly bound or adsorbed ammonia, moles/cm^3
- C''_{As} = Ammonia concentration in the solid found as strongly bound or as ammonium sulfite, moles/cm^3
- C_{As0} = Total initial ammonia concentration in the solid, moles/cm^3
- C_g = Total concentration of gas ($C_{g(\text{air})} + C_{gA}$), moles/cm^3
- C_{gA} = Concentration of ammonia in the gas phase, moles/cm^3
- C_L = Concentration of water in the reactor, moles/cm^3

ϵ_s	= Effective void fraction within the solids
f	= Fraction of the total initial ammonia that is weakly bound
H	= Henry's Law constant
H_g	= Gas loading, dimensionless
K_L	= Overall mass transfer coefficient for the liquid-gas interface, cm/min
k_R	= Reaction rate constant for the first order conversion of the strongly bound ammonia to the weakly bound ammonia, cm ³ /min
k_s	= Overall mass transfer coefficient between the particles and the surrounding liquid phase, cm/min
N_{As}	= Flux of ammonia from solid-to-liquid phase, moles/(cm ² -min)
N_{AG}	= Flux of ammonia from liquid-to-gas phase, moles/(cm ² -min)
r''_{As}	= Reaction rate for conversion of strongly bound ammonia to weakly bound ammonia, moles/cm ³ -min
S_L	= Solids loading, gram/liter
t	= Time, minutes
V_g	= Volume of gas (bubbles) in reactor interacting with liquid, cm ³
V_L	= Liquid volume in reactor, cm ³
V_s	= Volume of the solids whose weight is W_s , cm ³
V_t	= Total volume (liquid + gas) in the reactor, cm ³
W_A	= Molar flow rate of ammonia leaving the reactor, moles/min
W_s	= Weight of solids on an ammonia-free basis, g

x_A^* = Mole fraction of ammonia in the liquid phase in equilibrium with the gas phase

y_A = Mole fraction of ammonia in the gas phase

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APPENDIXES

APPENDIX A.
EXPERIMENTAL METHODS

Methods for Chemical Analysis of water and wastes
(Revised MARCH 1983) U.S. EPA, CINCINNATI, OHIO
NTIS: PB84-128677

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric - Distillation Procedure)

STORET NO. Total 00610

Dissolved 00608

1. Scope and Application
 - 1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
 - 1.2 The method covers the range from about 0.05 to 1.0 mg $\text{NH}_4\text{-N}$ l for the colorimetric procedure, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg. l for the electrode method.
 - 1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
 - 2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
 - 3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
 - 4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
 - 4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
 - 4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

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Issued 1971
Editorial revision 1974

5. Apparatus
 - 5.1 An all-glass distilling apparatus with an 800–1000 ml flask.
 - 5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.
 - 5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm $\pm$ 1.5 mm inside measurement from bottom.
 - 5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.
6. Reagents
 - 6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.
NOTE 1: All solutions must be made with ammonia-free water.
 - 6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg $\text{NH}_3\text{-N}$. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.
 - 6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.
 - 6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.
 - 6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.
NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 3D of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.
 - 6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.
NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).
 - 6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ or 9.5 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ per liter) and dilute to 1 liter.
 - 6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg $\text{NH}_3\text{-N}$). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2 -free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2 -free distilled water.
NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

- 6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3 , oven-dried at 140°C, and diluting to 1000 ml with CO_2 -free distilled water.
- 6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.
- 6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:
- Sodium thiosulfate (1/70 N): Dissolve 3.5 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.
 - Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO_2 in distilled water and dilute to 1 liter.

7. Procedure

- 7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.
- 7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

- 7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

- 7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

- 7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 , matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH ₃ -N	mg NH ₃ -N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH₃-N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 0.28 \times 1,000}{S}$$

where:

A = ml 0.02 N H₂SO₄ used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 1,000}{D} \times \frac{B}{C}$$

where:

A = mg NH₃-N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l NH}_3 - \text{N} = \frac{500}{D} \times A$$

where:

A = mg NH₃-N/l from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.21	0.122	-5.54	-0.01
0.26	0.070	-13.12	-0.03
1.71	0.244	-0.46	-0.01
1.92	0.279	-2.01	-0.04

(FWPCA Method Study 2, Nutrient Analyses)

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NITROGEN, AMMONIA

Method 350.3 (Potentiometric, Ion Selective Electrode)

STORET NO. Total 00610

Dissolved 00608

1. Scope and Application
 - 1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
 - 1.2 This method covers the range from 0.03 to 1400 mg $\text{NH}_3\text{-N/l}$. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.
2. Summary of Method
 - 2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
 - 2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.
3. Sample Handling and Preservation
 - 3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
 - 4.1 Volatile amines act as a positive interference.
 - 4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.
5. Apparatus
 - 5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
 - 5.2 Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.
 - 5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
6. Reagents
 - 6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.
 - 6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).
 - 6.3 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg $\text{NH}_3\text{-N}$. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

Issued 1974

* Approved for NPDES following preliminary distillation (method)
350.3-1 350.2

* This method added in March 1974 as a 350.2 EPA method

- 6.4 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg $\text{NH}_3\text{-N}$. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask.

NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350.1).

7. Procedure

- 7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

- 7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 2: The pH of the solution after the addition of NaOH must be above 11.

Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

- 7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg $\text{NH}_3\text{-N/l}$ on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

- 7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

- 7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample in 150 ml beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg $\text{NH}_3\text{-N/l}$.

8. Precision and Accuracy

- 8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg $\text{NH}_3\text{-N/l}$, standard deviations were ± 0.038 , ± 0.017 , ± 0.007 , and ± 0.003 , respectively.

- 8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg $\text{NH}_3\text{-N/l}$, recoveries were 96% and 91%, respectively.

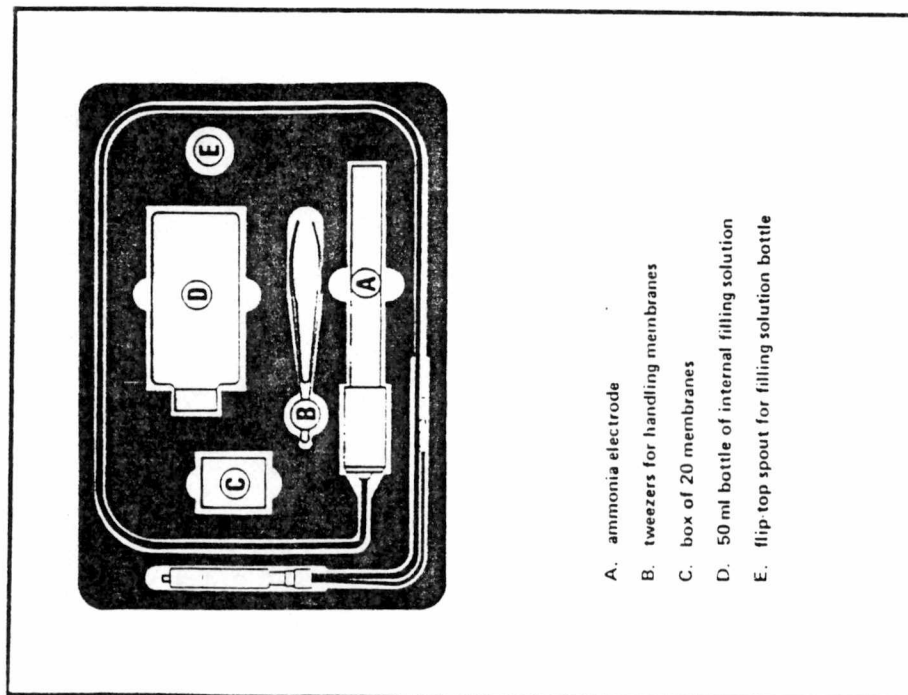
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ORION
RESEARCH

INSTRUCTION MANUAL
ammonia electrode
model 95-10

figure 1
contents of storage box



general information

introduction

The Model 95-10 Ammonia Electrode allows fast, simple, economical and accurate measurements of dissolved ammonia in aqueous solutions. This gas sensing electrode can also be used to measure the ammonium ion after conversion to ammonia, or organic nitrogen after Kjeldahl digestion of the sample. Sample color and turbidity do not affect the measurement, and samples need not be distilled. Anions, cations, and dissolved species, other than volatile amines, do not interfere.

All apparatus and solutions required for measurement, general analytical procedures, electrode characteristics and electrode theory are discussed in this manual. Methods are given for measuring ammonia in solutions that wet the membrane and for organic nitrogen measurements.

required equipment

meter — Orion Model 701A digital pH/mv meter or Model 901 ionalyzer for precision laboratory measurements, or Orion Model 407A specific ion meter for laboratory, field, or plant measurements.

magnetic stirrer — recommended for laboratory measurements.

graph paper — (for use with digital pH/mv laboratory meters) 4-cycle semilogarithmic paper for preparing calibration curves.

required solutions

distilled or deionized water — water must be ammonia-free. Pass distilled or demineralized water through an ion-exchange column containing a strongly acidic cation exchange resin, such as Dowex 50W-X8.

10 M NaOH — to adjust solution pH to the operating range of the electrode, add 1 ml of 10 M NaOH to each 100 ml of standard or sample. To prepare 10 M NaOH, add 40 g reagent-grade NaOH to 80 ml distilled water in a 100-ml volumetric flask, dissolve, and dilute to volume with distilled water, or dilute 80 ml of commercially available 50% NaOH to 100 ml with distilled water.

standard solution — 0.1 M ammonium chloride standard, Orion Cat. No. 95-10-06, or 1000 ppm as nitrogen standard, Orion Cat. No. 95-10-07. To prepare a 0.1 M ammonium chloride standard from laboratory supplies, add 0.535 g reagent grade NH_4Cl to 50 ml distilled water in a 100-ml volumetric flask, stir to dissolve, and dilute to volume with distilled water. To prepare a 1000 ppm as N standard from laboratory supplies, add 0.382 g reagent-grade NH_4Cl to 50 ml distilled water in a 100-ml volumetric flask. Stir to dissolve and dilute to volume with distilled water.

internal filling solution — to fill the electrode, Orion Cat. No. 95-10-02.

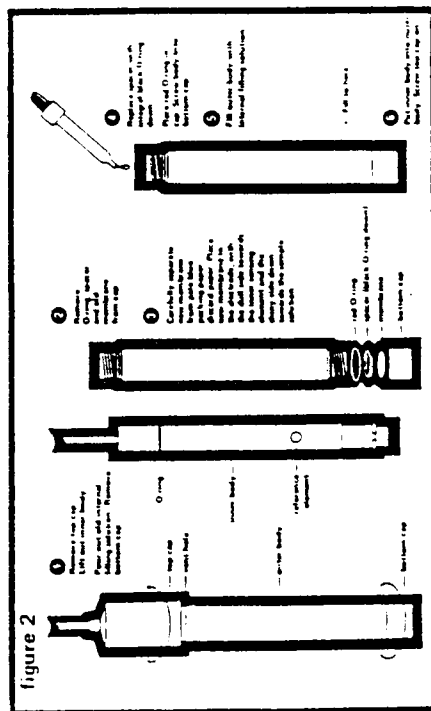
pH 4 buffer (with 0.1 M Cl^- added) — for checking inner body operation. Prepare 200 ml pH 4 buffer from Orion Cat. No. 91-00-04 buffer powder and add 1.16 g reagent-grade NaCl. Dissolve solid and store the buffer for repeated use.

pH 7 buffer (with 0.1 M Cl^- added) — for checking inner body operation. Prepare 200 ml pH 7 buffer from Orion Cat. No. 91-00-07 buffer powder and add 1.16 g reagent-grade NaCl. Dissolve solid and store the buffer for repeated use.

electrode assembly

Assemble the electrode according to instructions in figure 2. The electrode is shipped dry and without a membrane in place. After assembly, allow the electrode to stand for thirty minutes in internal filling solution.

Avoid touching the membrane during assembly; this might affect the membrane's hydrophobic properties, causing shortened membrane life. Use the tweezers provided. After assembly the membrane should be slightly distended by the inner body of the electrode. A membrane will last from one week to several months depending on usage. (Membrane failure is characterized by a shift in electrode potential, drift, and poor response. See the troubleshooting check list section in the centerfold. Membrane failure may be apparent on visual inspection as dark spots or discoloration of the membrane.)



electrode storage

Between measurements, keep the electrode tip immersed in a 10^{-4} M or 10 ppm standard with added NaOH. For low-level measurements, keep the electrode in a pH 4 buffer between measurements. Do not store overnight in pH 4 buffer.

For storage overnight or over a weekend, the electrode tip should be immersed in a 0.05 M standard without added NaOH. If the electrode is stored indefinitely, disassemble completely and rinse the inner body, outer body, and bottom cap with distilled water. Dry and reassemble electrode without filling solution or membrane. After dry storage, follow procedure in electrode assembly, page 4.

If the electrode is accidentally left in the air and erratic results are obtained, the space between the inside of the membrane and the sensing element may be dry. Wet the membrane with internal filling solution by unscrewing the top cap of the electrode and gently pumping the cable and inner sensing element up and down several times.

connecting electrode to meter

The large input jack and the small pin jack at the end of the electrode cable should be connected to the input connector and to the reference connector, respectively, on the meter. No external reference electrode is required with the ammonia electrode. Be sure to use an electrode holder that keeps the NH_3 electrode at a 20° angle to prevent air entrapment.

checking electrode slope with 701A digital pH/mV meter or 901 ionalyzer

NOTE: Check electrode slope daily.

1. Put 100 ml distilled water and 1 ml 10 M NaOH solution into a 150 ml beaker. Turn function switch to REL MV position. Place electrode in the solution. Use magnetic stirring throughout the procedure.
2. Pipet 1 ml 0.1 M or 1000 ppm standard into the solution. Set the reading to 000.0 by adjusting the calibration control on the 701A. With the 901, press CLEAR/READ MV, then SET CONC.
3. Add 10 ml 0.1 M standard or 1000 ppm standard to the solution. Correct electrode operation is indicated by a reading of -57 ± 3 mV, assuming the solution temperature is between 10° and 25°C . If the change in potential is not within this range, see the troubleshooting check list in the centerfold.

checking electrode slope with 407A specific ion meter

NOTE: Check electrode slope daily.

- 1 Put 100 ml distilled water into a 150 ml beaker. Add 1 ml 10 M NaOH. Place electrode in the solution. Turn function switch to "X". Stir throughout the procedure.
- 2 Pipet 1 ml 0.1 M or 1000 ppm standard into the solution. Turn the calibration control until the needle points to "1" on the red logarithmic scale.
- 3 Add 10 ml 0.1 M or 1000 ppm standard. Turn the temperature compensator until the needle points to "10" on the red logarithmic scale. Turn the slope indicator dial until the arrow on the temperature compensator points to the temperature of the solution. Read the percent electrode slope on the lower scale of the dial. Correct electrode operation is indicated by a percent slope between 90 and 100. If the slope is outside this range, see troubleshooting check list in the centerfold.

checking inner body with 701A digital pH/mv meter or 9011 ionalyzer

NOTE: This is a troubleshooting procedure. If electrode slope is found to be low during operation, disassemble electrode and check inner body.

Disassemble the ammonia electrode. If the electrode is dry, first soak the glass tip of the inner body in filling solution for at least two hours. Rinse the inner body with distilled water and immerse it in the pH 7 buffer (0.1 M Cl^- added) so that the reference element is covered. Stir throughout the procedure. Turn 901 MODE switch to REL MV. Press CLEAR/READ MV on the 901. Turn function switch of 701A to MV. The absolute mv reading should be between 95±20 mv. Rinse the inner body in distilled water and place in the pH 4 buffer (0.1 M Cl^- added). Watch the change in meter reading carefully. The reading should be greater than +200 mv in less than 30 seconds after immersion in the pH 4 buffer. The meter reading should stabilize in 3 to 4 minutes in the range of +230 to +250 absolute millivolts. The millivolt difference between pH 7 and pH 4 should be greater than 150 mv if the inner body sensing elements are operating correctly.

checking inner body with 407A specific ion meter

NOTE: This is a troubleshooting procedure. If electrode slope is found to be low during operation, disassemble electrode and check inner body.

Disassemble the ammonia electrode. If the electrode is dry, first soak the glass tip of the inner body in filling solution for at least two hours. Rinse the inner body with distilled water and immerse in the pH 7 buffer (0.1 M Cl^- added) so that the reference element is covered. Stir throughout the procedure. Turn function switch to pH. Adjust the calibration knob until the meter needle reads pH 7 (center scale). The meter needle should remain stable.

Rinse the inner body with distilled water and place in the pH 4 buffer (0.1 M Cl^- added). Turn the temperature compensator until the meter needle points to pH 4. If the meter can be calibrated and stabilizes at pH 4.3 to 4 minutes after immersion, the sensing elements of the inner body are operating properly.

using the electrode

units of measurement

Ammonia can be measured in units of moles per liter, parts per million as ammonia, parts per million as nitrogen, or any other convenient concentration unit. See table 1 below.

table 1

concentration unit conversion table		
moles per liter	ppm as N	ppm as NH_3
10^{-4}	1.4	1.7
10^{-3}	14	17
10^{-2}	140	170

sample requirements

Samples and standards should be at the same temperature. A 1°C difference in temperature will give rise to about a 2% measurement error.

In all analytical procedures 10 M NaOH must be added to all samples and standards immediately before measurement. After addition of NaOH, all solutions should fall within a pH 11 to 14 range and have a total level of dissolved species below 1 M. If the total level of dissolved species is above 1 M, see effect of dissolved species, page 23.

measuring hints

Minimize NH_3 loss from sample by:

storing samples according to the above procedure.

using beakers that minimize the ratio of surface area to volume.

keeping beakers containing standards and samples covered between measurements.

adding 1 ml 10 M NaOH to 100 ml sample or standard just before measurement.

Between measurements rinse the electrode with distilled water.

Be sure samples, standards, and electrode are at the same temperature.

Samples and standards should be stirred using a magnetic stirrer. Some magnetic stirrers generate enough heat to change solution temperature. This effect can be minimized by placing a piece of insulating material such as cork or styrofoam beneath the beaker.

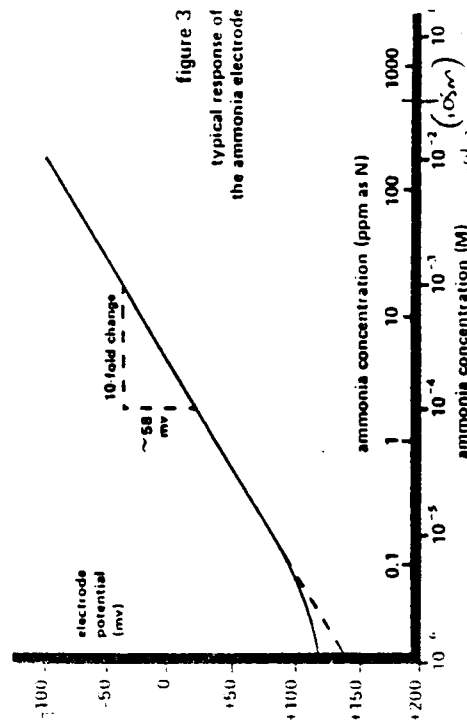
analytical procedures

Direct measurement is a simple, fast method for measuring a large number of samples over a wide range of concentration. Only one meter reading is required for each sample. The temperature of samples and standards must be the same.

Direct measurements are most conveniently made in the 6×10^{-5} M to 1 M ammonia range (1 to 17,000 ppm NH_3 or 0.8 to 14,000 ppm N). See an example of a calibration curve in figure 3. Below 6×10^{-5} M ammonia (1 ppm NH_3 or 0.8 ppm N), the rate of ammonia diffusion through the membrane is slow and the rate of equilibrium between ammonia and ammonium in the internal filling solution is slow. Special low-level direct measurement techniques must be used for such samples. Above 1 M, ammonia diffuses rapidly out of solution. Direct measurement can be used to measure samples above 1 M if samples are diluted.

Direct measurement results can be verified by a known addition procedure. The known addition procedure involves adding a standard of known concentration to a sample solution. From the change in electrode potential before and after addition, the original sample concentration is determined.

Known addition is also a useful method for measuring occasional samples, as the preparation of a calibration curve is not required. As in direct measurement, any convenient concentration unit can be used.



sample storage

If possible, alkaline samples should be measured at once. The rate of ammonia loss at room temperature from a stirred 100 ml basic solution in a 100 ml beaker is about 50% in six hours. If samples must be stored, make them slightly acidic (pH 6) by adding 0.5 ml of 1 M HCl to each liter of sample, and place them in tightly capped vessels. Basify these stored samples with 10 M NaOH just before measurement.

direct measurements using 701A digital pH/mv meter

1. Prepare 10^{-2} M, 10^{-3} M, and 10^{-4} M or 100 ppm, 10 ppm, and 1 ppm standards by serial dilution of the 0.1 M or 1000 ppm standards.
2. Place electrode in the 10^{-3} M or 10 ppm standard. Add 1 ml 10 M NaOH to each 100 ml of standard. Set the function switch to REL MV. Set the reading to 000.0 by adjusting the calibration control. Use magnetic stirring throughout the procedure.
3. Rinse electrode and place in the 10^{-4} M or 1 ppm standard. Add 1 ml 10 M NaOH to every 100 ml of standard. Stir thoroughly. Wait for a stable reading and record.
4. Rinse electrode and place in the 10^{-2} M or 100 ppm standard. Add 1 ml 10 M NaOH to each 100 ml of standard. Stir thoroughly. Wait for a stable reading and record.
5. Plot the millivolt reading (linear axis) against concentration (log axis) on standard 4 cycle semilogarithmic paper. See a calibration curve in figure 3.
6. Rinse electrode and place in sample. Add 1 ml 10 M NaOH to each 100 ml of sample. Stir thoroughly. Record the millivolt reading and determine sample concentration from the calibration curve.
7. Recalibrate every two hours. If ambient temperature has not changed, repeat step 2. If ambient temperature has changed, repeat steps 2-5.

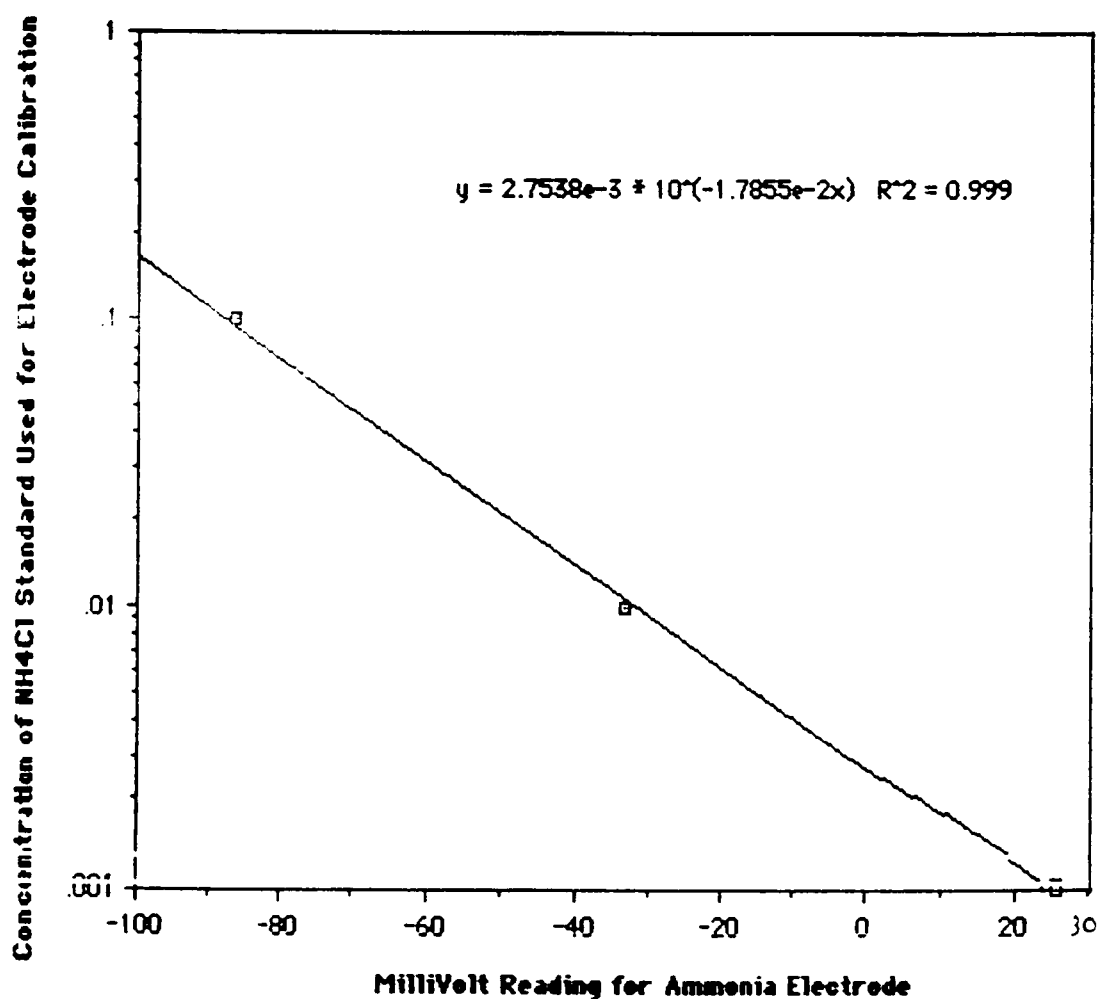
standard calibration method using 901 ionalyzer

1. Prepare a standard solution whose concentration is near the expected sample concentration. If desired, prepare a different standard for checking slope.
2. Turn the MODE switch to CONC. Set the STD VALUE switches to the concentration of the standard. Set the SLOPE switches to the slope of the electrode as determined in the daily electrode check. Set the sign switch to minus.
3. Place electrode in 100 ml of the first standard. Add 1 ml 10 M NaOH. Press HLT/AD/CLEAR MV and wait for a stable reading. Press SET CONC. Rinse electrode.
4. If desired, check the slope by placing electrode in 100 ml of a second standard. Add 1 ml 10 M NaOH. Wait for a stable reading, and slowly adjust the slope switches until the correct concentration is displayed.
5. If low-level measurements are to be made, place electrode in 100 ml distilled water and add 1 ml 10 M NaOH. Wait 4 minutes and press SET BLANK.
6. Rinse electrode and place in 100 ml sample. Add 1 ml 10 M NaOH. Wait for a stable reading and record sample concentration.
7. Recalibrate every two hours. Compensate for any temperature change by increasing the slope setting by 1 mv for every 5°C increase in temperature, then repeat step 3.

