DEVELOPMENT AND VALIDATION OF THERMODYNAMIC & PROCESS MODEL FOR A NOVEL AMINE-BASED SOLVENT IN CO_2 CAPTURE

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ABSTRACT

Accurate thermodynamic modeling is essential for the design and optimization of carbon capture processes, particularly those involving novel solvents with complex behavior. This study presents AVEVA's development and validation of the ION Clean Energy (ION) proprietary amine-based solvent and process modeling for post-combustion CO_2 capture. The thermodynamic model incorporates advanced electrolytic activity coefficient-based framework to represent phase equilibria and chemical speciation with high fidelity. The thermodynamic model integrates both the aspects of open modeling and an equation-oriented solver. Parameterization was achieved using a combination of laboratory measurements, with data regressed against a curated dataset, including vapor-liquid equilibrium, heat capacity, and enthalpy of absorption data. The thermodynamic model results for CO_2 partial pressure and transport properties align with the experimental data, achieving high accuracy over the lean and rich loading range of 0.05 to 0.6 mol CO_2/mol amine and the temperature range of 40 °C to 120 °C. The thermodynamic model was used with rigorous rate-based mass and heat transfer models and a novel enhancement factor formulation to account for reaction kinetics in the liquid phase. The process model was validated against ION's pilot plant data spanning multiple operating conditions. Results demonstrate a close match between model predictions and observed plant performance metrics, including CO_2 capture efficiency, temperature profiles, and energy consumption. The temperature profile in the absorber column aligns with the pilot plant data, with a maximum deviation of 2 °C throughout the