APPENDIX B.
EXPERIMENTAL GRAPHS

Calibration Data for the Ammonia Electrode on 6/10/91

Conc, M	mV Readings			Chart Paper Reading
	Before Exp.	After Exp.	Average	
0.100	-90.2	-82.3	-86.3	
0.010	-32.7	-34.0	-33.4	27.6
0.001	26.7	24.5	25.6	94.7



Typical Calibration Curve for the Ammonia Electrode

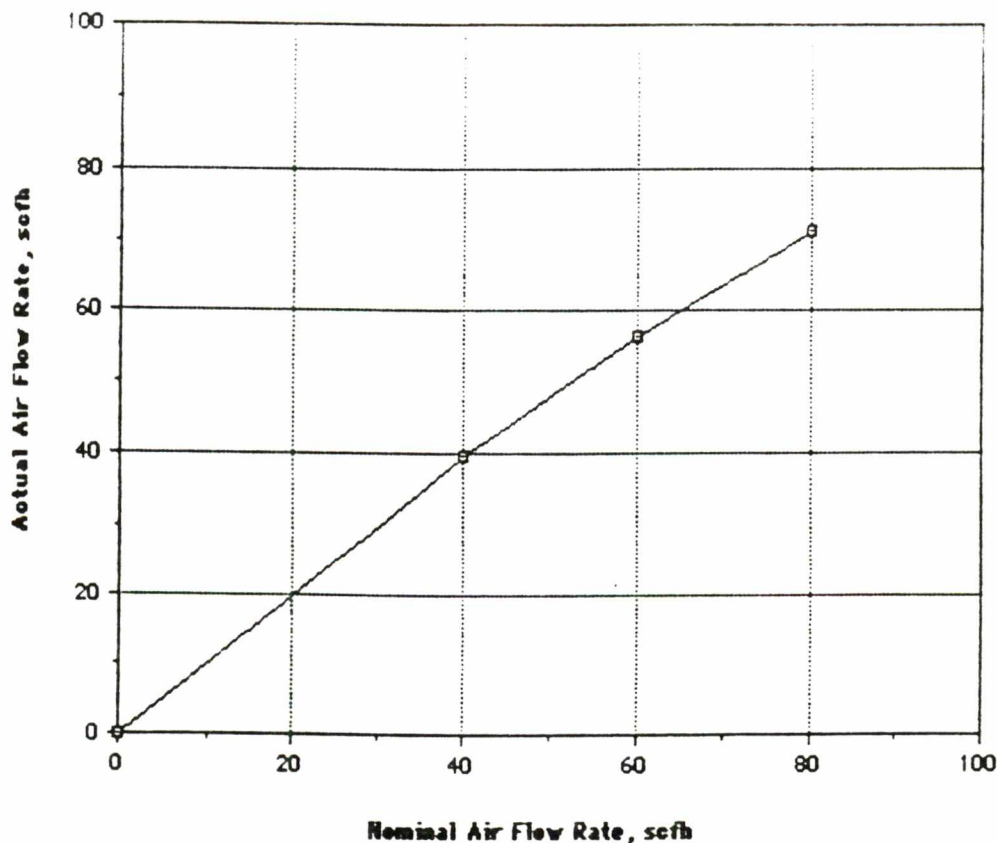
Calibration Data for the Air Flowmeter

Nominal Air Flow Rate, scfh	Time, sec	Volume of Air Through Wet Test Meter, liters	Actual Air Flow Rate, liters/min	Actual Air Flow Rate, scfh
40	115	36	18.75	39.71
40	116	36	18.62	39.44
40	115	36	18.78	39.78
60	108	48	26.67	56.49
60	109	48	26.42	55.96
60	108.5	48	26.54	56.21
60	142	63	26.62	56.38
80	107	60	33.64	71.25
80	107	60	33.64	71.25

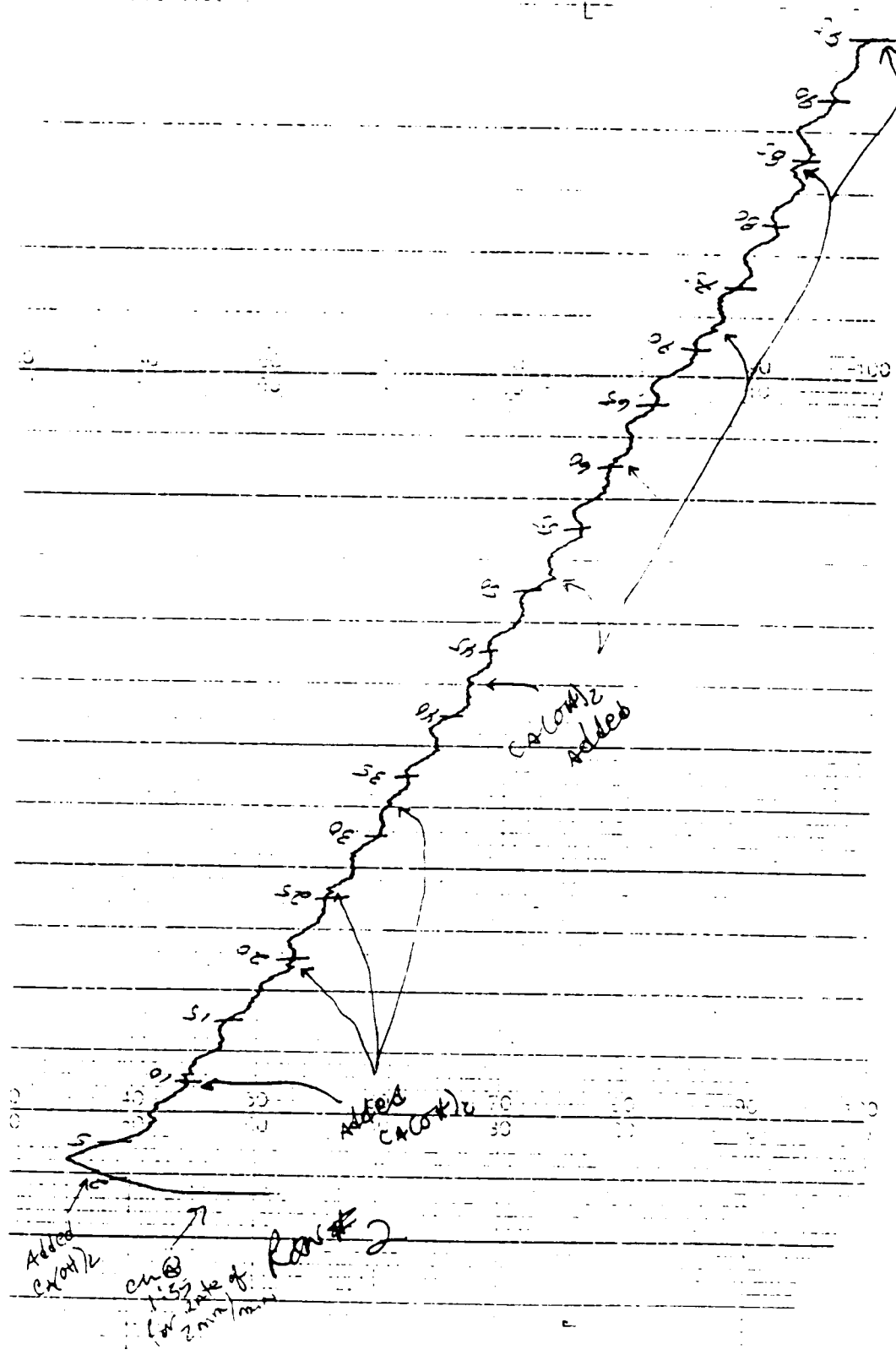
Linear Correlation of data:

$$\text{Nominal flow, scfh} = -10.524 + 2.6805 * (\text{actual flow, l/min})$$

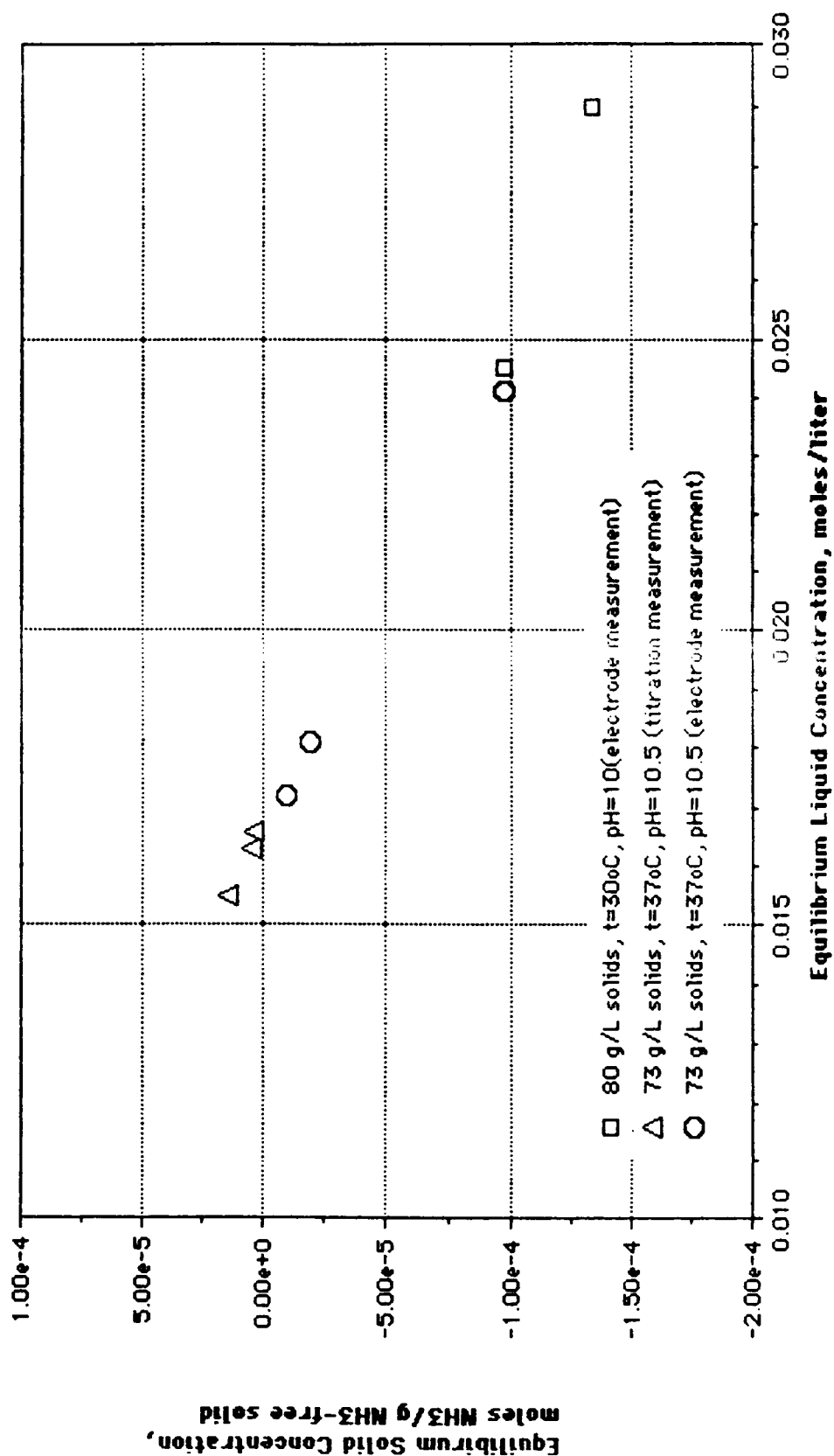
$$R^2 = 0.999$$



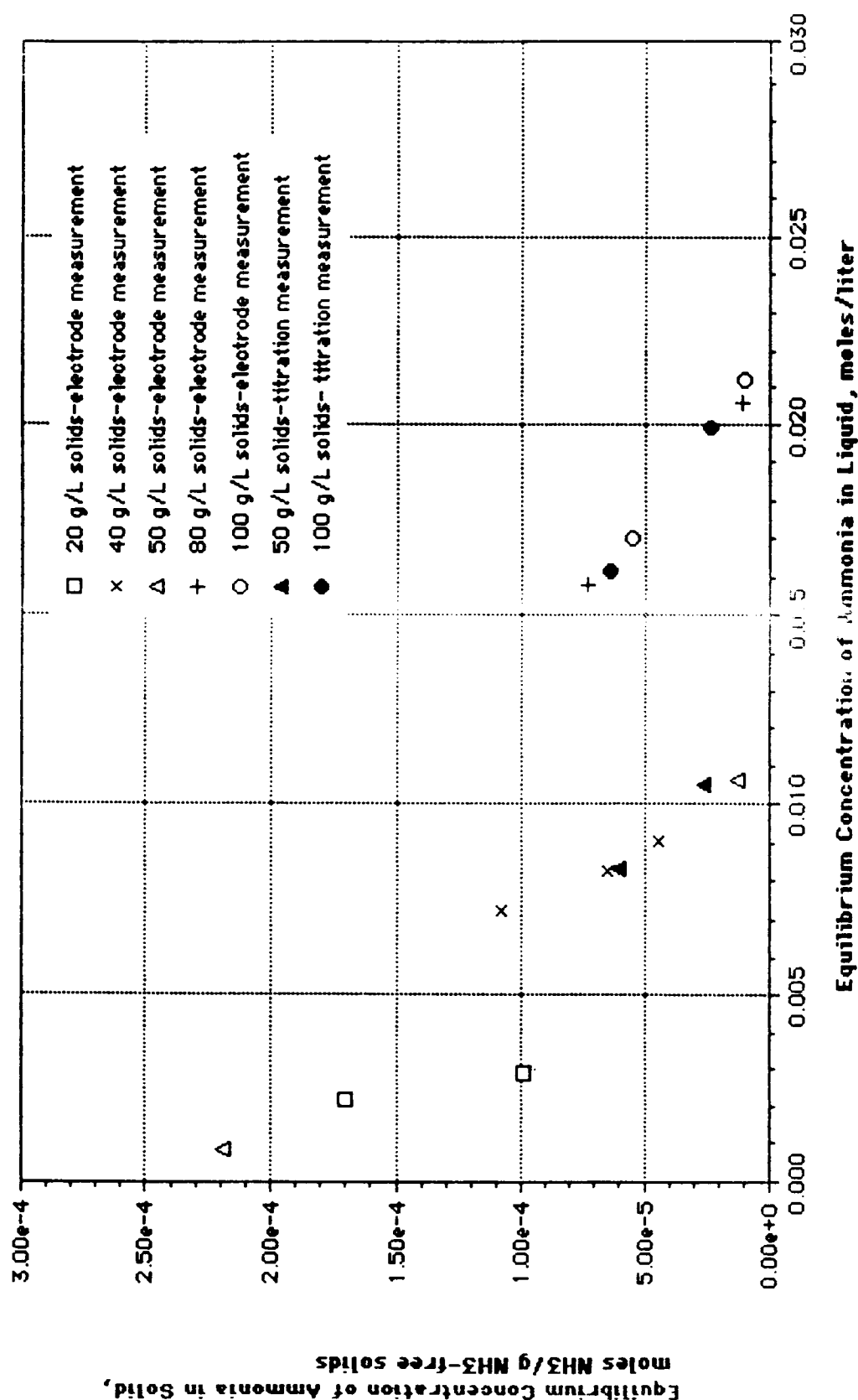
Calibration Curve Showing Approximately Linear Correlation up to about 60 scfh nominal air flow



Example of the Chart Paper Output from the Ammonia Electrode Giving an Experimental Reactor Run

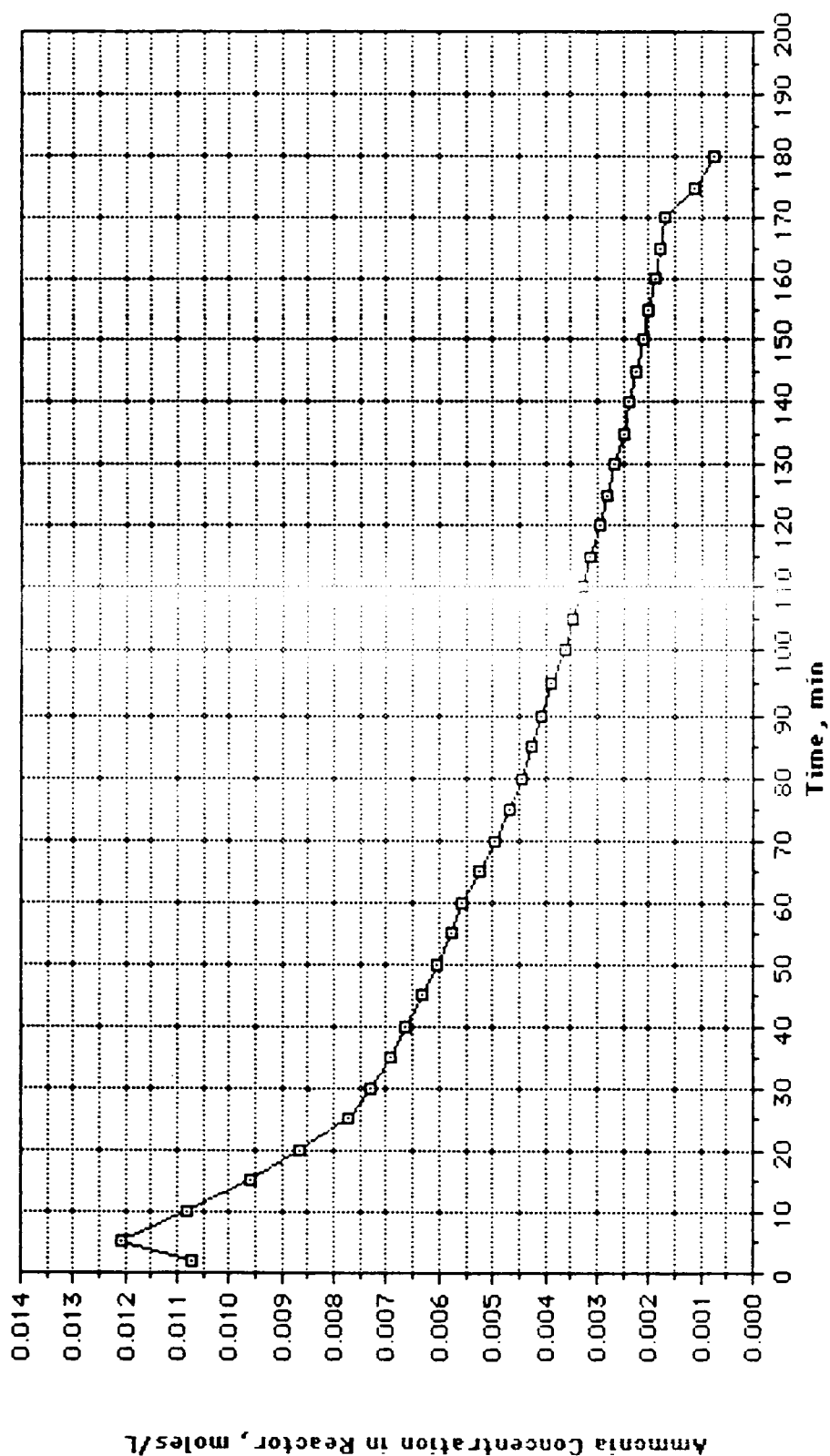


Solid/Liquid Equilibrium Data for Temp = 30 & 37°C,
pH = 10 & 10.5, and solids = 80 & 73 g/L

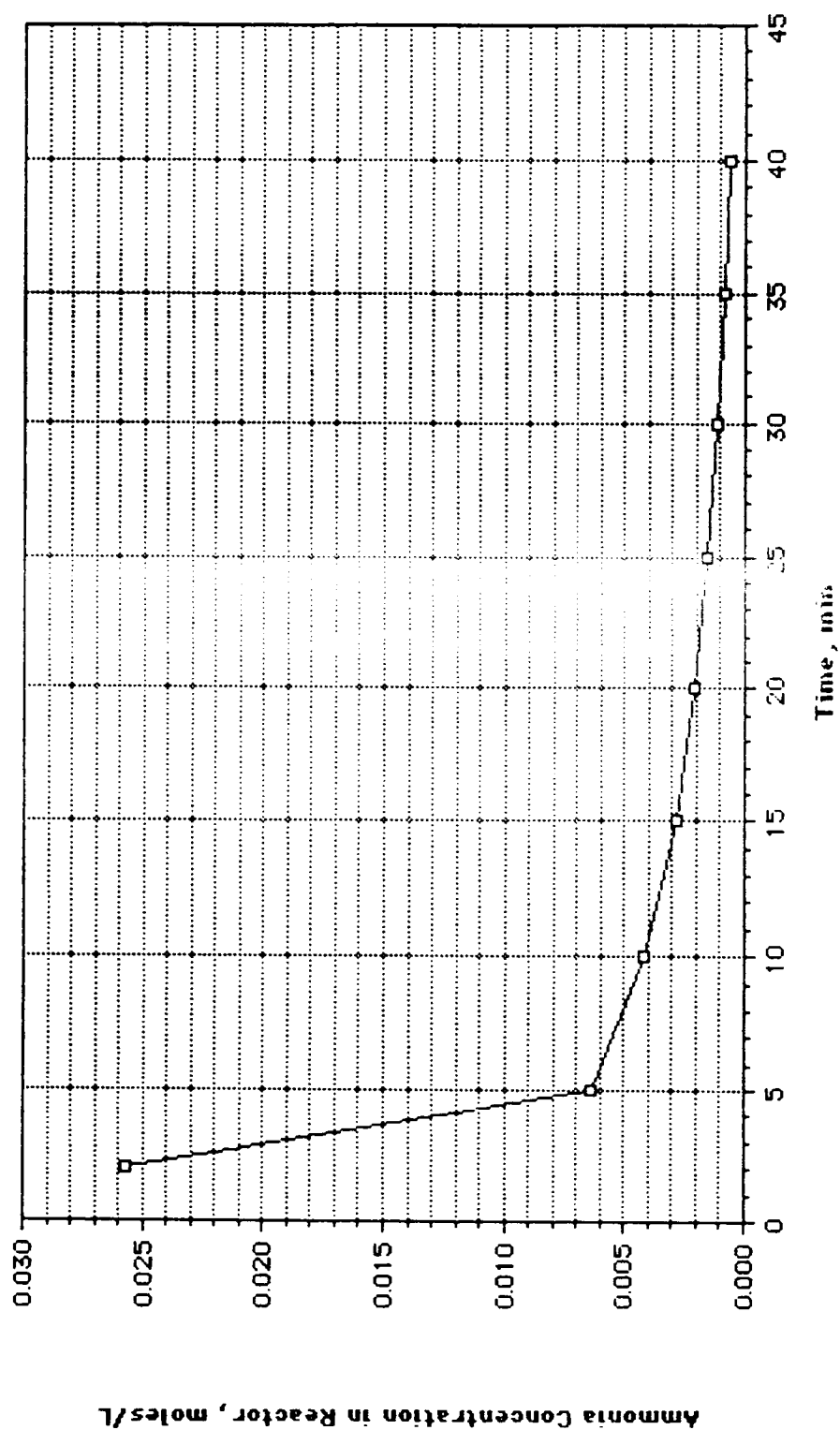


Solid/Liquid Equilibrium Data for Temperature = 45 C and pH = 10,
(data from both electrode and titration measurements)

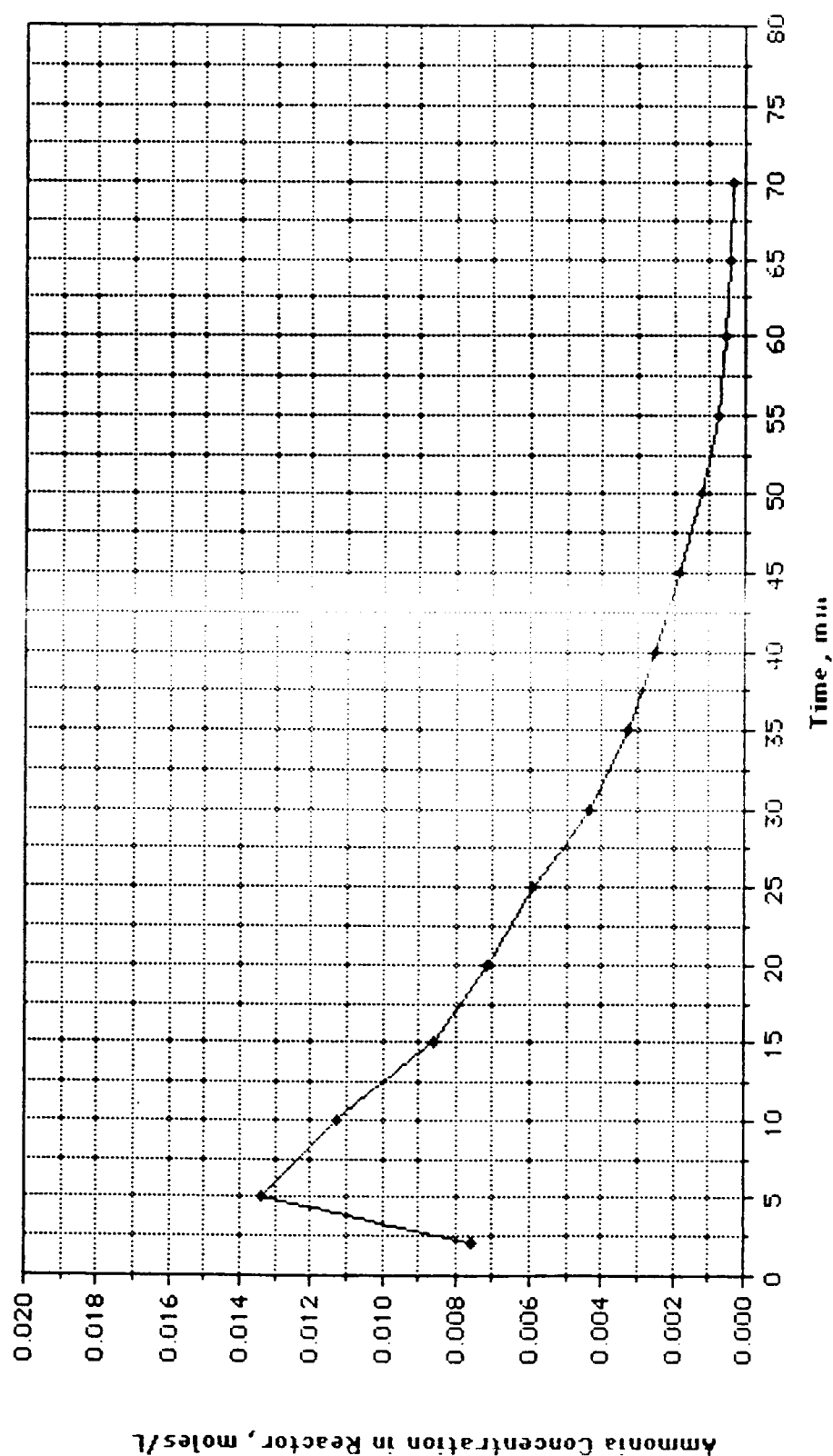
Anomaly Reactor Graphs



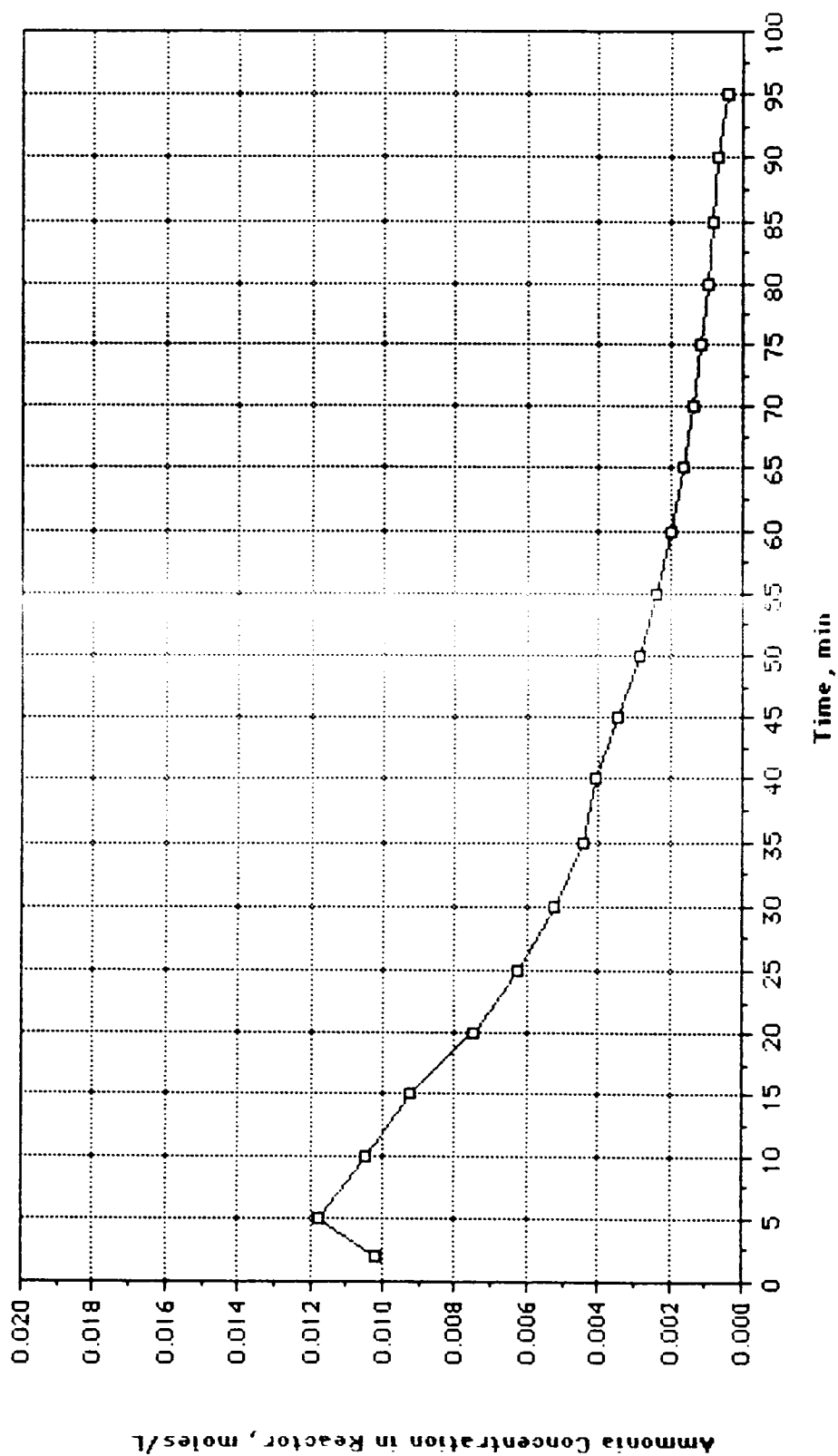
Reactor Data for 12/2/91 under conditions:
 300C, pH=10, 50 g/L solids, 40 scfh nominal air flow rate,
 $[NH_3]_i=0.00020672$ moles/g NH_3 -free solids



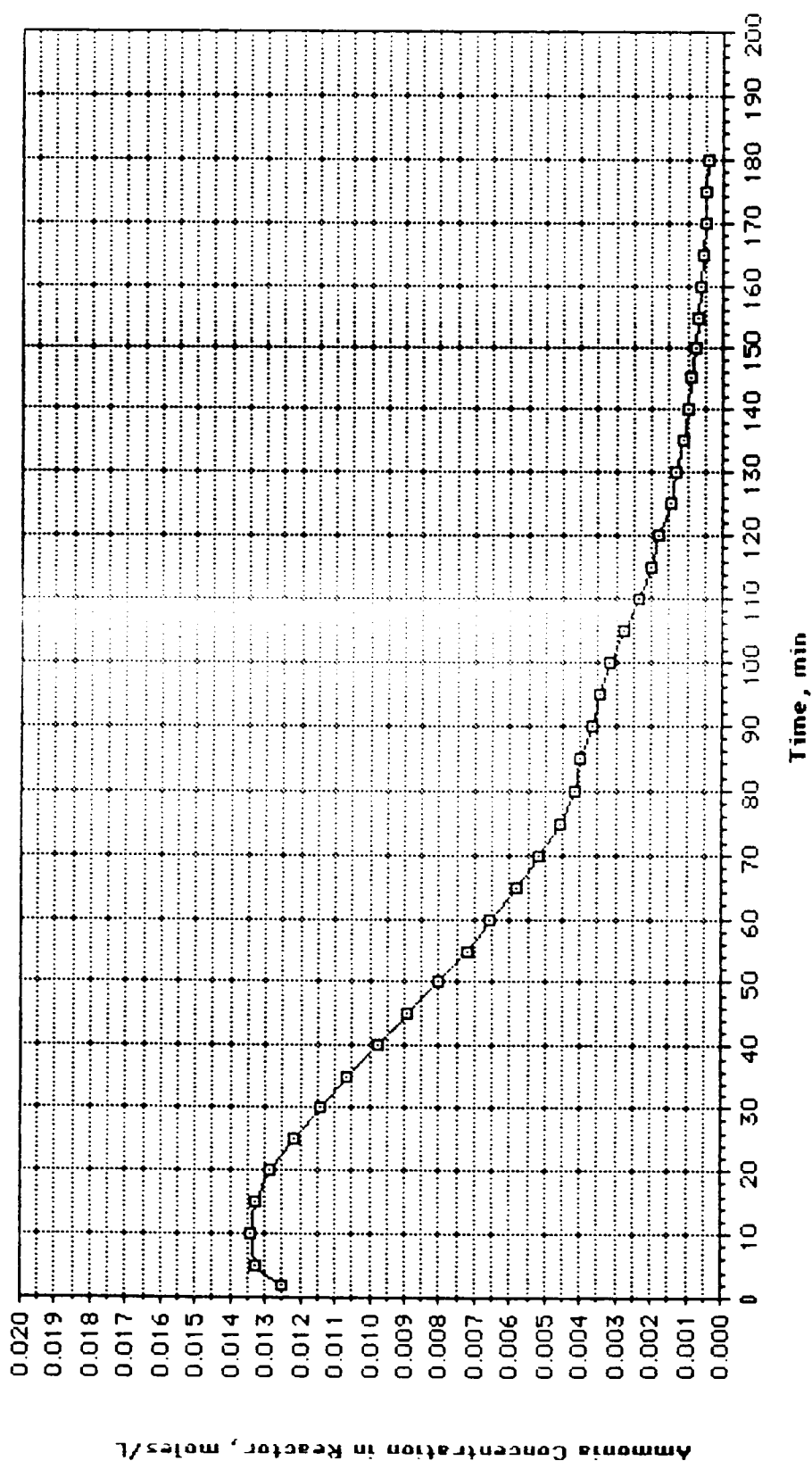
Reactor Data from 12/3/91 #2 under conditions:
30°C, pH = 11, 100g/L solids, 40 scfh nominal air flow rate,
[NH₃]_i = 0.00020471 moles NH₃/g NH₃-free solids



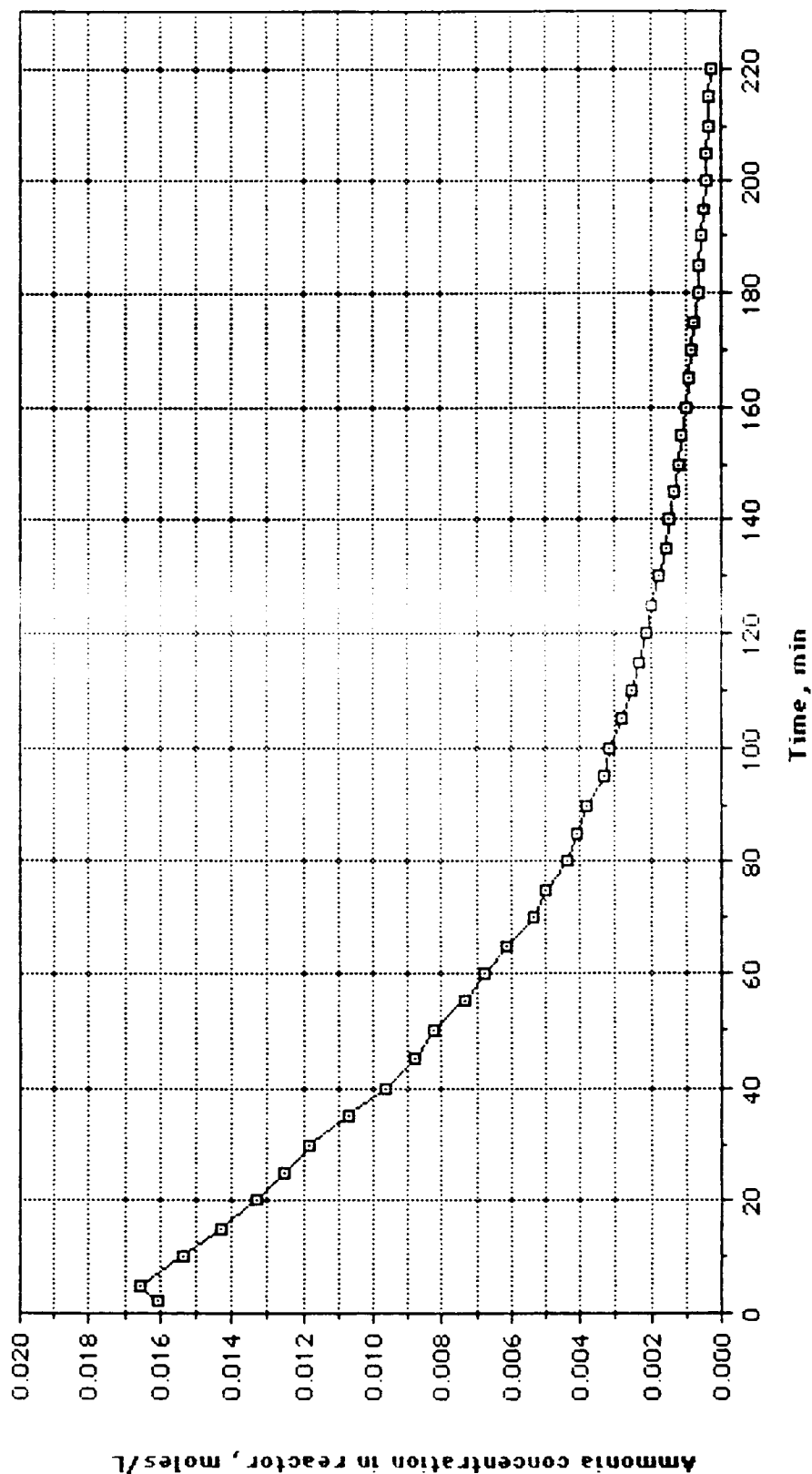
Reactor Data for 12/5/91 #2 under conditions:
 45°C, pH=11, 50 g/L solids, 60 scfh nominal air flow rate,
 $[NH_3]_i = 0.00020169$ moles/g NH_3 -free solids



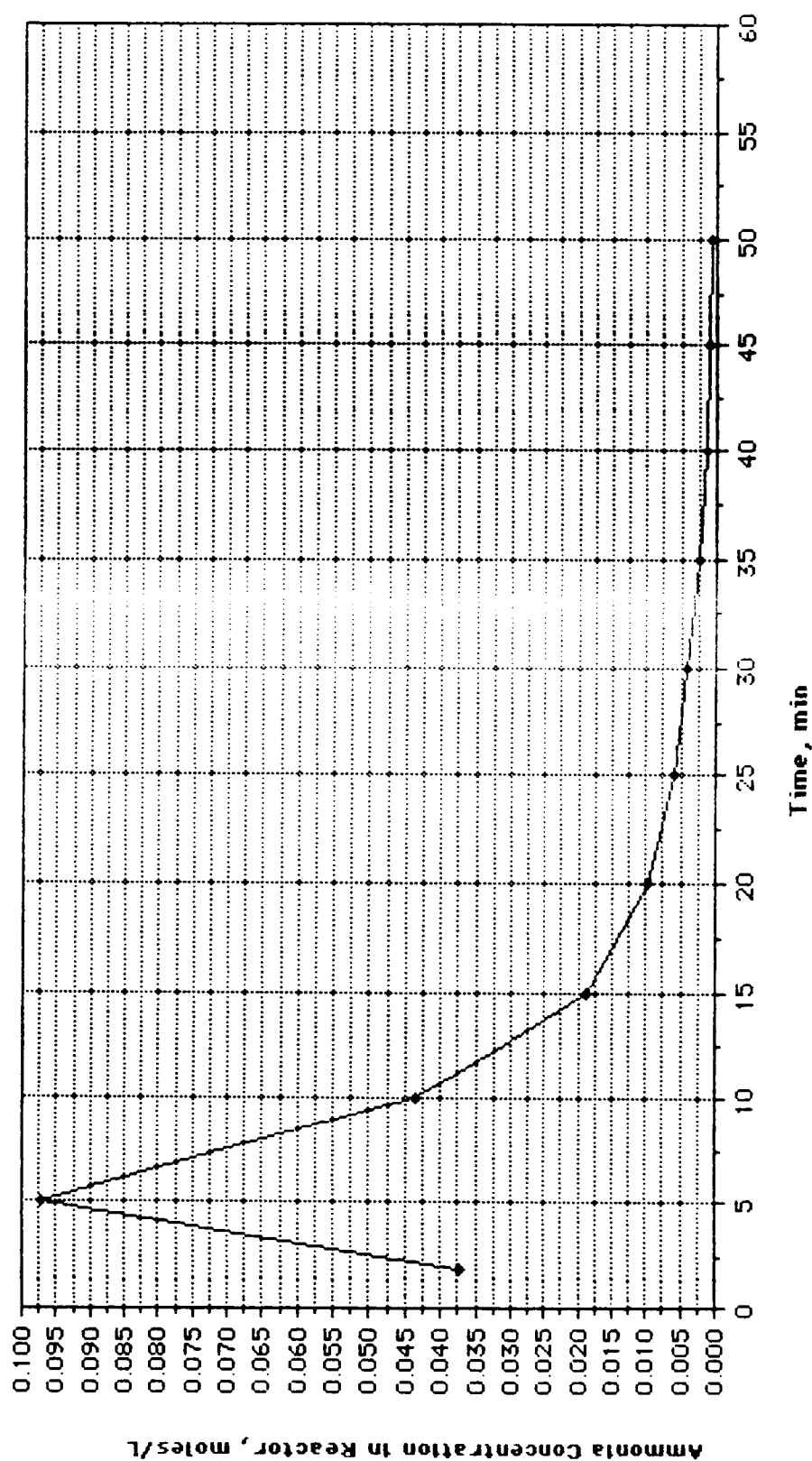
Reactor Data for 12/9/91 *1 under conditions:
45°C, pH=11, 50 g/L solids, 40 scfh nominal air flow rate,
[NH₃]_i=0.00020592 moles/g NH₃-free solids



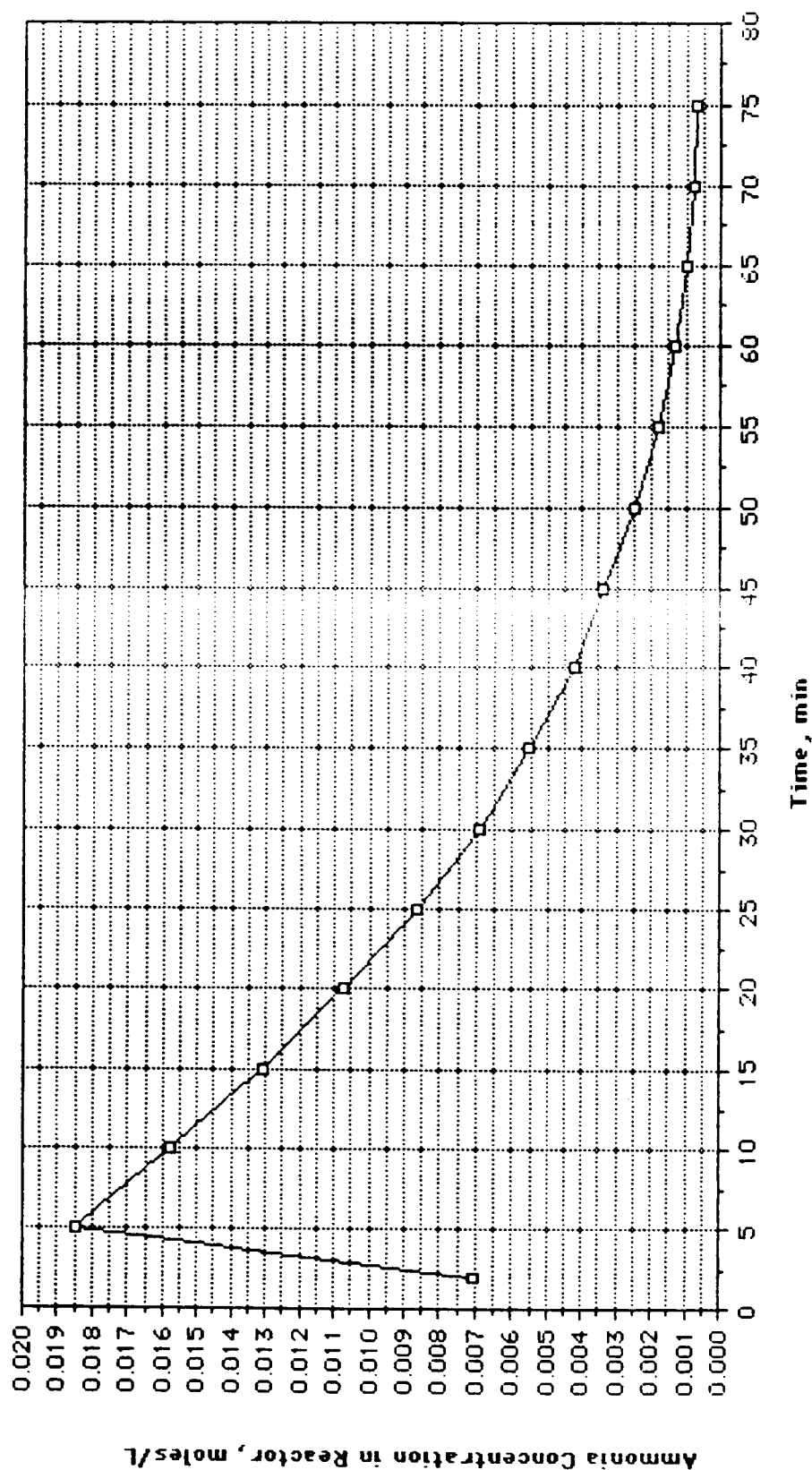
Reactor data for 12/13/91 #1 under conditions:
30 C, pH=11, 100 g/L solids, 80 scfh nominal air flow rate,
[NH₃]_i = 0.00021857 moles NH₃/g NH₃-free solid



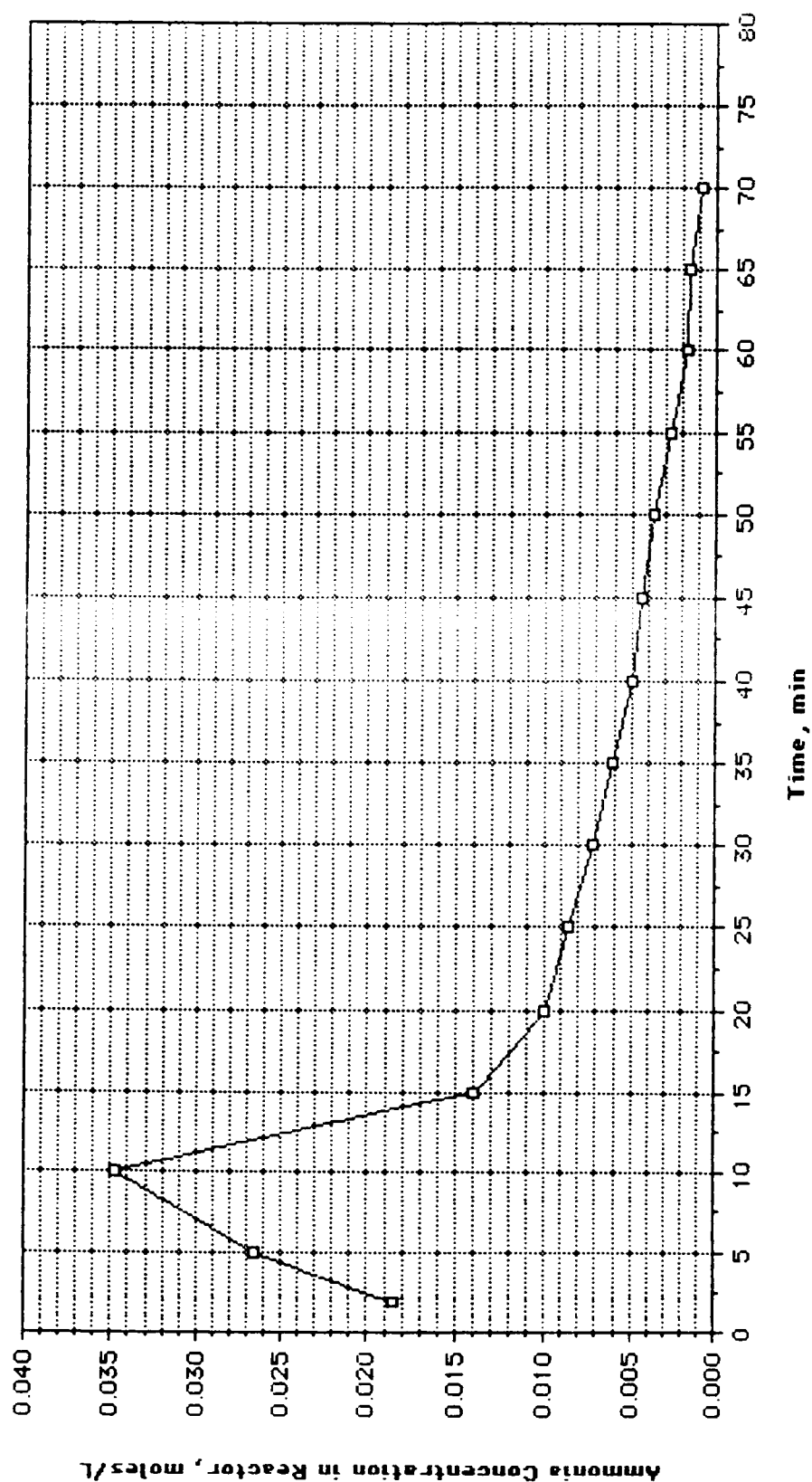
Reactor data for 12/13/91 #2 under conditions:
300C, pH= 11, 50 g/L solids, 40 scfh nominal air flow rate,
[NH3]i = 0.00021857 moles NH3/g NH3-free solid



Reactor Data for 12/16/91 #1 under conditions:
 45°C, pH=10, 100 g/L solids, air=80 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.00021156$ moles/g NH_3 -free solids

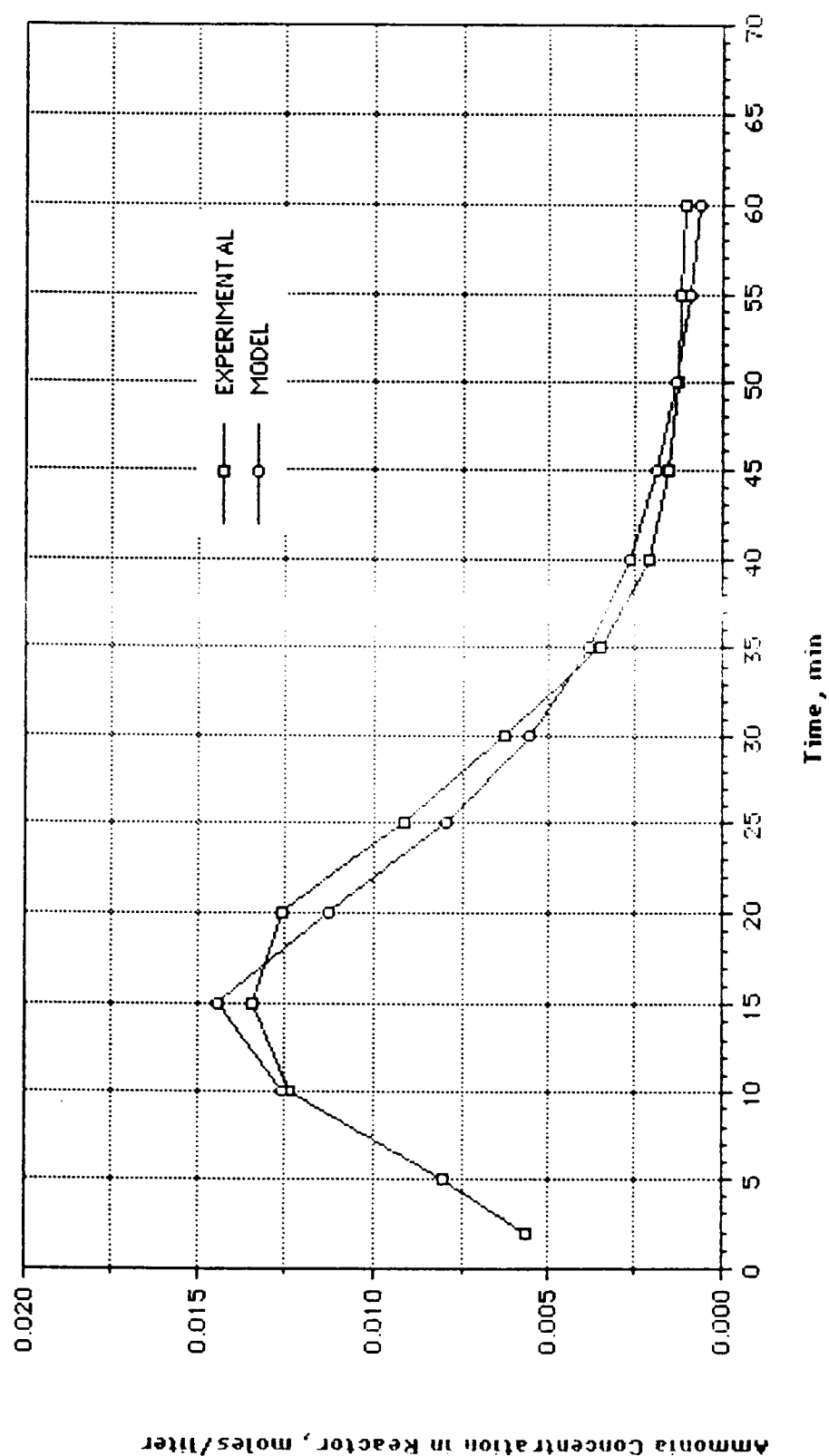


Reactor Data for 12/16/91 #2 under conditions:
 45°C, pH=10, 50 g/L solids, air=40 scfh nominal air flow rate,
 $[NH_3]_i=0.0002156$ moles/g NH_3 -free solids

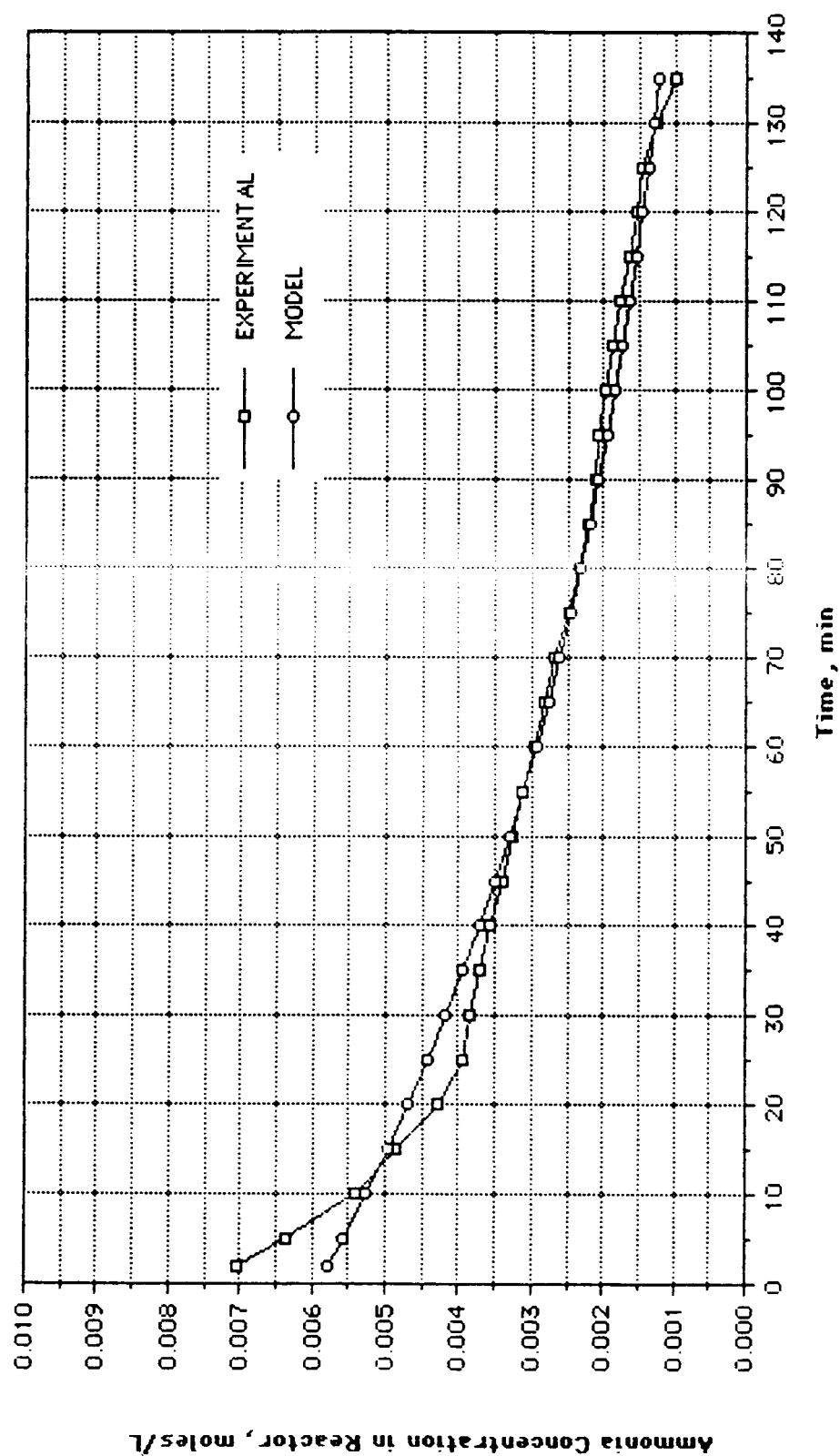


Reactor Data for 12/19/91 #2 under conditions:
45oC, pH=11, 100 g/L solids, 40 scfh nominal air flow rate,
[NH3]i=0.00020975 moles/g NH3-free solids

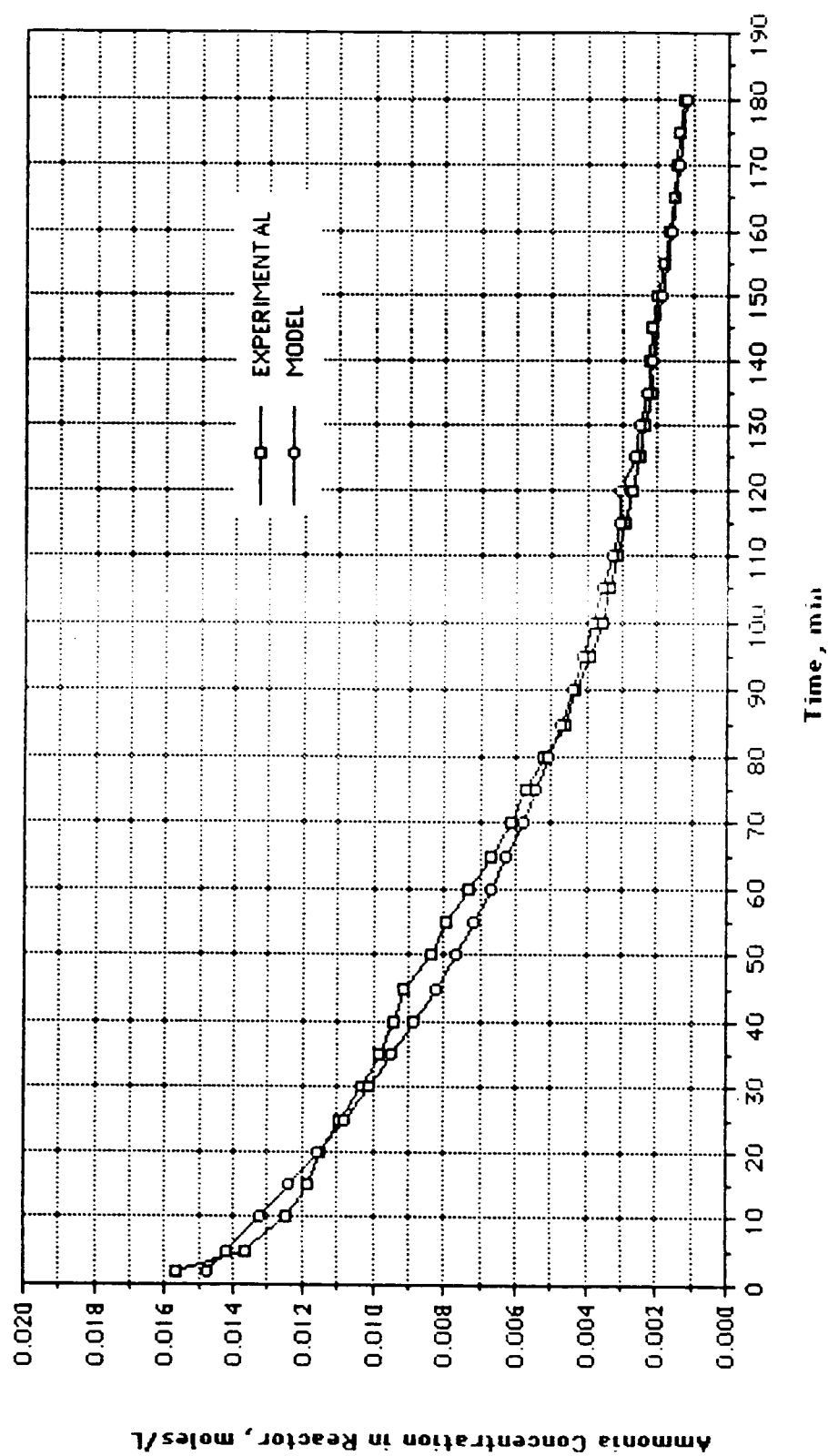
Other Modeled Reactor Graphs



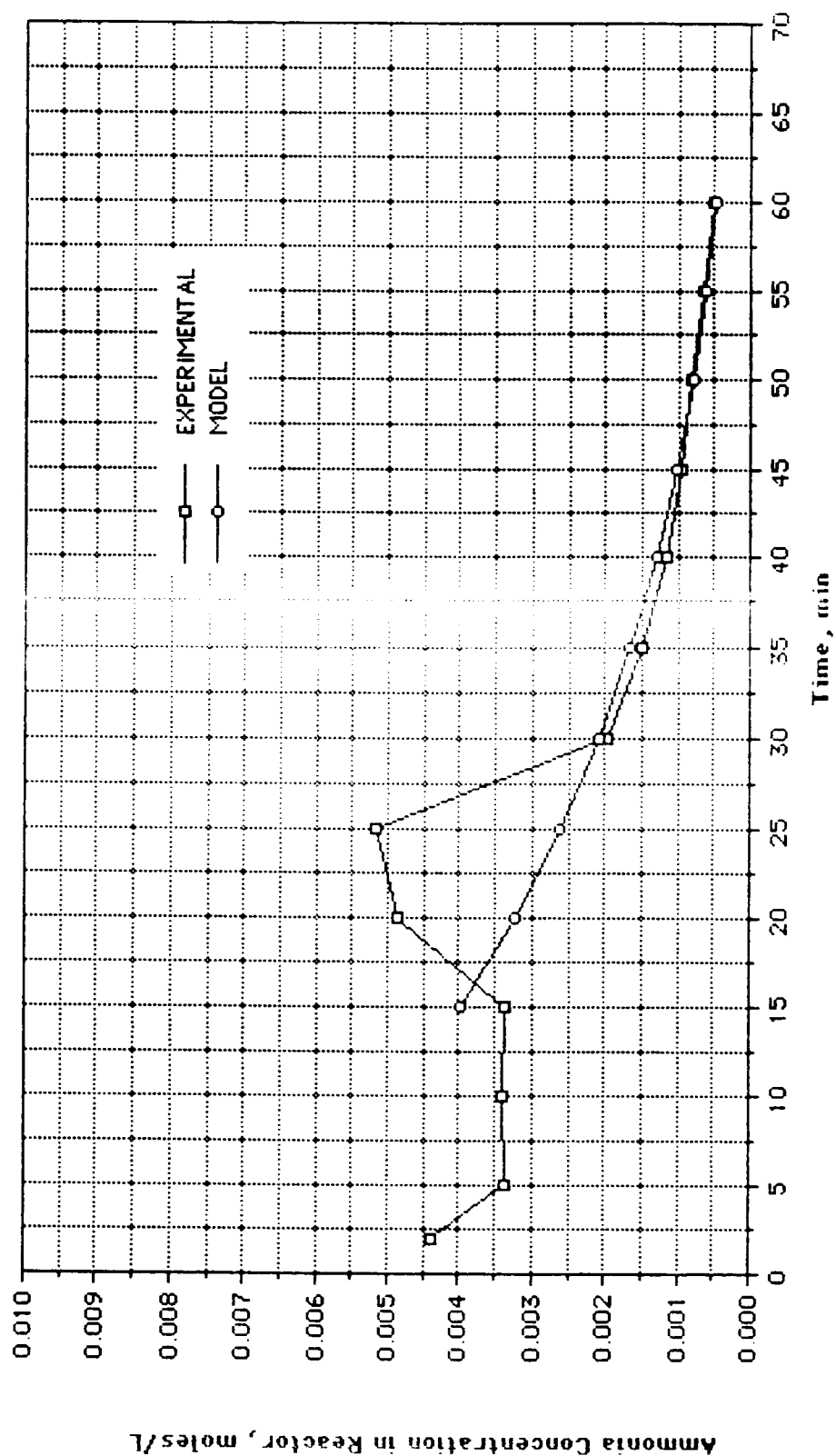
Reactor Data from 11/22/91 #2 under conditions:
45°C, pH = 11, 100g/L solids, 60 scfh nominal air flow rate,
[NH₃]i = .00020723 moles NH₃/g NH₃-free solids



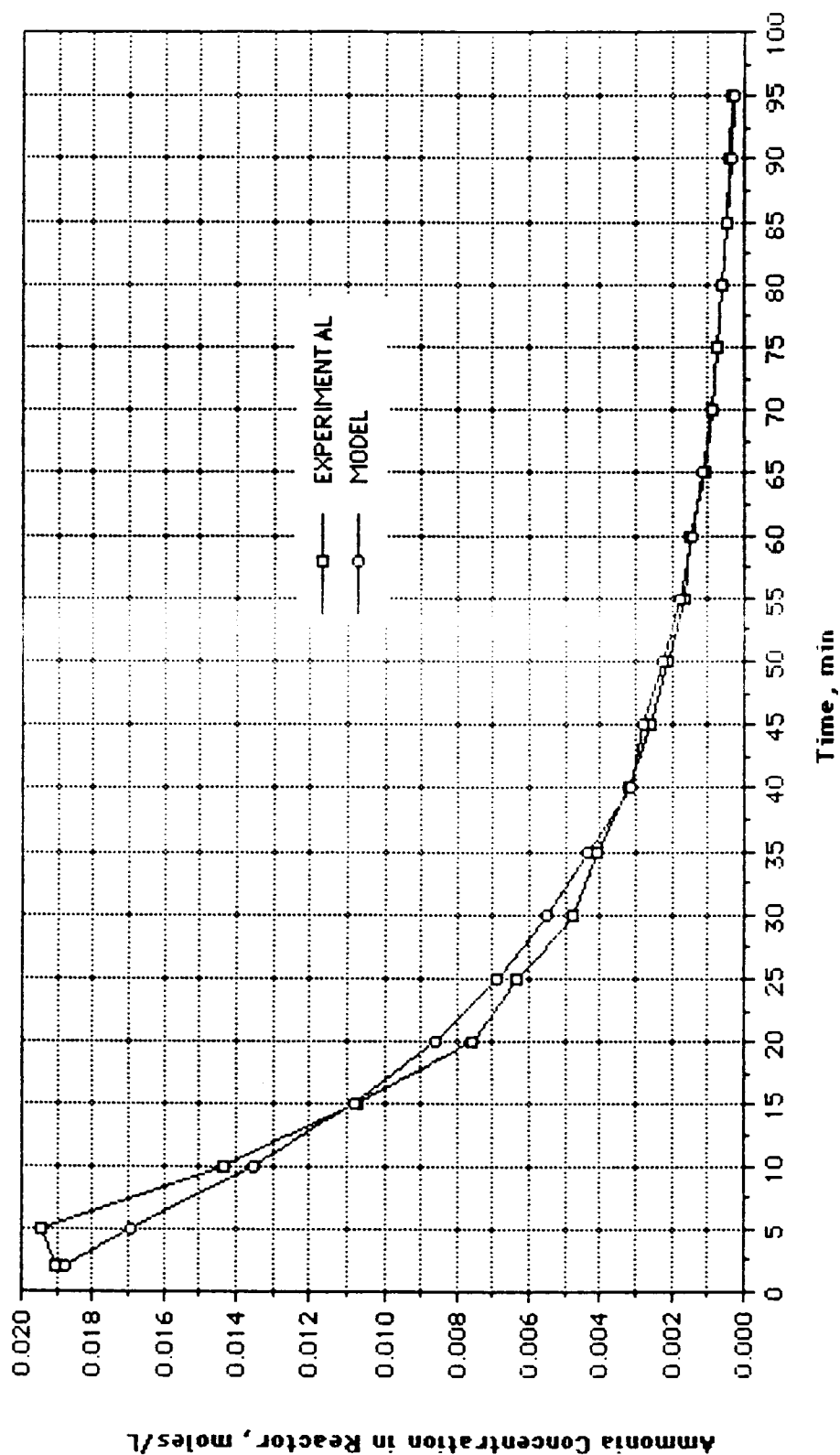
Reactor Data for 12/3/91*3 under conditions:
 300C, pH=11, 50 g/L solids, air=67.5 scfh nominal air flow rate,
 $[NH_3]_i=0.00020471$ moles/g NH_3 -free solids



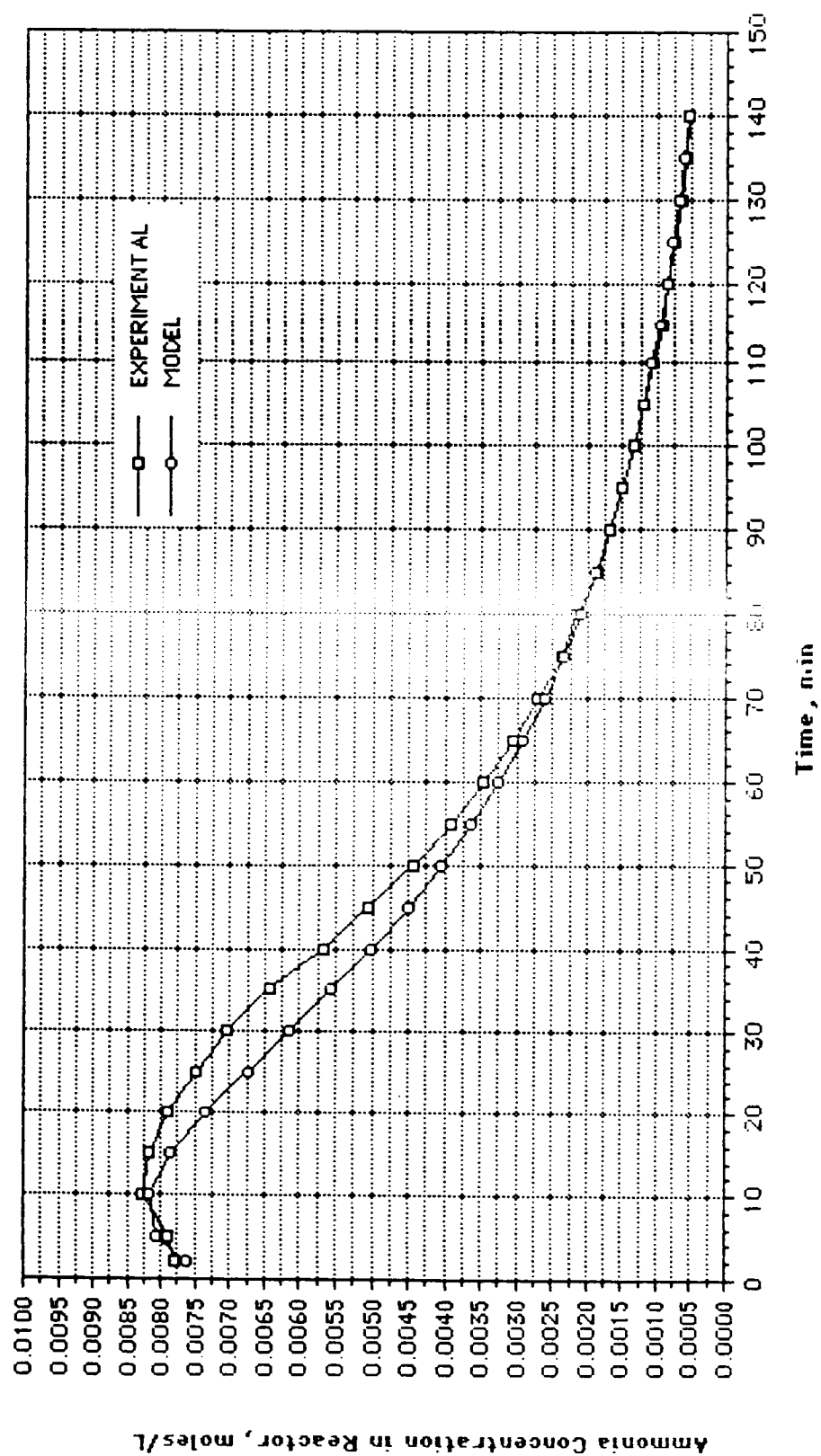
Reactor Data for 12/5/91 #1 under conditions:
300C, pH=10, 100 g/L solids, 80 scfh nominal air flow rate,
[NH₃]_i=0.00020169 moles/g NH₃-free solids



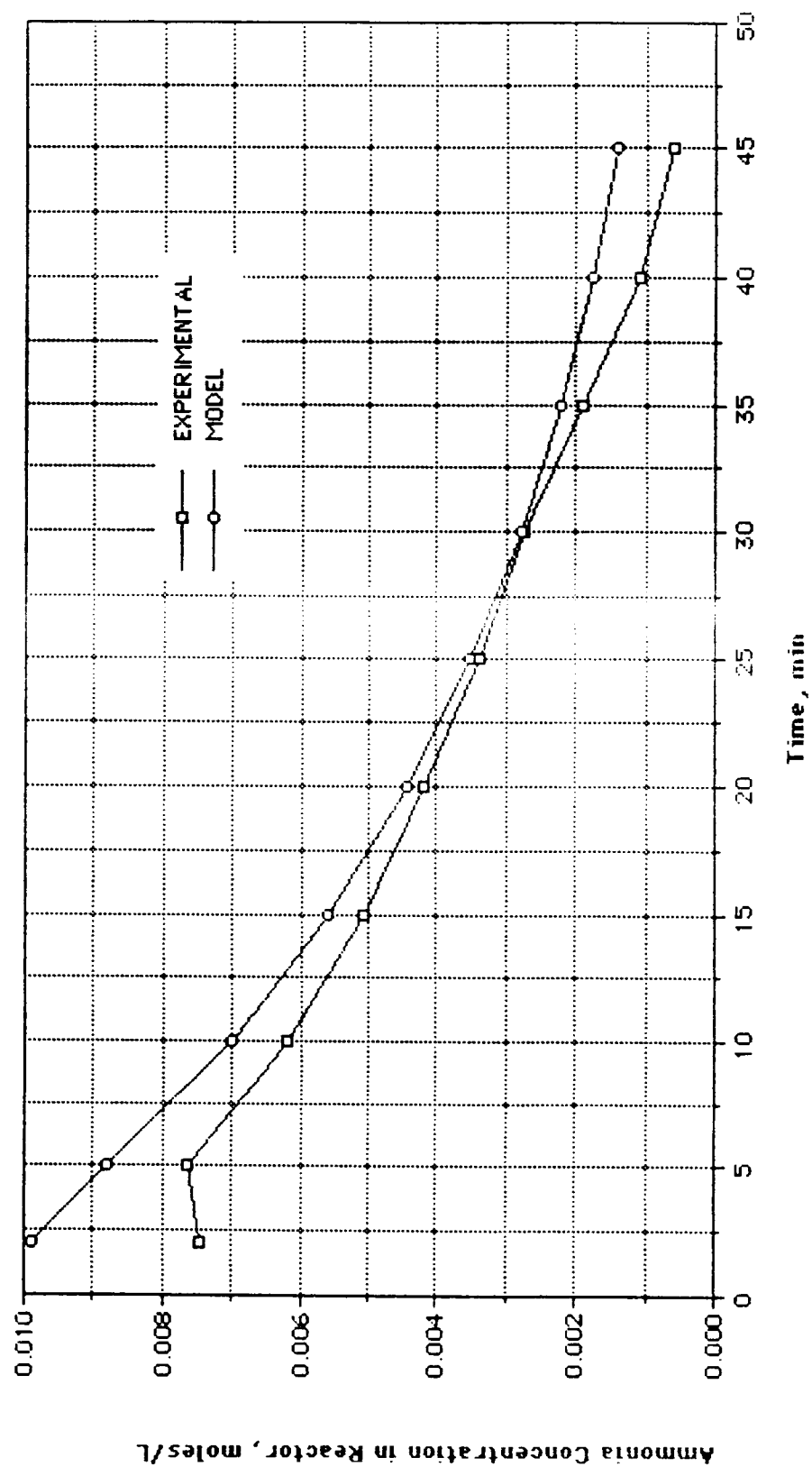
Reactor Data for 12/6/91 #1 under conditions:
45oC, pH=10, 50 g/L solids, 60 scfh nominal air flow rate,
[NH3]_i=0.00020572 moles/g NH₃-free solids



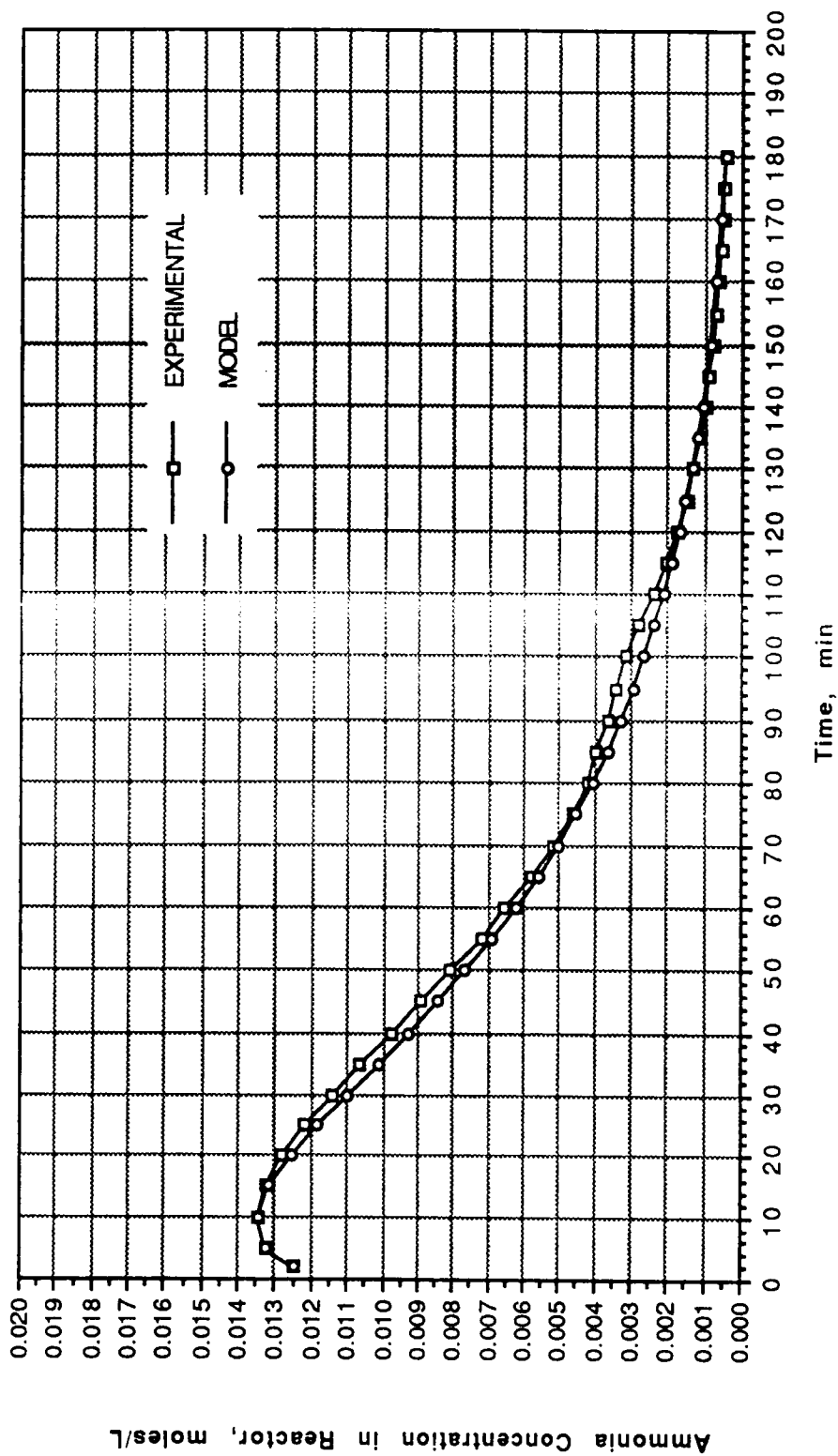
Reactor Data for 12/6/91 #2 under conditions:
45oC, pH=10, 100 g/L solids, 40 scfh nominal air flow rate,
[NH3]i=0.00020572 moles/g NH3-free solids



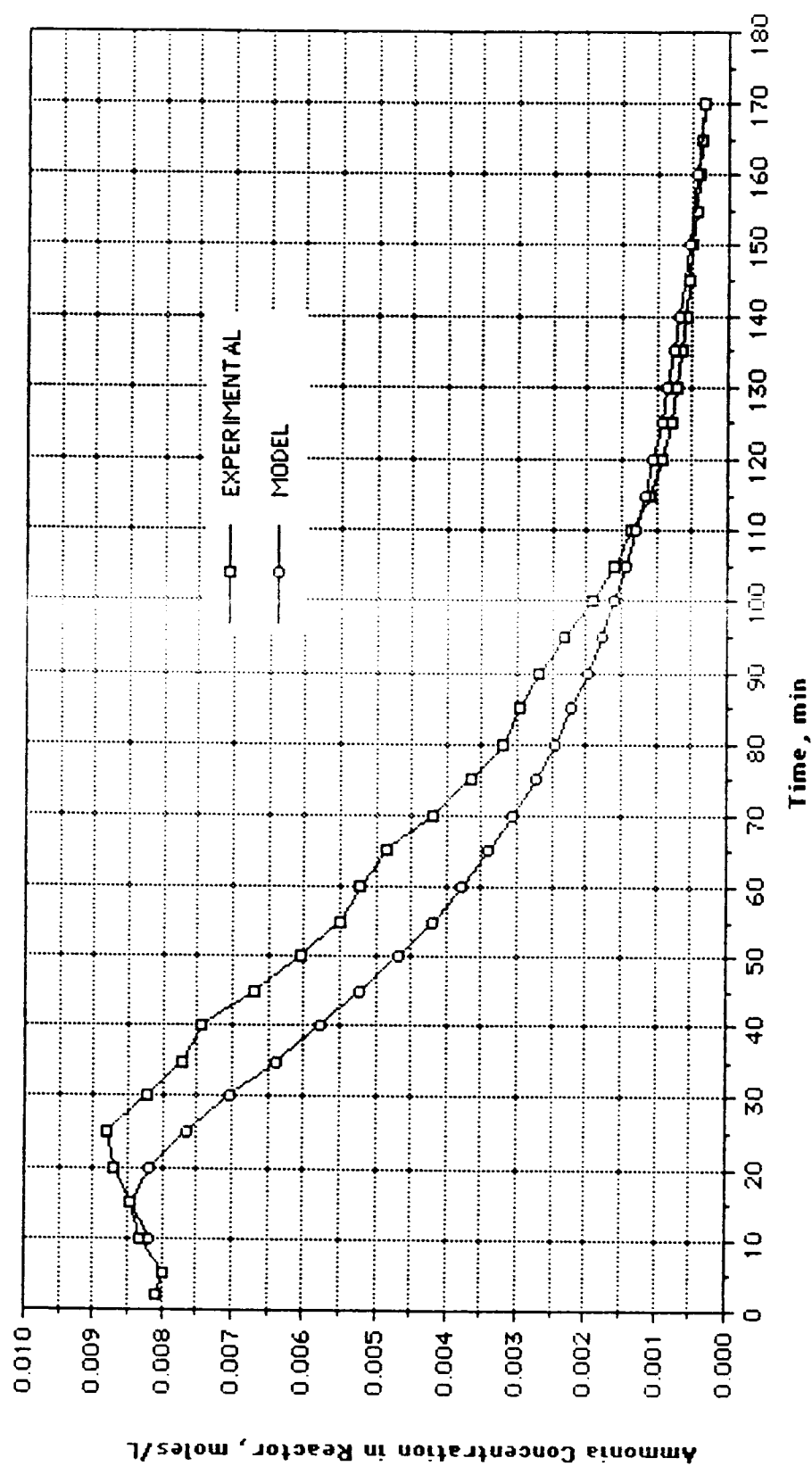
Reactor data form 12/11/91 #1 under conditions:
 300C, pH=11, 50g/L solids, 80 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.0002232$ moles NH_3/g NH_3 -free solid



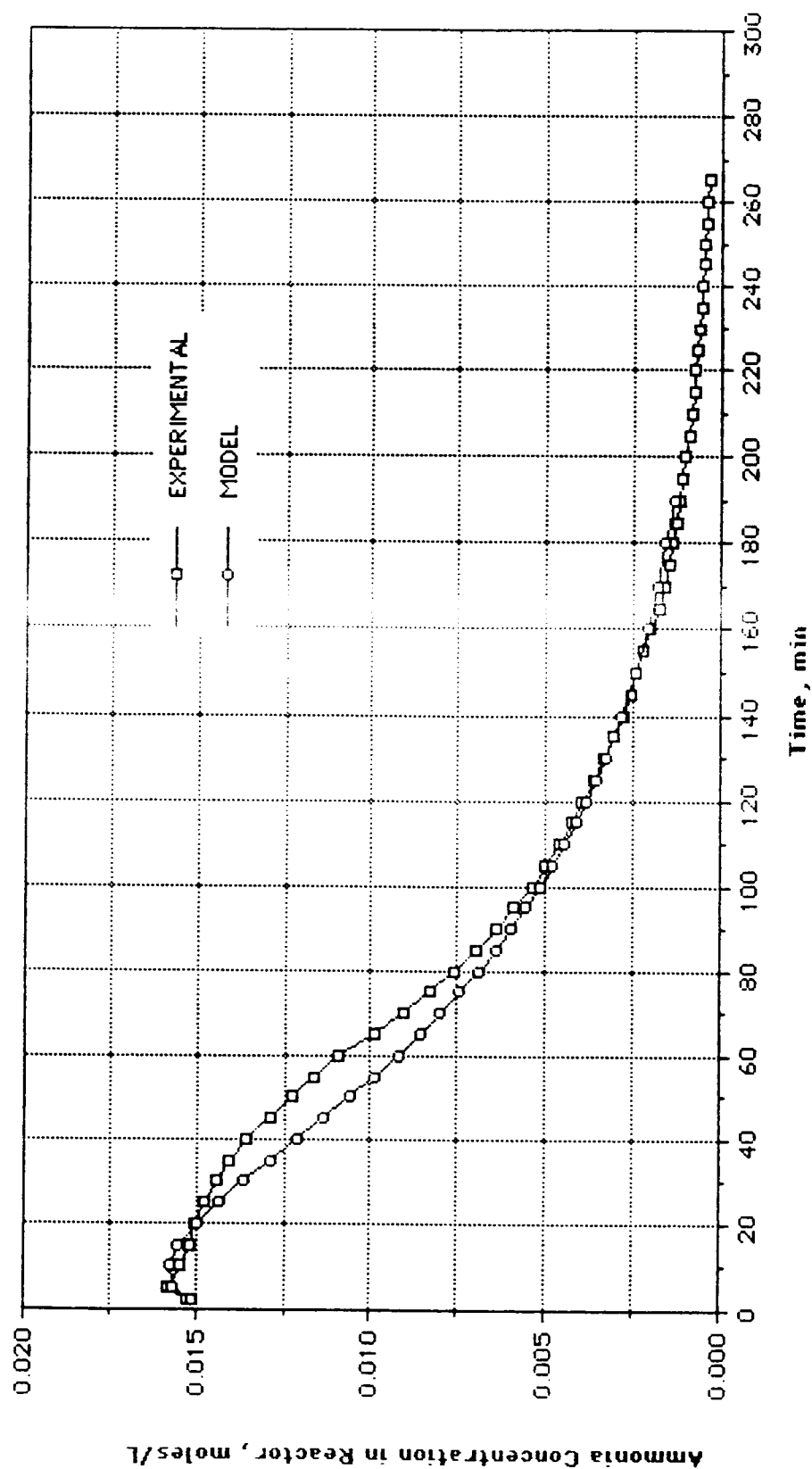
Reactor Data for 12/12/91 #1 under conditions:
45°C, pH=10, 50 g/L solids, 60 sccfh nominal air flow rate,
[NH₃]_i=0.00022091 moles/g NH₃-free solids



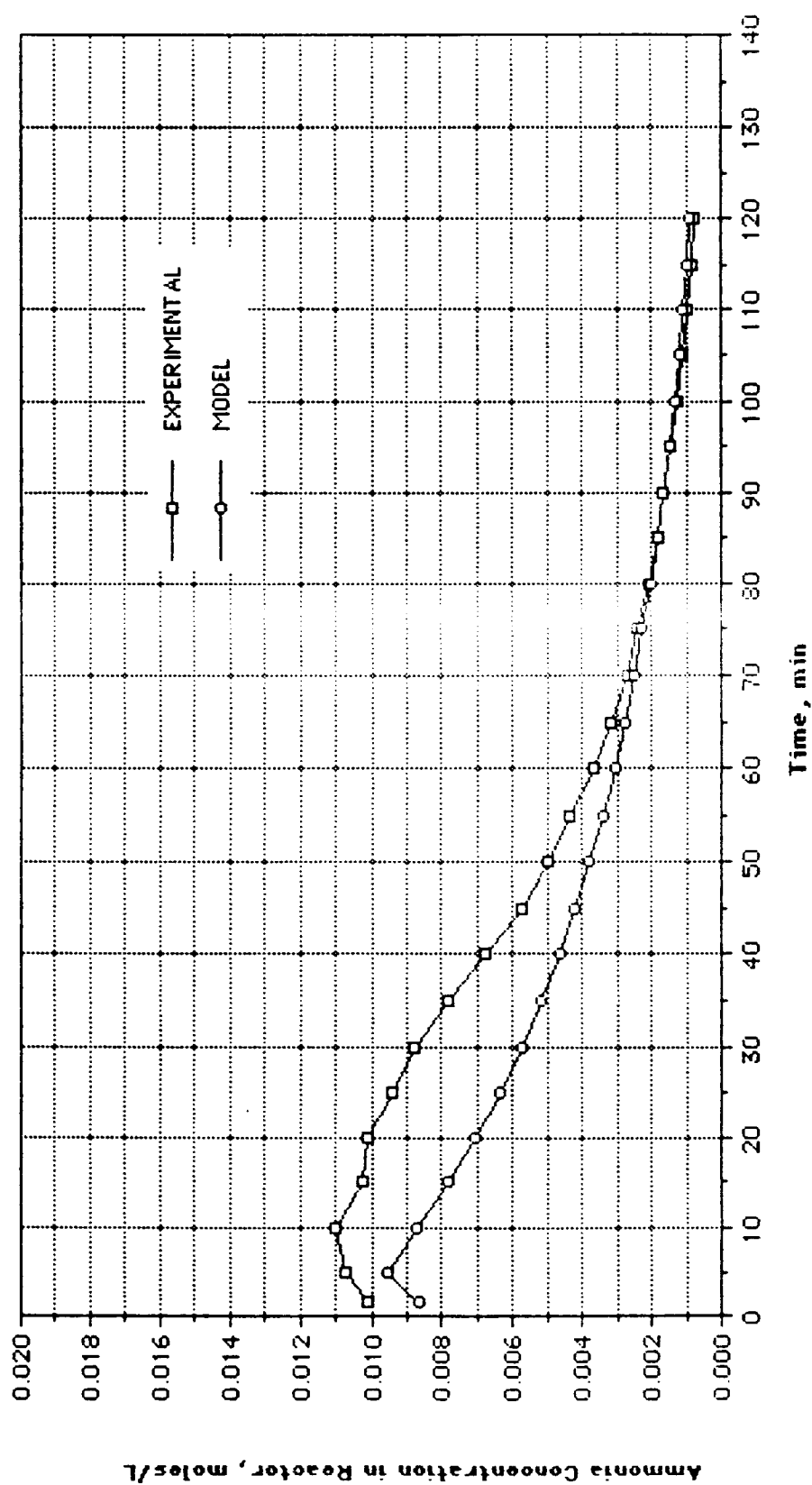
Reactor data for 12/13/91 #1 under conditions:
 30 °C, pH=11, 100 g/L solids, 80 sctm nominal air flow rate,
 $[NH_3]_i = 0.00021857$ moles NH_3/g NH_3 -free solid



Reactor Data for 12/17/91 #1 under conditions:
 300C, pH=10, 100 g/L solids, 60 scfm nominal air flow rate,
 $[NH_3]_i = 0.00021095$ moles/g NH_3 -free solids



Reactor Data for 12/18/91 #2 under conditions:
300C, pH=10, 100 g/L solids, 40 scfh nominal air flow rate,
[NH₃]_i=0.00021035 moles/g NH₃-free solids



Reactor Data for 12/19/91 #1 under conditions:
 300C, pH=10, 50 g/L solids, 80 scfh nominal air flow rate,
 $[\text{NH}_3]_i = 0.00020975$ moles/g NH_3 -free solids

APPENDIX C.
K_LA FORTRAN PROGRAM

```

C
C   SIAM6.FOR          GCF          10 MAR 92
C
C   THIS PROGRAM ADAPTS THE EXAMPLE INTEGRATION PROBLEM GIVEN
C   IN IMSL SUBROUTINE 'DIVPAG' TO THE MODEL AMMONIA STRIPING
C   PROBLEM OF CHRISTIE CLARK. SPECIFICALLY THE QUESTION OF THE
C   THE PARAMETER,  $KL_a$ , FOR THE SIAM5.FOR MODEL.
C
C   -----
C
C   IMPLICIT REAL*8 (A-H,O-Z)
C   INTEGER   NEQ,NPARAM,NPTS,NX,KZ(50)
C   PARAMETER (NEQ=2, NPARAM=50, NX=2)
C
C   INTEGER   IDO,IEND,NOUT
C   DIMENSION A(1,1),PARAM(NPARAM),Y(NEQ)
C   DIMENSION CY1(50),CY2(50),RTM(50),RCA(50)
C   DIMENSION CA(50),CAG(50),W(50)
C   DIMENSION X(NX),XMIN(NX),XMAX(NX)
C   DIMENSION Z(15),ZZ(9,NX)
C   CHARACTER*3 FIRST
C   CHARACTER*4 LAST
C   CHARACTER*6 INNAME
C   CHARACTER*9 ALLNAME
C   CHARACTER*10 OUTNAME
C   CHARACTER*35 TITLE
C
C   EXTERNAL  IVPAG, DSET,FCN,FCNJ
C
C   COMMON//ZZ
C   COMMON/PARK/AKLA,HG,BETA,GAMMA,CG
C
C   WRITE(6,*)'ENTER THE NAME OF THE INPUT FILE IN SINGLE
1 QUOTES, PREFIX ONLY'
C   READ(6,*)INNAME
C   FIRST='IN'
C   ALLNAME=INNAME//FIRST
C   LAST='OUT'
C   OUTNAME=INNAME//LAST
C   OPEN(FILE=ALLNAME,STATUS='OLD',UNIT=23)
C   OPEN(FILE=OUTNAME,STATUS='NEW',UNIT=24)
C
C   READ(23,*) TITLE
C   READ(23,*) XMIN(1),XMIN(2)
C   READ(23,*) X(1),X(2)

```

```

      READ(23,*) XMAX(1),XMAX(2)
      READ(23,*) NPTS,KFLAG,TOL
      READ(23,*) AKLA,HG,HC,CL,CG
      READ(23,*) VL,CAO,WAIR,TC
      DO 10 I = 1,NPTS
10    READ(23,*) RTM(I),RCA(I),W(I)
      C
      C  CONVERT AMMONIA CONCENTRATIONS FROM MOLS/L BASIS TO
      C  MOLS/ML BASIS.
      C
      CAO=CAO/1000.0
      DO 20 I = 1,NPTS
20    RCA(I) = RCA(I)/1000.0
      C
      C  INITIALIZE ESOPDP BY SETTING KOUT FOR NO OUTPUT (CALL
      C  ESOPDP WITH KPHAS = -1 AND AN ARBITRARY COST VALUE)
      C
      KOUT = 0
      KPHAS = -1
      COST = 1
      CALL ESOPDP(COST,X,XMIN,XMAX,NX,KPHAS,KOUT,ZZ)
      C
      WRITE(6,50) KPHAS
50    FORMAT(3X,'KPHAS AFTER INITIALIZATION CALL = ',I4)
      C
      C  OPTIMIZATION LOOP, STATEMENTS 500 THROUGH 2000
      C
      KOUNT = 0
500  CONTINUE
      C
      C  INITIALIZE THE OBJECTIVE FUNCTION
      C
      COST = 0.0
      C
      C  PROVIDE THE UPDATED VALUES OF THE PARAMETERS TO BE OPTIMIZED
      C
      AKLA = X(1)
      HG = X(2)
      C
      C  UPDATE THE PARAMETER BETA AND GAMMA
      C
      BETA = CL/(HC*CG)
      GAMMA = ((1.0-HG)/HG)*WAIR/(CG*VL)
      C
      WRITE(6,5020) X(1),X(2)

```

```

C
C  INITIALIZE THE DIFFERENTIAL EQUATIONS SOLVER SUBROUTINE,
C  'DIVPAG' IN THE IMSL SUBROUTINE LIBRARY
C
  CALL DSET (NPARAM,0.000,PARAM,1)
  PARAM(12) = 2
  PARAM(13) = 2
C
  IDO      = 1
  T        = 0.0
C
C  SET THE INITIAL VALUES OF THE VARIABLES:
C
  Y(1)     = CAO           ! LIQUID PHASE CONCENTRATION
  Y(2)     = 0.0           ! GAS PHASE CONCENTRATION
C
  DO 1000 J = 1,NPTS
    TEND    = RTM(J)
C
    CALL DIVPAG (IDO,NEQ,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
    CY1(J) = Y(1)
    CY2(J) = Y(2)
  1000 CONTINUE
    IDO     = 3
    CALL DIVPAG (IDO,NEQ,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
    IF(KFLAG) 1010,1010,2000
  1010 CONTINUE
C  COMPUTE THE VALUE OF THE OBJECTIVE FUNCTION BASED ON THE
C  SUM OF THE SQUARES OF THE FRACTION ERRORS
C
  DO 1200 I = 1,NPTS
  1200 COST    = COST + W(I)*((CY1(I) - RCA(I))/RCA(I))**2
C
    KOUNT     = KOUNT + 1
    WRITE(6,1290)
  1290 FORMAT(/)
    WRITE(6,1295) KOUNT
  1295 FORMAT(1X,'***** CALL NO. ',I5,' TO ESOPDP *****')
    CALL ESOPDP(COST,X,XMIN,XMAX,NX,KPHAS,KOUT,ZZ)
    WRITE(6,1300) KPHAS
  1300 FORMAT(1X,'***** RETURN FROM ESOPDP ***** KPHAS =',I4)
    IF (KPHAS) 500,500,2000
C
  2000 CONTINUE

```

```

WRITE(24,*) TITLE
WRITE(24,5000)
5000 FORMAT(3X,'OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:')
WRITE(24,1290)
WRITE(24,5010)X(1),X(2)
5010 FORMAT(8X,'KLa = ',D11.4,7X,'HG = ',D11.4)
WRITE(24,1290)
WRITE(24,1290)
5020 FORMAT(2X,2D12.4)
WRITE(24,5015)
5015 FORMAT(8X,'VL',10X,'VG',9X,'TEMP',7X,'HC',9X,'WAIR')
WRITE(24,5018)
5018 FORMAT(8X,'ML',10X,'ML',11X,'C',18X,'MOLS/MIN')
C
  VG = VL*X(2)/(1.0 - X(2))
  WRITE(24,5040)VL,VG,TC,HC,WAIR
5040 FORMAT(2X,2D12.4,F10.2,2X,2D12.4)
WRITE(24,1290)
WRITE(24,1290)
WRITE(24,5050)
5050 FORMAT (5X,'TIME',8X,'EXPTL CA',5X,'CALC CA',
16X,'CALC CAG',7X,'YAG')
WRITE(24,5060)
5060 FORMAT(4X,'MINUTES',7X,'L-PHASE',6X,'L-PHASE',6X,'G-PHASE')
WRITE(24,5070)
5070 FORMAT(19X,'MOL/L',7X,'MOL/L',8X,'MOL/L')
WRITE(24,1290)
DO 5080 I = 1,NPTS
  RCA(I) = RCA(I)*1000.0
  CA(I) = CY1(I)*1000.0
  CAG(I) = CY2(I)*1000.0
  YAG = CY2(I)/CG
5080 WRITE(24,5090) RTM(I),RCA(I),CA(I),CAG(I),YAG
5090 FORMAT(F10.2,5X,4D13.4)
C
  END
C -----
C
SUBROUTINE FCN (NEQ, T, Y, YPRIME)
C
  IMPLICIT REAL*8 (A-H,O-Z)
  INTEGER NEQ
  DIMENSION Y(NEQ),YPRIME(NEQ)
C
  COMMON/PARK/AKLA,HG,BETA,GAMMA,CG

```

```

C
C  ASSUME Y(NH3) IS NEGLIGIBLE
C
C  MODEL EQUATIONS:
C
  YPRIME(1) = - AKLA*(1.0/(1.0-HG))*(Y(1) - BETA*Y(2))
  YPRIME(2) = (AKLA/HG)*(Y(1) - BETA*Y(2)) - GAMMA*Y(2)
  RETURN
  END
C  -----
C
C  SUBROUTINE FCNJ (NEQ,T,Y,DYPDY)
C
C  IMPLICIT REAL*8 (A-H,O-Z)
C  INTEGER    NEQ
C  DIMENSION  Y(NEQ),DYPDY(NEQ,*)
C
C  RETURN
C  END

```

APPENDIX D.
HENRY'S CONSTANT FORTRAN PROGRAM

```

C
C  AMHC.FOR          GCF          4 FEB 92
C
C  THIS PROGRAM COMPUTES THE VALUE OF HENRY'S CONSTANT, HC,
C  FOR AMMONIA IN WATER AS A FUNCTION OF PH, TEMPERATURE IN
C  DEGREES CELCIUS, AND TOTAL AMMONIA CONCENTRATION IN MOLS
C  PER LITER, CAM, USING THE FORMULA GIVEN BY CLICK AND REED,
C  1975.
C
C  -----
C
C  IMPLICIT REAL*8 (A-H,O-Z)
C
C  DIMENSION CAM(20),ACAM(20),PNH3(20),HC(20)
C
C  OPEN(FILE='AMHC.IN',STATUS='OLD',UNIT=23)
C  OPEN(FILE='AMHC.OUT',STATUS='NEW',UNIT=24)
C
C  READ(23,*) NPTS,TC,PH,SG,PT
C  DO 10 I = 1,NPTS
10  READ(23,*) CAM(I)
C
C  CONVERT THE INPUT TEMPERATURE FROM DEGREES CELCIUS TO
C  DEGREES RANKINE.
C
C  TR    = (TC + 273.15)*1.8
C
C  CONVERT TOTAL AMMONIA CONCENTRATION FROM MOLS/LITER TO
C  MILLIGRAMS/LITER.
C
C  DO 50 I = 1,NPTS
50  ACAM(I) = CAM(I)*14.01*1000.0
C
C  HC1    = 183.8*DEXP(-2213.0/TR)
C  FPHT1   = 10**(PH - 0.2401 - 4756.0/TR - 41097.0/TR**2)
C  FSG     = SG*1.0D+06/18.02
C
C  DO 500 I = 1,NPTS
C  ANUM1   = (ACAM(I)/14.01)*FPHT1
C  DENOM1  = 1.0 + FPHT1
C  ANUM    = ANUM1/DENOM1
C  DENOM   = (ANUM1/DENOM1) + FSG
500  PNH3(I) = HC1*ANUM/DENOM
C
C  COMPUTE THE NON-DIMENSIONAL HENRY'S CONSTANT FOR EACH OF

```

```

C   THE SPECIFIED TOTAL AMMONIA CONCENTRATIONS, CAM(I)
C
      DO 600 I = 1,NPTS
600  HC(I)  = (PNH3(I)/PT)*(CAM(I) + SG*55.556)/CAM(I)
C
      DO 1950 I = 1,NPTS
1950  WRITE(24,2000) CAM(I),HC(I)
2000  FORMAT(//,5X,2D15.4)
C
      CALL EXIT
end

```

APPENDIX E.
MATERIAL BALANCE FORTRAN PROGRAM AND OUTPUT

SIAM4FOR GCF 18 MAR 92

THIS PROGRAM ADAPTS THE EXAMPLE INTEGRATION PROBLEM GIVEN
IN IMSL SUBROUTINE 'DIVPAG' TO THE MODEL AMMONIA STRIPPING
PROBLEM OF CHRISTIE CLARK.

THE LIQUID AND GAS PHASES ARE CONSIDERED WELL-MIXED IN THIS
MODEL. THE AMMONIA IN THE SOLID PHASE IS CONSIDERED TO BE
COMPOSED OF A WEAKLY BOUND PORTION PLUS A STRONGLY BOUND
PART.

THE STRONGLY BOUND AMMONIA CONVERTS TO WEKLY BOUND NH3 BY
WAY OF AN IRREVERSIBLE, PSEUDO-FIRST ORDER REACTION WITH
RATE COEFFICIENT AKR.

A SEARCH IS MADE BY USE OF 'ESOPDP.F' FOR THE OPTIMAL VALUES
OF THE FOLLOWING PARAMETERS:

AKSA = SOLID-TO-LIQUID MASS TRANSFER COEF.

EPS = VOID FRACTION WITHIN THE PARTICLES

F = FRACTION OF THE AMMONIA IN THE SOLID
THAT IS WEAKLY BOUND

AKR = PSEUDO FIRST-ORDER RATTTE COEFFICIENT FOR
CONVERSION OF STRONGLY BOUND AMMONIA TO
WEAKLY BOUND AMMONIA.

AKLA = OVERALL LIQUID-TO-GAS VOLUMETRIC MASS
TRANSFER COEFFICIENT

THE VALUE OF HG (GAS HOLD UP FRACTION) USED IS THAT WHICH
WAS DETERMINED IN THE AMMONIA-FREE ASH STRIPPING EXPTS.

IMPLICIT REAL*8 (A-H,O-Z)
INTEGER NEQ,NPARAM,NPTS,NX,KZ(50)
PARAMETER (NEQ=4, NPARAM=50, NX=5)

INTEGER IDO,IEND,NOUT
DIMENSION A(1,1),PARAM(NPARAM),Y(NEQ)
DIMENSION CY1(50),CY2(50),CY3(50),RTM(50),RCA(50)
DIMENSION CA(50),CAS1(50),CAS2(50),W(50)
DIMENSION X(NX),XMIN(NX),XMAX(NX),CY4(50)
DIMENSION Z(15),ZZ(9,NX)
CHARACTER*3 FIRST
CHARACTER*4 LAST

```

CHARACTER*6 INNAME
CHARACTER*9 ALLNAME
CHARACTER*10 OUTNAME
CHARACTER*35 TITLE
C
EXTERNAL  IVPAG, DSET, FCN, FCNJ
C
COMMON//ZZ
COMMON/PARK/AO,A1,A2,BO,B1,BETA,AKR
C
C THIS INPUT SECTION ACCEPTS THE PREFIX TITLE OF THE INPUT
C FILE USED. THEN AN OUTPUT FILE IS WRITTEN TO WITH THE
C SAME PREFIX AND .OUT
C
WRITE(6,*)'ENTER THE NAME OF THE INPUT FILE IN SINGLE
1 QUOTES, PREFIX ONLY'
READ(6,*)INNAME
FIRST='IN'
ALLNAME=INNAME//FIRST
LAST='OUT'
OUTNAME=INNAME//LAST
OPEN(FILE=ALLNAME,STATUS='OLD',UNIT=23)
OPEN(FILE=OUTNAME,STATUS='NEW',UNIT=24)
C
READ(23,*) TITLE
READ(23,*) XMIN(1),XMIN(2),XMIN(3),XMIN(4),XMIN(5)
READ(23,*) X(1),X(2),X(3),X(4),X(5)
READ(23,*) XMAX(1),XMAX(2),XMAX(3),XMAX(4),XMAX(5)
READ(23,*) NPTS,KFLAG,TOL
READ(23,*) AKSA,EPS,AKR,F,AKLA
READ(23,*) VL,VS,WS,WAIR,SL,CASO,HG
READ(23,*) HC,CL,CG
DO 10 I = 1,NPTS
10 READ(23,*) W(I),RTM(I),RCA(I)
C
C
C CONVERT AMMONIA CONCENTRATIONS FROM MOLS/L BASIS TO
C MOLS/ML BASIS.
C
DO 20 I = 1,NPTS
20 RCA(I) = RCA(I)/1000.0
C
C INITIALIZE ESOPDP BY SETTING KOUT FOR NO OUTPUT (CALL
C ESOPDP WITH KPHAS = -1 AND AN ARBITRARY COST VALUE)
C

```

```

KOUT      = 0
KPHAS     = -1
COST      = 1
CALL ESOPDP(COST,X,XMIN,XMAX,NX,KPHAS,KOUT,ZZ)
C
  WRITE(6,50) KPHAS
50  FORMAT(3X,'KPHAS AFTER INITIALIZATION CALL = ',I4)
C
C  OPTIMIZATION LOOP, STATEMENTS 500 THROUGH 2000
C
  KOUNT    = 0
500  CONTINUE
C
C  INITIALIZE THE OBJECTIVE FUNCTION
C
  COST     = 0.0
C
C  PROVIDE THE UPDATED VALUES OF THE PARAMETERS TO BE OPTIMIZED
C
  AKSA     = X(1)
  EPS      = X(2)
  AKR      = X(3)
  F        = X(4)
  AKLA     = X(5)
C
C  UPDATE THE PARAMETERS
C
  AO       = AKSA*SL
  A1       = AKLA/HG
  A2       = AKSA*WS/(EPS*VS)
  B0       = AKLA/((1.0 - HG)
  B1       = ((1.0 - HG)/HG)*WAIR/(VL*CG)
  BETA     = CL/(HC*CG)
C
  WRITE(6,5010)
  WRITE(6,5020) X(1),X(2),X(3),X(4),X(5)
C
C  INITIALIZE THE DIFFERENTIAL EQUATIONS SOLVER SUBROUTINE,
C  'DIVPAG' IN THE IMSL SUBROUTINE LIBRARY.
C
  CALL DSET (NPARAM,0.0D0,PARAM,1)
  PARAM(12) = 2
  PARAM(13) = 2
C
  IDO      = 1

```

```

      T      = 0.0
C
C   SET THE INITIAL VALUES OF THE VARIABLES:
C
      Y(1)   = 0.0           ! LIQUID PHASE CONC
      Y(2)   = 0.0           ! GAS PHASE CONC
      Y(3)   = F*WS*CASO/(EPS*VS)   ! WEAKLY BOUND SOLID CONC
      Y(4)   = (1.0-F)*WS*CASO/(EPS*VS) ! STRONGLY BOUND SOLID CONC
C
      DO 1000 J = 1,NPTS
      TEND    = RTM(J)
C
      CALL DIVPAG (IDO,NEQ,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
      CY1(J) = Y(1)
      CY2(J) = Y(2)
      CY3(J) = Y(3)
      CY4(J) = Y(4)
1000 CONTINUE
      IDO    = 3
      CALL DIVPAG (IDO,NEQ,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
      IF(KFLAG) 1010,1010,2000
1010 CONTINUE
C   COMPUTE THE VALUE OF THE OBJECTIVE FUNCTION BASED ON THE
C   SUM OF THE SQUARES OF THE FRACTION ERRORS
C
      DO 1200 I = 1,NPTS
1200 COST      = COST + W(I)*((CY1(I) - RCA(I))/RCA(I))**2
C
      KOUNT     = KOUNT + 1
      WRITE(6,1290)
1290 FORMAT(/)
      WRITE(6,1295) KOUNT
1295 FORMAT(1X,'***** CALL NO. ',I5,' TO ESOPDP *****')
      CALL ESOPDP(COST,X,XMIN,XMAX,NX,KPHAS,KOUT,ZZ)
      WRITE(6,1300) KPHAS
1300 FORMAT(1X,'***** RETURN FROM ESOPDP ***** KPHAS =',I4)
      IF (KPHAS) 500,500,2000
C
2000 CONTINUE
      WRITE(24,*) TITLE
      WRITE(24,5000)
5000 FORMAT(3X,'OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE')
      WRITE(24,1290)
      WRITE(24,5010)

```

```

5010 FORMAT(7X,'AKSA',9X,'EPS',9X,'AKR',10X,'F',11X,'KLA')
      WRITE(24,1290)
      WRITE(24,5020) X(1),X(2),X(3),X(4),X(5)
5020 FORMAT(2X,5D12.4)
      WRITE(24,1290)
      WRITE(24,5050)
5050 FORMAT (5X,'TIME',8X,'EXPTL CA',5X,'CALC CA',
      16X,'CALC CAS1',4X,'CALC CAS2')
      WRITE(24,5060)
5060 FORMAT(4X,'MINUTES',7X,'L-PHASE',6X,'L-PHASE',6X,'S-PHASE',
      16X,'S-PHASE')
      WRITE(24,5070)
5070 FORMAT(19X,'MOL/L',7X,'MOL/L',8X,'MOL/GRAM',5X,'MOL/GRAM')
      WRITE(24,1290)
      DO 5080 I = 1,NPTS
      RCA(I) = RCA(I)*1000.0
      CA(I) = CY1(I)*1000.0
      CAS1(I) = EPS*VS*CY3(I)/WS
      CAS2(I) = EPS*VS*CY4(I)/WS
5080 WRITE(24,5090) RTM(I),RCA(I),CA(I),CAS1(I),CAS2(I)
5090 FORMAT(F10.2,5X,5D13.4)
      WRITE(24,1290)
      WRITE(24,1290)
      WRITE(24,6000)
6000 FORMAT(1X,'TIME',5X,'TOTAL NH3',5X,'FRACTION',5X,
      1'FRACTIONAL',6X,'YAG',7X,'FRACTION')
      WRITE(24,6010)
6010 FORMAT(1X,'MINUTES',4X,'IN SOLIDS',5X,'AMMONIA',6X,
      1'CONVERSION',6X,'MOL',7X,'OF NH3')
      WRITE(24,6020)
6020 FORMAT(11X,'MOL/GRAM',6X,'REMOVED',6X,'OF (NH4)2SO3',
      12X,'FRACTION',4X,'REMOVED')
      WRITE(24,6030)
6030 FORMAT(24X,'FROM SOLIDS',3X,'TO NH3(AQ)',16X,'FROM SYSTEM')
      WRITE(24,1290)
      DO 6200 I = 1,NPTS
      CAT = CAS1(I) + CAS2(I)
      FM = 1.0 - CAT/CASO
      XA = 1.0 - CAS2(I)/((1.0 - F)*CASO)
      YAG = CY2(I)/CG
      FS = (WS*CASO - (CA(I)*1 + CAS1(I)*WS + CAS2(I)*WS))/
      1(CASO*WS)
C
6200 WRITE(24,6210) RTM(I),CAT,FM,XA,YAG,FS
6210 FORMAT(F6.2,1X,5D13.4)

```

```

C
C  END
C  -----
C
C  SUBROUTINE FCN (NEQ, T, Y, YPRIME)
C
C  IMPLICIT REAL*8 (A-H,O-Z)
C  INTEGER    NEQ
C  DIMENSION  Y(NEQ),YPRIME(NEQ)
C
C  COMMON/PARK/A0,A1,A2,B0,B1,BETA,AKR
C
C  SOLID-LIQUID EQUILIBRIUM MODEL:
C
C  CASS      = DSL*Y(3)
C
C  FIRST ORDER REACTION FOR CONVERSION OF STRONGLY BOUND NH3
C  TO WEAKLY BOUND NH3 IN THE SOLID PHASE
C
C  TRANSPORT MODEL EQUATIONS
C
C  YPRIME(1) = A0*(Y(3) - Y(1)) - B0*(Y(1) - BETA*Y(2))
C  YPRIME(2) = A1*(Y(1) - BETA*Y(2)) - B1*Y(2)
C  YPRIME(3) = - A2*(Y(3) - Y(1)) + AKR*Y(4)
C  YPRIME(4) = -Y(4)*AKR
C  RETURN
C  END
C  -----
C
C  SUBROUTINE FCNJ (NEQ,T,Y,DYPDY)
C
C  IMPLICIT REAL*8 (A-H,O-Z)
C  INTEGER    NEQ
C  DIMENSION  Y(NEQ),DYPDY(NEQ,*)
C
C  RETURN
C  END

```

Computer Output Table For Experimental Conditions on 11/22/91
 Experiment #1, 45oC, pH=11, 50 g/L solids, and 40 scfh nominal
 air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.0107	0.2306D-01	0.4293D+00	0.5821D+00	0.1221D+00

TIME	EXPTL CA	CALC CA	CALC CAS1	CALC CAS2
MINUTES	L - PHASE	S - PHASE	S - PHASE	S - PHASE
	MOL/L	MOL/L	MOL/GRAM	MOLE/GRAM
2	0.5850D-02	0.5820D-02	0.4850D-04	0.3670D-04
5	0.8050D-02	0.8037D-02	0.1299D-04	0.1012D-04
10	0.9440D-02	0.7454D-02	0.1588D-05	0.1184D-05
15	0.8580D-02	0.6192D-02	0.2628D-06	0.1384D-06
20	0.6520D-02	0.5071D-02	0.9416D-07	0.1617D-07
25	0.4440D-02	0.4144D-02	0.6285D-07	0.1891D-08
30	0.3740D-02	0.3386D-02	0.4970D-07	0.2200D-09
35	0.2860D-02	0.2766D-02	0.4041D-07	0.2506D-10
40	0.2200D-02	0.2260D-02	0.3299D-07	0.2444D-11
45	0.1760D-02	0.1846D-02	0.2695D-07	0.1680D-12
50	0.1440D-02	0.1508D-02	0.2201D-07	0.2874D-12
55	0.1160D-02	0.1232D-02	0.1798D-07	0.4819D-12
60	0.9500D-03	0.1006D-02	0.1469D-07	0.2122D-12
65	0.7900D-03	0.8221D-03	0.1200D-07	0.4307D-13
70	0.6700D-03	0.6716D-03	0.9804D-08	0.1474D-13
75	0.5800D-03	0.5487D-03	0.8009D-08	0.7228D-13

TIME,	TOTAL NH3	FRACTION	FRACTIONAL	YAG	FRACTION
MINUTES	IN SOLIDS	AMMONIA	CONVERSION	MOLES OF	NH3
	MOL/GRAM	REMOVED	OF (NH4)2SO3	FRACTION	REMOVED
		FROM SOLIDS	TO NH3(AQ)		FROM SYSTEM
2	0.8520D-04	0.5889D+00	0.5762D+00	0.3153D-03	0.2716D-01
5	0.2311D-04	0.8885D+00	0.8831D+00	0.4363D-03	0.1128D+00
10	0.2771D-05	0.9866D+00	0.9863D+00	0.4055D-03	0.2672D+00
15	0.4011D-06	0.9981D+00	0.9984D+00	0.3361D-03	0.4004D+00

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOLES OF FRACTION	FRACTION NH3 REMOVED FROM SYSTEM
20	0.1103D-06	0.9995D+00	0.9998D+00	0.2747D-03	0.5101D+00
25	0.6474D-07	0.9997D+00	0.1000D+01	0.2249D-03	0.5997D+00
30	0.4992D-07	0.9998D+00	0.1000D+01	0.1838D-03	0.6730D+00
35	0.4043D-07	0.9998D+00	0.1000D+01	0.1501D-03	0.7329D+00
40	0.3299D-07	0.9998D+00	0.1000D+01	0.1226D-03	0.7818D+00
45	0.2695D-07	0.9999D+00	0.1000D+01	0.1002D-03	0.8217D+00
50	0.2201D-07	0.9999D+00	0.1000D+01	0.8185D-04	0.8544D+00
55	0.1798D-07	0.9999D+00	0.1000D+01	0.6687D-04	0.8810D+00
60	0.1469D-07	0.9999D+00	0.1000D+01	0.5463D-04	0.9028D+00
65	0.1200D-07	0.9999D+00	0.1000D+01	0.4462D-04	0.9206D+00
70	0.9805D-08	0.1000D+01	0.1000D+01	0.3645D-04	0.9351D+00
75	0.8009D-08	0.1000D+01	0.1000D+01	0.2978D-04	0.9470D+00

COMPUTER OUTPUT TABLE FOR EXPERIMENTAL CONDITIONS ON 11/22/91
 EXPERIMENT #2, 45oC, pH = 11, 100 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.4009	0.1692D-02	0.4307D+00	0.2362D+00	0.1603D+00

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.1245D-01	0.1261D-01	0.8583D-07	0.6688D-04
5	0.1341D-01	0.1439D-01	0.3466D-07	0.1837D-04
10	0.1258D-01	0.1127D-01	0.1377D-07	0.2132D-05
15	0.9150D-02	0.7978D-02	0.8371D-08	0.2474D-06
20	0.6310D-02	0.5560D-02	0.5677D-08	0.2873D-07
25	0.3510D-02	0.3865D-02	0.3928D-08	0.3340D-08
30	0.2120D-02	0.2665D-02	0.2727D-08	0.3946D-09
35	0.1530D-02	0.1865D-02	0.1894D-08	0.4746D-10
40	0.1230D-02	0.1296D-02	0.1316D-08	0.5848D-11
45	0.1170D-02	0.9003D-03	0.9142D-09	0.9714D-12
50	0.1050D-02	0.6263D-03	0.6360D-09	0.2084D-11

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.6697D-04	0.6768D+00	0.5775D+00	0.7063D-03	0.6836D-01
5	0.1840D-04	0.9112D+00	0.8839D+00	0.8069D-03	0.2170D+00
10	0.2146D-05	0.9896D+00	0.9865D+00	0.6325D-03	0.4458D+00
15	0.2558D-06	0.9988D+00	0.9984D+00	0.4478D-03	0.6138D+00
20	0.3441D-07	0.9998D+00	0.9998D+00	0.3120D-03	0.7315D+00
25	0.7268D-08	0.1000D+01	0.1000D+01	0.2169D-03	0.8135D+00
30	0.3121D-08	0.1000D+01	0.1000D+01	0.1507D-03	0.8704D+00
35	0.1942D-08	0.1000D+01	0.1000D+01	0.1047D-03	0.9100D+00
40	0.1322D-08	0.1000D+01	0.1000D+01	0.7272D-04	0.9375D+00
45	0.9151D-09	0.1000D+01	0.1000D+01	0.5053D-04	0.9566D+00
50	0.6381D-09	0.1000D+01	0.1000D+01	0.3515D-04	0.9698D+00

Computer Output Table for Experimental Conditions on 12/03/91
 Experiment #3, 300C, pH = 11, 50 g/L solids, 67.5 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.05165	0.6039D-03	0.1166D-01	0.5794D+00	0.2341D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.7050D-02	0.5792D-02	0.9134D-08	0.8414D-04
5	0.6350D-02	0.5592D-02	0.8820D-08	0.8125D-04
10	0.5400D-02	0.5274D-02	0.8320D-08	0.7665D-04
15	0.4860D-02	0.4974D-02	0.7848D-08	0.7230D-04
20	0.4280D-02	0.4691D-02	0.7403D-08	0.6821D-04
25	0.3930D-02	0.4424D-02	0.6984D-08	0.6435D-04
30	0.3850D-02	0.4173D-02	0.6588D-08	0.6070D-04
35	0.3720D-02	0.3936D-02	0.6214D-08	0.5726D-04
40	0.3560D-02	0.3712D-02	0.5862D-08	0.5402D-04
45	0.3420D-02	0.3501D-02	0.5530D-08	0.5096D-04
50	0.3280D-02	0.3302D-02	0.5216D-08	0.4807D-04
55	0.3140D-02	0.3115D-02	0.4920D-08	0.4535D-04
60	0.2970D-02	0.2938D-02	0.4642D-08	0.4278D-04
65	0.2810D-02	0.2771D-02	0.4378D-08	0.4036D-04
70	0.2690D-02	0.2613D-02	0.4130D-08	0.3807D-04
75	0.2470D-02	0.2465D-02	0.3896D-08	0.3591D-04
80	0.2350D-02	0.2325D-02	0.3675D-08	0.3388D-04
85	0.2210D-02	0.2193D-02	0.3467D-08	0.3196D-04
90	0.2120D-02	0.2069D-02	0.3271D-08	0.3015D-04
95	0.2090D-02	0.1951D-02	0.3085D-08	0.2844D-04
100	0.1990D-02	0.1840D-02	0.2910D-08	0.2683D-04
105	0.1880D-02	0.1736D-02	0.2745D-08	0.2531D-04
110	0.1760D-02	0.1638D-02	0.2590D-08	0.2388D-04
115	0.1640D-02	0.1545D-02	0.2443D-08	0.2252D-04
120	0.1540D-02	0.1457D-02	0.2305D-08	0.2125D-04
125	0.1450D-02	0.1374D-02	0.2174D-08	0.2004D-04
130	0.1260D-02	0.1296D-02	0.2051D-08	0.1891D-04
135	0.1000D-02	0.1223D-02	0.1935D-08	0.1784D-04

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.8415D-04	0.5889D+00	0.2306D-01	0.1015D-03	0.2306D-01
5	0.8126D-04	0.6031D+00	0.5665D-01	0.9797D-04	0.5674D-01
10	0.7666D-04	0.6255D+00	0.1101D+00	0.9239D-04	0.1103D+00
15	0.7231D-04	0.6468D+00	0.1605D+00	0.8714D-04	0.1608D+00
20	0.6822D-04	0.6668D+00	0.2081D+00	0.8218D-04	0.2085D+00
25	0.6435D-04	0.6856D+00	0.2529D+00	0.7751D-04	0.2534D+00
30	0.6071D-04	0.7034D+00	0.2952D+00	0.7311D-04	0.2958D+00
35	0.5727D-04	0.7202D+00	0.3352D+00	0.6895D-04	0.3357D+00
40	0.5402D-04	0.7361D+00	0.3728D+00	0.6503D-04	0.3734D+00
45	0.5096D-04	0.7510D+00	0.4083D+00	0.6134D-04	0.4090D+00
50	0.4808D-04	0.7651D+00	0.4419D+00	0.5785D-04	0.4425D+00
55	0.4535D-04	0.7785D+00	0.4735D+00	0.5457D-04	0.4742D+00
60	0.4278D-04	0.7910D+00	0.5033D+00	0.5147D-04	0.5040D+00
65	0.4036D-04	0.8028D+00	0.5314D+00	0.4854D-04	0.5321D+00
70	0.3807D-04	0.8140D+00	0.5580D+00	0.4579D-04	0.5587D+00
75	0.3592D-04	0.8245D+00	0.5830D+00	0.4319D-04	0.5837D+00
80	0.3388D-04	0.8345D+00	0.6066D+00	0.4073D-04	0.6073D+00
85	0.3196D-04	0.8439D+00	0.6289D+00	0.3842D-04	0.6296D+00
90	0.3015D-04	0.8527D+00	0.6499D+00	0.3624D-04	0.6506D+00
95	0.2844D-04	0.8610D+00	0.6698D+00	0.3418D-04	0.6704D+00
100	0.2683D-04	0.8689D+00	0.6885D+00	0.3224D-04	0.6891D+00
105	0.2531D-04	0.8763D+00	0.7061D+00	0.3041D-04	0.7067D+00
110	0.2388D-04	0.8834D+00	0.7228D+00	0.2869D-04	0.7234D+00
115	0.2253D-04	0.8900D+00	0.7385D+00	0.2706D-04	0.7391D+00
120	0.2125D-04	0.8962D+00	0.7533D+00	0.2552D-04	0.7538D+00
125	0.2005D-04	0.9021D+00	0.7673D+00	0.2408D-04	0.7678D+00
130	0.1891D-04	0.9076D+00	0.7805D+00	0.2271D-04	0.7810D+00
135	0.1784D-04	0.9129D+00	0.7929D+00	0.2142D-04	0.7934D+00

Computer Output Table for Experimental Conditions on 12/05/91
 Experiment* 1, 30oC, pH = 10, 100 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.02301	0.3210D-02	0.1570D-01	0.7516D+00	0.1994D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.1568D-01	0.1477D-01	0.9810D-07	0.4856D-04
5	0.1364D-01	0.1419D-01	0.9379D-07	0.4633D-04
10	0.1246D-01	0.1327D-01	0.8702D-07	0.4284D-04
15	0.1187D-01	0.1241D-01	0.8074D-07	0.3961D-04
20	0.1147D-01	0.1159D-01	0.7490D-07	0.3663D-04
25	0.1092D-01	0.1083D-01	0.6948D-07	0.3387D-04
30	0.1033D-01	0.1012D-01	0.6445D-07	0.3131D-04
35	0.9840D-02	0.9451D-02	0.5978D-07	0.2895D-04
40	0.9440D-02	0.8824D-02	0.5544D-07	0.2677D-04
45	0.9110D-02	0.8236D-02	0.5142D-07	0.2476D-04
50	0.8380D-02	0.7686D-02	0.4769D-07	0.2289D-04
55	0.7930D-02	0.7172D-02	0.4422D-07	0.2117D-04
60	0.7300D-02	0.6690D-02	0.4101D-07	0.1957D-04
65	0.6710D-02	0.6240D-02	0.3803D-07	0.1810D-04
70	0.6130D-02	0.5818D-02	0.3526D-07	0.1673D-04
75	0.5720D-02	0.5424D-02	0.3269D-07	0.1547D-04
80	0.5220D-02	0.5056D-02	0.3031D-07	0.1431D-04
85	0.4610D-02	0.4712D-02	0.2810D-07	0.1323D-04
90	0.4300D-02	0.4391D-02	0.2605D-07	0.1223D-04
95	0.3870D-02	0.4091D-02	0.2415D-07	0.1131D-04
100	0.3590D-02	0.3811D-02	0.2238D-07	0.1046D-04
105	0.3350D-02	0.3549D-02	0.2075D-07	0.9669D-05
110	0.3120D-02	0.3305D-02	0.1923D-07	0.8940D-05
115	0.2910D-02	0.3077D-02	0.1782D-07	0.8267D-05
120	0.2720D-02	0.2865D-02	0.1652D-07	0.7644D-05
125	0.2520D-02	0.2666D-02	0.1531D-07	0.7068D-05
130	0.2350D-02	0.2482D-02	0.1419D-07	0.6535D-05
135	0.2170D-02	0.2309D-02	0.1315D-07	0.6043D-05

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
140	0.2240D-02	0.2149D-02	0.1218D-07	0.5587D-05
150	0.2000D-02	0.1859D-02	0.1046D-07	0.4777D-05
160	0.1690D-02	0.1608D-02	0.8982D-08	0.4084D-05
170	0.1470D-02	0.1391D-02	0.7711D-08	0.3492D-05
180	0.1250D-02	0.1202D-02	0.6618D-08	0.2985D-05

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.4866D-04	0.7587D+00	0.3085D-01	0.2100D-03	0.2627D-01
5	0.4642D-04	0.7698D+00	0.7535D-01	0.2018D-03	0.6615D-01
10	0.4293D-04	0.7872D+00	0.1450D+00	0.1887D-03	0.1292D+00
15	0.3969D-04	0.8032D+00	0.2095D+00	0.1764D-03	0.1881D+00
20	0.3670D-04	0.8180D+00	0.2690D+00	0.1649D-03	0.2431D+00
25	0.3394D-04	0.8317D+00	0.3241D+00	0.1540D-03	0.2946D+00
30	0.3138D-04	0.8444D+00	0.3750D+00	0.1439D-03	0.3427D+00
35	0.2901D-04	0.8561D+00	0.4221D+00	0.1344D-03	0.3876D+00
40	0.2683D-04	0.8670D+00	0.4657D+00	0.1255D-03	0.4295D+00
45	0.2481D-04	0.8770D+00	0.5059D+00	0.1171D-03	0.4686D+00
50	0.2294D-04	0.8863D+00	0.5432D+00	0.1093D-03	0.5052D+00
55	0.2121D-04	0.8948D+00	0.5776D+00	0.1020D-03	0.5393D+00
60	0.1961D-04	0.9028D+00	0.6094D+00	0.9512D-04	0.5711D+00
65	0.1813D-04	0.9101D+00	0.6389D+00	0.8872D-04	0.6007D+00
70	0.1677D-04	0.9169D+00	0.6661D+00	0.8273D-04	0.6284D+00
75	0.1550D-04	0.9231D+00	0.6912D+00	0.7712D-04	0.6542D+00
80	0.1434D-04	0.9289D+00	0.7145D+00	0.7189D-04	0.6782D+00
85	0.1326D-04	0.9343D+00	0.7360D+00	0.6700D-04	0.7006D+00
90	0.1226D-04	0.9392D+00	0.7559D+00	0.6243D-04	0.7215D+00
95	0.1133D-04	0.9438D+00	0.7743D+00	0.5816D-04	0.7410D+00
100	0.1048D-04	0.9480D+00	0.7913D+00	0.5418D-04	0.7591D+00
105	0.9690D-05	0.9520D+00	0.8070D+00	0.5046D-04	0.7760D+00
110	0.8960D-05	0.9556D+00	0.8216D+00	0.4699D-04	0.7917D+00
115	0.8284D-05	0.9589D+00	0.8350D+00	0.4375D-04	0.8064D+00

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
120	0.7660D-05	0.9620D+00	0.8474D+00	0.4073D-04	0.8200D+00
125	0.7083D-05	0.9649D+00	0.8589D+00	0.3791D-04	0.8327D+00
130	0.6549D-05	0.9675D+00	0.8696D+00	0.3528D-04	0.8445D+00
135	0.6056D-05	0.9700D+00	0.8794D+00	0.3283D-04	0.8555D+00
140	0.5600D-05	0.9722D+00	0.8885D+00	0.3055D-04	0.8657D+00
150	0.4787D-05	0.9763D+00	0.9047D+00	0.2644D-04	0.8841D+00
160	0.4093D-05	0.9797D+00	0.9185D+00	0.2287D-04	0.9000D+00
170	0.3500D-05	0.9826D+00	0.9303D+00	0.1977D-04	0.9137D+00
180	0.2992D-05	0.9852D+00	0.9404D+00	0.1709D-04	0.9256D+00

Computer Output Table for Experimental Conditions on 12/06/91

Experiment #1, 45oC, pH = 10, 50 g/L solids, 60 scfm nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.7742	0.7332D-03	0.6566D-01	0.6419D+00	0.4245D+00

TIME	EXPTL CA	CALC CA	CALC CAS1	CALC CAS2
MINUTES	L-PHASE	L-PHASE	S-PHASE	S-PHASE
	MOL/L	MOL/L	MOL/GRAM	MOL/GRAM

15	0.3360D-02	0.3984D-02	0.2779D-08	0.2752D-04
20	0.4850D-02	0.3246D-02	0.2168D-08	0.1982D-04
25	0.5150D-02	0.2615D-02	0.1683D-08	0.1427D-04
30	0.1970D-02	0.2086D-02	0.1301D-08	0.1028D-04
35	0.1510D-02	0.1651D-02	0.1002D-08	0.7402D-05
40	0.1160D-02	0.1297D-02	0.7696D-09	0.5330D-05
45	0.9500D-03	0.1014D-02	0.5593D-09	0.3839D-05
50	0.8000D-03	0.7887D-03	0.4501D-09	0.2764D-05
55	0.6300D-03	0.6108D-03	0.3430D-09	0.1991D-05
60	0.5100D-03	0.4713D-03	0.2608D-09	0.1434D-05

TIME,	TOTAL NH3	FRACTION	FRACTIONAL	YAG	FRACTION
MINUTES	IN SOLIDS	AMMONIA	CONVERSION	MOL	OF NH3
	MOL/GRAM	REMOVED	OF (NH4)2SO3	FRACTION	REMOVED
		FROM SOLIDS	TO NH3(AQ)		FROM SYSTEM

15	0.2752D-04	0.8662D+00	0.6265D+00	0.2370D-03	0.4789D+00
20	0.1982D-04	0.9037D+00	0.7310D+00	0.1932D-03	0.5880D+00
25	0.1427D-04	0.9306D+00	0.8063D+00	0.1556D-03	0.6764D+00
30	0.1028D-04	0.9500D+00	0.8605D+00	0.1234D-03	0.7473D+00
35	0.7403D-05	0.9640D+00	0.8995D+00	0.9821D-04	0.8035D+00
40	0.5331D-05	0.9741D+00	0.9277D+00	0.7720D-04	0.8479D+00
45	0.3839D-05	0.9813D+00	0.9479D+00	0.5969D-04	0.8827D+00
50	0.2765D-05	0.9866D+00	0.9625D+00	0.4693D-04	0.9099D+00
55	0.1991D-05	0.9903D+00	0.9730D+00	0.3635D-04	0.9309D+00
60	0.1434D-05	0.9930D+00	0.9805D+00	0.2621D-04	0.9472D+00

Computer Output Table for Experimental Conditions on 12/06/91
 Experiment #2, 45oC, pH = 10, 100g/L solids, 40 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.0217	0.1823D-01	0.1982D+01	0.8865D+00	0.4503D+00

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.1906D-01	0.1876D-01	0.5414D-05	0.4459D-06
5	0.1945D-01	0.1690D-01	0.2094D-06	0.1168D-08
10	0.1431D-01	0.1350D-01	0.1511D-06	0.6927D-13
15	0.1074D-01	0.1079D-01	0.1207D-06	0.2677D-14
20	0.7590D-02	0.8619D-02	0.9643D-07	0.1296D-14
25	0.6380D-02	0.6886D-02	0.7704D-07	0.1130D-14
30	0.4760D-02	0.5501D-02	0.6155D-07	0.4056D-15
35	0.4110D-02	0.4395D-02	0.4917D-07	0.1406D-15
40	0.3230D-02	0.3511D-02	0.3929D-07	0.2856D-17
45	0.2630D-02	0.2805D-02	0.3139D-07	0.5591D-15
50	0.2150D-02	0.2241D-02	0.2508D-07	0.1689D-15
55	0.1610D-02	0.1791D-02	0.2003D-07	0.4087D-15
60	0.1500D-02	0.1431D-02	0.1601D-07	0.5766D-15
65	0.1100D-02	0.1143D-02	0.1279D-07	0.2325D-14
70	0.8900D-03	0.9133D-03	0.1022D-07	0.1538D-14
75	0.7200D-03	0.7298D-03	0.8166D-08	0.2279D-15
80	0.5900D-03	0.5832D-03	0.6525D-08	0.5841D-15
85	0.4900D-03	0.4660D-03	0.5214D-08	0.3098D-16
90	0.4200D-03	0.3723D-03	0.4166D-08	0.2854D-15
95	0.3500D-03	0.2975D-03	0.3329D-08	0.2829D-16

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.5860D-05	0.9717D+00	0.9810D+00	0.1164D-02	0.6413D-01
5	0.2106D-06	0.9990D+00	0.1000D+01	0.1049D-02	0.1815D+00
10	0.1511D-06	0.9993D+00	0.1000D+01	0.8379D-03	0.3461D+00
15	0.1207D-06	0.9994D+00	0.1000D+01	0.6694D-03	0.4776D+00
20	0.9643D-07	0.9995D+00	0.1000D+01	0.5348D-03	0.5826D+00
25	0.7704D-07	0.9996D+00	0.1000D+01	0.4273D-03	0.6665D+00
30	0.6155D-07	0.9997D+00	0.1000D+01	0.3414D-03	0.7336D+00
35	0.4917D-07	0.9998D+00	0.1000D+01	0.2727D-03	0.7872D+00
40	0.3929D-07	0.9998D+00	0.1000D+01	0.2179D-03	0.8300D+00
45	0.3139D-07	0.9998D+00	0.1000D+01	0.1741D-03	0.8641D+00
50	0.2508D-07	0.9999D+00	0.1000D+01	0.1391D-03	0.8915D+00
55	0.2003D-07	0.9999D+00	0.1000D+01	0.1111D-03	0.9133D+00
60	0.1601D-07	0.9999D+00	0.1000D+01	0.8876D-04	0.9307D+00
65	0.1279D-07	0.9999D+00	0.1000D+01	0.7093D-04	0.9446D+00
70	0.1022D-07	0.1000D+01	0.1000D+01	0.5668D-04	0.9558D+00
75	0.8166D-08	0.1000D+01	0.1000D+01	0.4529D-04	0.9647D+00
80	0.6525D-08	0.1000D+01	0.1000D+01	0.3619D-04	0.9718D+00
85	0.5214D-08	0.1000D+01	0.1000D+01	0.2892D-04	0.9774D+00
90	0.4166D-08	0.1000D+01	0.1000D+01	0.2310D-04	0.9820D+00
95	0.3329D-08	0.1000D+01	0.1000D+01	0.1846D-04	0.9856D+00

Computer Output Table for Experimental Conditions on 12/11/91
 Experiment #1, 30oC, pH = 11, 50 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.006054	0.2271D-02	0.1142D+00	0.6527D+00	0.2411D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.7790D-02	0.7634D-02	0.3469D-05	0.6168D-04
5	0.7800D-02	0.8082D-02	0.1980D-05	0.4379D-04
10	0.8270D-02	0.8179D-02	0.1126D-05	0.2474D-04
15	0.8160D-02	0.7857D-02	0.6438D-06	0.1398D-04
20	0.7900D-02	0.7339D-02	0.3703D-06	0.7896D-05
25	0.7500D-02	0.6744D-02	0.2152D-06	0.4461D-05
30	0.7060D-02	0.6138D-02	0.1269D-06	0.2520D-05
35	0.6430D-02	0.5553D-02	0.7644D-07	0.1424D-05
40	0.5670D-02	0.5006D-02	0.4746D-07	0.8043D-06
45	0.5040D-02	0.4502D-02	0.3064D-07	0.4544D-06
50	0.4440D-02	0.4043D-02	0.2074D-07	0.2567D-06
55	0.3920D-02	0.3628D-02	0.1479D-07	0.1450D-06
60	0.3480D-02	0.3254D-02	0.1111D-07	0.8193D-07
65	0.3050D-02	0.2917D-02	0.8740D-08	0.4628D-07
70	0.2700D-02	0.2614D-02	0.7147D-08	0.2615D-07
75	0.2380D-02	0.2343D-02	0.6017D-08	0.1477D-07
80	0.2170D-02	0.2099D-02	0.5172D-08	0.8346D-08
85	0.1840D-02	0.1881D-02	0.4511D-08	0.4715D-08
90	0.1680D-02	0.1685D-02	0.3972D-08	0.2664D-08
95	0.1520D-02	0.1510D-02	0.3519D-08	0.1505D-08
100	0.1350D-02	0.1353D-02	0.3131D-08	0.8504D-09
105	0.1210D-02	0.1212D-02	0.2792D-08	0.4805D-09
110	0.1060D-02	0.1086D-02	0.2495D-08	0.2716D-09
115	0.9300D-03	0.9731D-03	0.2231D-08	0.1535D-09
120	0.8500D-03	0.8719D-03	0.1997D-08	0.8678D-10
125	0.7600D-03	0.7811D-03	0.1788D-08	0.4906D-10
130	0.6700D-03	0.6999D-03	0.1601D-08	0.2772D-10
135	0.5800D-03	0.6270D-03	0.1434D-08	0.1567D-10
140	0.5500D-03	0.5618D-03	0.1285D-08	0.8856D-11

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.6515D-04	0.7081D+00	0.2042D+00	0.1251D-03	0.2406D-01
5	0.4577D-04	0.7949D+00	0.4351D+00	0.1317D-03	0.7073D-01
10	0.2587D-04	0.8841D+00	0.6808D+00	0.1341D-03	0.1513D+00
15	0.1462D-04	0.9345D+00	0.8197D+00	0.1288D-03	0.2305D+00
20	0.8266D-05	0.9630D+00	0.8981D+00	0.1204D-03	0.3054D+00
25	0.4676D-05	0.9791D+00	0.9425D+00	0.1108D-03	0.3747D+00
30	0.2647D-05	0.9881D+00	0.9675D+00	0.1013D-03	0.4382D+00
35	0.1500D-05	0.9933D+00	0.9816D+00	0.9104D-04	0.4957D+00
40	0.8517D-06	0.9962D+00	0.9896D+00	0.8209D-04	0.5476D+00
45	0.4850D-06	0.9978D+00	0.9941D+00	0.7383D-04	0.5944D+00
50	0.2774D-06	0.9988D+00	0.9967D+00	0.6631D-04	0.6364D+00
55	0.1598D-06	0.9993D+00	0.9981D+00	0.5950D-04	0.6742D+00
60	0.9303D-07	0.9996D+00	0.9989D+00	0.5356D-04	0.7080D+00
65	0.5502D-07	0.9998D+00	0.9994D+00	0.4753D-04	0.7384D+00
70	0.3329D-07	0.9999D+00	0.9997D+00	0.4287D-04	0.7656D+00
75	0.2079D-07	0.9999D+00	0.9998D+00	0.3842D-04	0.7900D+00
80	0.1352D-07	0.9999D+00	0.9999D+00	0.3443D-04	0.8118D+00
85	0.9226D-08	0.1000D+01	0.9999D+00	0.3088D-04	0.8314D+00
90	0.6636D-08	0.1000D+01	0.1000D+01	0.2784D-04	0.8489D+00
95	0.5024D-08	0.1000D+01	0.1000D+01	0.2474D-04	0.8647D+00
100	0.3981D-08	0.1000D+01	0.1000D+01	0.2219D-04	0.8787D+00
105	0.3273D-08	0.1000D+01	0.1000D+01	0.1987D-04	0.8914D+00
110	0.2766D-08	0.1000D+01	0.1000D+01	0.1776D-04	0.9027D+00
115	0.2385D-08	0.1000D+01	0.1000D+01	0.1561D-04	0.9128D+00
120	0.2084D-08	0.1000D+01	0.1000D+01	0.1497D-04	0.9219D+00
125	0.1837D-08	0.1000D+01	0.1000D+01	0.1219D-04	0.9300D+00
130	0.1629D-08	0.1000D+01	0.1000D+01	0.1351D-04	0.9373D+00
135	0.1450D-08	0.1000D+01	0.1000D+01	0.1085D-04	0.9438D+00
140	0.1293D-08	0.1000D+01	0.1000D+01	0.8326D-05	0.9497D+00

Computer Output for Experimental Conditions on 12/12/91

Experiment #1, 45°C, pH = 10, 50 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.1316	0.3494D-02	0.1229D+01	0.8937D+00	0.2485D+00

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
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2	0.7460D-02	0.9991D-02	0.6108D-07	0.2008D-05
5	0.7640D-02	0.8804D-02	0.1948D-07	0.5030D-07
10	0.6210D-02	0.7011D-02	0.1471D-07	0.1122D-09
15	0.5080D-02	0.5581D-02	0.1171D-07	0.5633D-12
20	0.4180D-02	0.4440D-02	0.9316D-08	0.8765D-13
25	0.3410D-02	0.3526D-02	0.7398D-08	0.3384D-13
30	0.2740D-02	0.2799D-02	0.5872D-08	0.1050D-13
35	0.1900D-02	0.2221D-02	0.4660D-08	0.2560D-16
40	0.1100D-02	0.1768D-02	0.3709D-08	0.4682D-14
45	0.6100D-03	0.1411D-02	0.2961D-08	0.2502D-14

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
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2	0.2070D-05	0.9906D+00	0.9144D+00	0.6126D-03	0.8607D-01
5	0.6977D-07	0.9997D+00	0.9979D+00	0.5398D-03	0.2026D+00
10	0.1482D-07	0.9999D+00	0.1000D+01	0.4299D-03	0.3652D+00
15	0.1171D-07	0.9999D+00	0.1000D+01	0.3422D-03	0.4947D+00
20	0.9316D-08	0.1000D+01	0.1000D+01	0.2722D-03	0.5980D+00
25	0.7398D-08	0.1000D+01	0.1000D+01	0.2162D-03	0.6807D+00
30	0.5872D-08	0.1000D+01	0.1000D+01	0.1716D-03	0.7466D+00
35	0.4660D-08	0.1000D+01	0.1000D+01	0.1362D-03	0.7989D+00
40	0.3709D-08	0.1000D+01	0.1000D+01	0.1084D-03	0.8399D+00
45	0.2961D-08	0.1000D+01	0.1000D+01	0.8654D-04	0.8722D+00

Computer Output for Experimental Conditions on 12/12/91

Experiment #3, 45oC, pH = 11, 50 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.02409	0.3748D-01	0.1364D+01	0.6950D+00	0.7081D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
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2	0.1044D-01	0.8434D-02	0.3460D-04	0.4406D-05
5	0.1552D-01	0.8665D-02	0.2077D-05	0.7367D-07
10	0.1194D-01	0.6497D-02	0.1650D-06	0.8074D-10
15	0.8960D-02	0.4815D-02	0.1148D-06	0.1033D-12
20	0.6720D-02	0.3569D-02	0.8504D-07	0.1276D-15
25	0.5080D-02	0.2645D-02	0.6302D-07	0.9161D-16
30	0.3370D-02	0.1960D-02	0.4671D-07	0.2808D-16
35	0.1950D-02	0.1452D-02	0.3461D-07	0.3039D-16
40	0.1120D-02	0.1076D-02	0.2565D-07	0.5146D-17
45	0.6500D-03	0.7976D-03	0.1901D-07	0.1323D-16
50	0.4500D-03	0.5910D-03	0.1408D-07	0.2019D-17

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
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2	0.3901D-04	0.8234D+00	0.9346D+00	0.3772D-03	0.5983D-01
5	0.2151D-05	0.9903D+00	0.9989D+00	0.3888D-03	0.2058D+00
10	0.1650D-06	0.9993D+00	0.1000D+01	0.2916D-03	0.4110D+00
15	0.1148D-06	0.9995D+00	0.1000D+01	0.2161D-03	0.5635D+00
20	0.8504D-07	0.9996D+00	0.1000D+01	0.1601D-03	0.6765D+00
25	0.6302D-07	0.9997D+00	0.1000D+01	0.1187D-03	0.7603D+00
30	0.4671D-07	0.9998D+00	0.1000D+01	0.8796D-04	0.8223D+00
35	0.3461D-07	0.9998D+00	0.1000D+01	0.6518D-04	0.8683D+00
40	0.2565D-07	0.9999D+00	0.1000D+01	0.4830D-04	0.9024D+00
45	0.1901D-07	0.9999D+00	0.1000D+01	0.3580D-04	0.9277D+00
50	0.1408D-07	0.9999D+00	0.1000D+01	0.2652D-04	0.9464D+00

Computer Output Table for Experimental Conditions on 12/13/91
 Experiment #1, 30oC, pH = 11, 100 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.008015	0.7173D-02	0.6833D-01	0.6089D+00	0.2497D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.1251D-01	0.1246D-01	0.5631D-05	0.6955D-04
5	0.1327D-01	0.1322D-01	0.2227D-05	0.5667D-04
10	0.1345D-01	0.1343D-01	0.1593D-05	0.4027D-04
15	0.1327D-01	0.1315D-01	0.1148D-05	0.2862D-04
20	0.1284D-01	0.1257D-01	0.8296D-06	0.2034D-04
25	0.1218D-01	0.1182D-01	0.6022D-06	0.1446D-04
30	0.1141D-01	0.1098D-01	0.4392D-06	0.1027D-04
35	0.1068D-01	0.1011D-01	0.3222D-06	0.7302D-05
40	0.9740D-02	0.9248D-02	0.2380D-06	0.5190D-05
45	0.8940D-02	0.8418D-02	0.1772D-06	0.3688D-05
50	0.8050D-02	0.7634D-02	0.1331D-06	0.2621D-05
55	0.7200D-02	0.6901D-02	0.1010D-06	0.1863D-05
60	0.6560D-02	0.6225D-02	0.7755D-07	0.1324D-05
65	0.5790D-02	0.5605D-02	0.6026D-07	0.9410D-06
70	0.5180D-02	0.5040D-02	0.4743D-07	0.6688D-06
75	0.4600D-02	0.4526D-02	0.3782D-07	0.4753D-06
80	0.4170D-02	0.4062D-02	0.3056D-07	0.3378D-06
85	0.3980D-02	0.3642D-02	0.2501D-07	0.2401D-06
90	0.3650D-02	0.3264D-02	0.2072D-07	0.1706D-06
95	0.3440D-02	0.2924D-02	0.1736D-07	0.1213D-06
100	0.3160D-02	0.2619D-02	0.1469D-07	0.8619D-07
105	0.2770D-02	0.2345D-02	0.1255D-07	0.6125D-07
110	0.2380D-02	0.2099D-02	0.1080D-07	0.4353D-07
115	0.2020D-02	0.1878D-02	0.9359D-08	0.3094D-07
120	0.1770D-02	0.1681D-02	0.8158D-08	0.2199D-07
125	0.1480D-02	0.1504D-02	0.7145D-08	0.1563D-07
130	0.1300D-02	0.1345D-02	0.6283D-08	0.1111D-07
135	0.1140D-02	0.1204D-02	0.5543D-08	0.7894D-08

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
140	0.9900D-03	0.1077D-02	0.4903D-08	0.5610D-08
150	0.7900D-03	0.8615D-03	0.3860D-08	0.2834D-08
160	0.6300D-03	0.6892D-03	0.3057D-08	0.1432D-08
170	0.5000D-03	0.5514D-03	0.2429D-08	0.7234D-09
180	0.4000D-03	0.4411D-03	0.1935D-08	0.3656D-09

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.7518D-04	0.6313D+00	0.1277D+00	0.2135D-03	0.2042D-01
5	0.5889D-04	0.7112D+00	0.2893D+00	0.2266D-03	0.6301D-01
10	0.4187D-04	0.7947D+00	0.4949D+00	0.2303D-03	0.1383D+00
15	0.2977D-04	0.8540D+00	0.6410D+00	0.2255D-03	0.2092D+00
20	0.2117D-04	0.8962D+00	0.7449D+00	0.2156D-03	0.2797D+00
25	0.1506D-04	0.9261D+00	0.8187D+00	0.2027D-03	0.3466D+00
30	0.1071D-04	0.9475D+00	0.8711D+00	0.1890D-03	0.4090D+00
35	0.7625D-05	0.9626D+00	0.9084D+00	0.1734D-03	0.4668D+00
40	0.5428D-05	0.9734D+00	0.9349D+00	0.1588D-03	0.5198D+00
45	0.3866D-05	0.9810D+00	0.9537D+00	0.1437D-03	0.5682D+00
50	0.2755D-05	0.9865D+00	0.9671D+00	0.1312D-03	0.6121D+00
55	0.1964D-05	0.9904D+00	0.9766D+00	0.1192D-03	0.6519D+00
60	0.1402D-05	0.9931D+00	0.9834D+00	0.1068D-03	0.6878D+00
65	0.1001D-05	0.9951D+00	0.9882D+00	0.9615D-04	0.7202D+00
70	0.7162D-06	0.9965D+00	0.9916D+00	0.8645D-04	0.7493D+00
75	0.5131D-06	0.9975D+00	0.9940D+00	0.7764D-04	0.7755D+00
80	0.3684D-06	0.9982D+00	0.9958D+00	0.6967D-04	0.7990D+00
85	0.2651D-06	0.9987D+00	0.9970D+00	0.6247D-04	0.8201D+00
90	0.1913D-06	0.9991D+00	0.9979D+00	0.5599D-04	0.8390D+00
95	0.1386D-06	0.9993D+00	0.9985D+00	0.5016D-04	0.8559D+00
100	0.1009D-06	0.9995D+00	0.9989D+00	0.4492D-04	0.8711D+00
105	0.7380D-07	0.9996D+00	0.9992D+00	0.4022D-04	0.8846D+00
110	0.5433D-07	0.9997D+00	0.9995D+00	0.3600D-04	0.8968D+00
115	0.4030D-07	0.9998D+00	0.9996D+00	0.3212D-04	0.9077D+00

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
120	0.3015D-07	0.9999D+00	0.9997D+00	0.2936D-04	0.9174D+00
125	0.2277D-07	0.9999D+00	0.9998D+00	0.2613D-04	0.9261D+00
130	0.1739D-07	0.9999D+00	0.9999D+00	0.2270D-04	0.9339D+00
135	0.1344D-07	0.9999D+00	0.9999D+00	0.2176D-04	0.9409D+00
140	0.1051D-07	0.9999D+00	0.9999D+00	0.1890D-04	0.9471D+00
150	0.6694D-08	0.1000D+01	0.1000D+01	0.1464D-04	0.9577D+00
160	0.4488D-08	0.1000D+01	0.1000D+01	0.1184D-04	0.9662D+00
170	0.3153D-08	0.1000D+01	0.1000D+01	0.9458D-05	0.9729D+00
180	0.2301D-08	0.1000D+01	0.1000D+01	0.7570D-05	0.9784D+00

Computer Output Table for Experimental Conditions on 12/17/91
 Experiment #1, 30oC, pH = 10, 100 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.009465	0.9010D-02	0.1295D+00	0.7883D+00	0.2297D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.8330D-02	0.8177D-02	0.7713D-05	0.3446D-04
5	0.8450D-02	0.8477D-02	0.1940D-05	0.2336D-04
10	0.8700D-02	0.8180D-02	0.1022D-05	0.1222D-04
15	0.8820D-02	0.7642D-02	0.5531D-06	0.6394D-05
20	0.8220D-02	0.7017D-02	0.3059D-06	0.3345D-05
25	0.7710D-02	0.6383D-02	0.1749D-06	0.1750D-05
30	0.7440D-02	0.5774D-02	0.1048D-06	0.9157D-06
35	0.6690D-02	0.5207D-02	0.6680D-07	0.4790D-06
40	0.6050D-02	0.4687D-02	0.4569D-07	0.2506D-06
45	0.5480D-02	0.4215D-02	0.3355D-07	0.1311D-06
50	0.5210D-02	0.3788D-02	0.2622D-07	0.6860D-07
55	0.4860D-02	0.3404D-02	0.2150D-07	0.3589D-07
60	0.4210D-02	0.3057D-02	0.1823D-07	0.1877D-07
65	0.3660D-02	0.2746D-02	0.1581D-07	0.9822D-08
70	0.3220D-02	0.2466D-02	0.1391D-07	0.5138D-08
75	0.2950D-02	0.2214D-02	0.1233D-07	0.2688D-08
80	0.2710D-02	0.1989D-02	0.1100D-07	0.1406D-08
85	0.2320D-02	0.1786D-02	0.9832D-08	0.7349D-09
90	0.1930D-02	0.1604D-02	0.8807D-08	0.3839D-09
95	0.1600D-02	0.1440D-02	0.7897D-08	0.2006D-09
100	0.1350D-02	0.1293D-02	0.7085D-08	0.1046D-09
105	0.1110D-02	0.1161D-02	0.6359D-08	0.5449D-10
110	0.9200D-03	0.1043D-02	0.5709D-08	0.2841D-10
115	0.7900D-03	0.9363D-03	0.5126D-08	0.1471D-10
120	0.7200D-03	0.8408D-03	0.4602D-08	0.7488D-11
125	0.6500D-03	0.7550D-03	0.4133D-08	0.3789D-11

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
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130	0.5900D-03	0.6780D-03	0.3711D-08	0.1939D-11
140	0.5000D-03	0.5467D-03	0.2992D-08	0.4285D-12
150	0.4000D-03	0.4408D-03	0.2413D-08	0.4619D-13
160	0.3300D-03	0.3554D-03	0.1945D-08	0.1048D-12

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
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2	0.4217D-04	0.8001D+00	0.2283D+00	0.1351D-03	0.4124D+00
5	0.2530D-04	0.8801D+00	0.4768D+00	0.1401D-03	0.4782D+00
10	0.1324D-04	0.9372D+00	0.7263D+00	0.1352D-03	0.5495D+00
15	0.6948D-05	0.9671D+00	0.8568D+00	0.1263D-03	0.6048D+00
20	0.3651D-05	0.9827D+00	0.9251D+00	0.1160D-03	0.6500D+00
25	0.1925D-05	0.9909D+00	0.9608D+00	0.1055D-03	0.6883D+00
30	0.1020D-05	0.9952D+00	0.9795D+00	0.9630D-04	0.7215D+00
35	0.5458D-06	0.9974D+00	0.9893D+00	0.8614D-04	0.7506D+00
40	0.2963D-06	0.9986D+00	0.9944D+00	0.7746D-04	0.7764D+00
45	0.1647D-06	0.9992D+00	0.9971D+00	0.6949D-04	0.7994D+00
50	0.9482D-07	0.9996D+00	0.9985D+00	0.6480D-04	0.8200D+00
55	0.5739D-07	0.9997D+00	0.9992D+00	0.5667D-04	0.8384D+00
60	0.3701D-07	0.9998D+00	0.9996D+00	0.5120D-04	0.8549D+00
65	0.2563D-07	0.9999D+00	0.9998D+00	0.4465D-04	0.8697D+00
70	0.1904D-07	0.9999D+00	0.9999D+00	0.4115D-04	0.8830D+00
75	0.1502D-07	0.9999D+00	0.9999D+00	0.3666D-04	0.8950D+00
80	0.1240D-07	0.9999D+00	0.1000D+01	0.3288D-04	0.9057D+00
85	0.1057D-07	0.9999D+00	0.1000D+01	0.2952D-04	0.9153D+00
90	0.9191D-08	0.1000D+01	0.1000D+01	0.2651D-04	0.9239D+00
95	0.8098D-08	0.1000D+01	0.1000D+01	0.2388D-04	0.9317D+00
100	0.7190D-08	0.1000D+01	0.1000D+01	0.2138D-04	0.9387D+00
105	0.6414D-08	0.1000D+01	0.1000D+01	0.1920D-04	0.9449D+00

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
110	0.5737D-08	0.1000D+01	0.1000D+01	0.1724D-04	0.9505D+00
115	0.5140D-08	0.1000D+01	0.1000D+01	0.1548D-04	0.9556D+00
120	0.4610D-08	0.1000D+01	0.1000D+01	0.1390D-04	0.9601D+00
125	0.4136D-08	0.1000D+01	0.1000D+01	0.1248D-04	0.9642D+00
130	0.3713D-08	0.1000D+01	0.1000D+01	0.1121D-04	0.9678D+00
140	0.2993D-08	0.1000D+01	0.1000D+01	0.9038D-05	0.9741D+00
150	0.2413D-08	0.1000D+01	0.1000D+01	0.7288D-05	0.9791D+00
160	0.1945D-08	0.1000D+01	0.1000D+01	0.5377D-05	0.9831D+00

Computer Output Table for Experimental Conditions on 12/18/91
 Experiment #2, 300C, pH = 10, 100 g/L solids, 40 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.005159	0.3922D-02	0.7037D-01	0.7162D+00	0.2085D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.1528D-01	0.1514D-01	0.3608D-05	0.5187D-04
5	0.1583D-01	0.1565D-01	0.1432D-05	0.4200D-04
10	0.1550D-01	0.1577D-01	0.1017D-05	0.2954D-04
15	0.1518D-01	0.1551D-01	0.7257D-06	0.2078D-04
20	0.1507D-01	0.1501D-01	0.5202D-06	0.1461D-04
25	0.1476D-01	0.1437D-01	0.3749D-06	0.1028D-04
30	0.1445D-01	0.1365D-01	0.2721D-06	0.7229D-05
35	0.1405D-01	0.1288D-01	0.1991D-06	0.5085D-05
40	0.1356D-01	0.1211D-01	0.1473D-06	0.3577D-05
45	0.1291D-01	0.1135D-01	0.1103D-06	0.2516D-05
50	0.1229D-01	0.1061D-01	0.8382D-07	0.1769D-05
55	0.1162D-01	0.9904D-02	0.6474D-07	0.1245D-05
60	0.1091D-01	0.9232D-02	0.5090D-07	0.8754D-06
65	0.9880D-02	0.8598D-02	0.4079D-07	0.6157D-06
70	0.9080D-02	0.8001D-02	0.3332D-07	0.4331D-06
75	0.8290D-02	0.7441D-02	0.2773D-07	0.3046D-06
80	0.7570D-02	0.6918D-02	0.2350D-07	0.2142D-06
85	0.6950D-02	0.6429D-02	0.2023D-07	0.1507D-06
90	0.6390D-02	0.5974D-02	0.1767D-07	0.1060D-06
95	0.5920D-02	0.5549D-02	0.1562D-07	0.7455D-07
100	0.5400D-02	0.5155D-02	0.1395D-07	0.5244D-07
105	0.5000D-02	0.4787D-02	0.1257D-07	0.3688D-07
110	0.4630D-02	0.4446D-02	0.1139D-07	0.2594D-07
115	0.4250D-02	0.4129D-02	0.1039D-07	0.1825D-07
120	0.3960D-02	0.3834D-02	0.9510D-08	0.1283D-07
125	0.3640D-02	0.3560D-02	0.8734D-08	0.9027D-08
130	0.3320D-02	0.3305D-02	0.8043D-08	0.6349D-08

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
135	0.3080D-02	0.3069D-02	0.7420D-08	0.4466D-08
140	0.2810D-02	0.2850D-02	0.6856D-08	0.3141D-08
150	0.2420D-02	0.2457D-02	0.5873D-08	0.1554D-08
160	0.2050D-02	0.2118D-02	0.5044D-08	0.7689D-09
170	0.1610D-02	0.1826D-02	0.4338D-08	0.3805D-09
180	0.1380D-02	0.1574D-02	0.3735D-08	0.1884D-09
190	0.1180D-02	0.1357D-02	0.3218D-08	0.9324D-10

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.5547D-04	0.7363D+00	0.1313D+00	0.3098D-03	0.1668D-01
5	0.4343D-04	0.7935D+00	0.2966D+00	0.3205D-03	0.4947D-01
10	0.3055D-04	0.8547D+00	0.5053D+00	0.3229D-03	0.1051D+00
15	0.2150D-04	0.8978D+00	0.6520D+00	0.3176D-03	0.1604D+00
20	0.1513D-04	0.9281D+00	0.7553D+00	0.3074D-03	0.2143D+00
25	0.1065D-04	0.9494D+00	0.8279D+00	0.2943D-03	0.2662D+00
30	0.7501D-05	0.9643D+00	0.8789D+00	0.2794D-03	0.3156D+00
35	0.5284D-05	0.9749D+00	0.9148D+00	0.2638D-03	0.3625D+00
40	0.3724D-05	0.9823D+00	0.9401D+00	0.2480D-03	0.4066D+00
45	0.2626D-05	0.9875D+00	0.9579D+00	0.2323D-03	0.4480D+00
50	0.1853D-05	0.9912D+00	0.9704D+00	0.2176D-03	0.4867D+00
55	0.1309D-05	0.9938D+00	0.9792D+00	0.2026D-03	0.5229D+00
60	0.9263D-06	0.9956D+00	0.9853D+00	0.1891D-03	0.5567D+00
65	0.6565D-06	0.9969D+00	0.9897D+00	0.1761D-03	0.5881D+00
70	0.4664D-06	0.9978D+00	0.9927D+00	0.1638D-03	0.6174D+00
75	0.3323D-06	0.9984D+00	0.9949D+00	0.1524D-03	0.6447D+00
80	0.2377D-06	0.9989D+00	0.9964D+00	0.1417D-03	0.6700D+00
85	0.1709D-06	0.9992D+00	0.9975D+00	0.1317D-03	0.6935D+00
90	0.1237D-06	0.9994D+00	0.9982D+00	0.1223D-03	0.7154D+00
95	0.9017D-07	0.9996D+00	0.9988D+00	0.1136D-03	0.7358D+00
100	0.6639D-07	0.9997D+00	0.9991D+00	0.1056D-03	0.7546D+00
105	0.4945D-07	0.9998D+00	0.9994D+00	0.9791D-04	0.7722D+00

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
110	0.3734D-07	0.9998D+00	0.9996D+00	0.8985D-04	0.7885D+00
115	0.2863D-07	0.9999D+00	0.9997D+00	0.8458D-04	0.8036D+00
120	0.2234D-07	0.9999D+00	0.9998D+00	0.7883D-04	0.8176D+00
125	0.1776D-07	0.9999D+00	0.9998D+00	0.7229D-04	0.8307D+00
130	0.1439D-07	0.9999D+00	0.9999D+00	0.6806D-04	0.8428D+00
135	0.1189D-07	0.9999D+00	0.9999D+00	0.6324D-04	0.8540D+00
140	0.9998D-08	0.1000D+01	0.9999D+00	0.5944D-04	0.8645D+00
150	0.7427D-08	0.1000D+01	0.1000D+01	0.5028D-04	0.8832D+00
160	0.5812D-08	0.1000D+01	0.1000D+01	0.4337D-04	0.8993D+00
170	0.4719D-08	0.1000D+01	0.1000D+01	0.3739D-04	0.9132D+00
180	0.3924D-08	0.1000D+01	0.1000D+01	0.3223D-04	0.9252D+00
190	0.3311D-08	0.1000D+01	0.1000D+01	0.2778D-04	0.9355D+00

Computer Output Table for Experimental Conditions on 12/19/91
 Experiment #1, 30oC, pH = 10, 50 g/L solids, 80 scfh nominal air flow rate

OPTIMAL VALUES OF THE PARAMETERS FOR THIS CASE:

AKSA	EPS	AKR	F	KLA
0.01064	0.1050D-01	0.1004D+01	0.5316D+00	0.2166D-01

TIME MINUTES	EXPTL CA L-PHASE MOL/L	CALC CA L-PHASE MOL/L	CALC CAS1 S-PHASE MOL/GRAM	CALC CAS2 S-PHASE MOL/GRAM
2	0.1012D-01	0.8679D-02	0.1827D-04	0.1320D-04
5	0.1070D-01	0.9579D-02	0.1005D-05	0.6502D-06
10	0.1101D-01	0.8706D-02	0.6183D-07	0.4303D-08
15	0.1026D-01	0.7847D-02	0.5010D-07	0.2859D-10
20	0.1012D-01	0.7072D-02	0.4512D-07	0.1727D-12
25	0.9430D-02	0.6374D-02	0.4066D-07	0.1130D-13
30	0.8790D-02	0.5744D-02	0.3665D-07	-0.2680D-14
35	0.7850D-02	0.5177D-02	0.3303D-07	0.7844D-15
40	0.6770D-02	0.4666D-02	0.2977D-07	-0.4696D-16
45	0.5760D-02	0.4205D-02	0.2683D-07	-0.1211D-14
50	0.5010D-02	0.3790D-02	0.2418D-07	-0.2194D-14
55	0.4350D-02	0.3416D-02	0.2179D-07	-0.8802D-15
60	0.3670D-02	0.3078D-02	0.1964D-07	0.1262D-15
65	0.3170D-02	0.2774D-02	0.1770D-07	0.1229D-15
70	0.2710D-02	0.2500D-02	0.1595D-07	-0.3823D-16
75	0.2390D-02	0.2253D-02	0.1438D-07	-0.7386D-16
80	0.2090D-02	0.2031D-02	0.1296D-07	-0.1669D-15
85	0.1830D-02	0.1830D-02	0.1168D-07	-0.3480D-16
90	0.1650D-02	0.1649D-02	0.1052D-07	0.2968D-16
95	0.1430D-02	0.1486D-02	0.9483D-08	0.3503D-16
100	0.1240D-02	0.1340D-02	0.8546D-08	0.2234D-16
105	0.1100D-02	0.1207D-02	0.7702D-08	-0.7097D-17
110	0.9600D-03	0.1088D-02	0.6941D-08	-0.6687D-17
115	0.8400D-03	0.9806D-03	0.6256D-08	-0.7776D-17
120	0.7300D-03	0.8837D-03	0.5638D-08	0.3021D-18

TIME, MINUTES	TOTAL NH3 IN SOLIDS MOL/GRAM	FRACTION AMMONIA REMOVED FROM SOLIDS	FRACTIONAL CONVERSION OF (NH4)2SO3 TO NH3(AQ)	YAG MOL FRACTION	FRACTION OF NH3 REMOVED FROM SYSTEM
2	0.3147D-04	0.8500D+00	0.8656D+00	0.1345D-03	0.2243D-01
5	0.1656D-05	0.9921D+00	0.9934D+00	0.1473D-03	0.7870D-01
10	0.6614D-07	0.9997D+00	0.1000D+01	0.1351D-03	0.1695D+00
15	0.5013D-07	0.9998D+00	0.1000D+01	0.1229D-03	0.2515D+00
20	0.4512D-07	0.9998D+00	0.1000D+01	0.1098D-03	0.3255D+00
25	0.4066D-07	0.9998D+00	0.1000D+01	0.9894D-04	0.3921D+00
30	0.3665D-07	0.9998D+00	0.1000D+01	0.8917D-04	0.4521D+00
35	0.3303D-07	0.9998D+00	0.1000D+01	0.8036D-04	0.5062D+00
40	0.2977D-07	0.9999D+00	0.1000D+01	0.7243D-04	0.5550D+00
45	0.2683D-07	0.9999D+00	0.1000D+01	0.6527D-04	0.5989D+00
50	0.2418D-07	0.9999D+00	0.1000D+01	0.5883D-04	0.6385D+00
55	0.2179D-07	0.9999D+00	0.1000D+01	0.5302D-04	0.6742D+00
60	0.1964D-07	0.9999D+00	0.1000D+01	0.4778D-04	0.7064D+00
65	0.1770D-07	0.9999D+00	0.1000D+01	0.4306D-04	0.7354D+00
70	0.1595D-07	0.9999D+00	0.1000D+01	0.3881D-04	0.7615D+00
75	0.1438D-07	0.9999D+00	0.1000D+01	0.3498D-04	0.7851D+00
80	0.1296D-07	0.9999D+00	0.1000D+01	0.3152D-04	0.8063D+00
85	0.1168D-07	0.9999D+00	0.1000D+01	0.2841D-04	0.8254D+00
90	0.1052D-07	0.9999D+00	0.1000D+01	0.2560D-04	0.8427D+00
95	0.9483D-08	0.1000D+01	0.1000D+01	0.2307D-04	0.8582D+00
100	0.8546D-08	0.1000D+01	0.1000D+01	0.2079D-04	0.8722D+00
105	0.7702D-08	0.1000D+01	0.1000D+01	0.1874D-04	0.8848D+00
110	0.6941D-08	0.1000D+01	0.1000D+01	0.1689D-04	0.8962D+00
115	0.6256D-08	0.1000D+01	0.1000D+01	0.1522D-04	0.9065D+00
120	0.5638D-08	0.1000D+01	0.1000D+01	0.1372D-04	0.9157D+00

VITA

C. Christie Clark was born in Birmingham, Alabama on June 11, 1961. She received her undergraduate degree in Chemistry/Math from the Birmingham-Southern College in May 1985. For the next three years, she worked for Southern Research Institute, located in Birmingham, in their Environmental Services Department as an Assistant Chemist. In the Summer of 1988, she received a research assistantship from the University of Tennessee to work on their flue gas desulfurization pilot plant system while working towards a Master's degree in chemical engineering.

In May of 1991, she was married to Stephen Prout. Ms. Clark, now Mrs. Prout, will be employed by International Paper in their Pine Bluff, Arkansas mill after graduation.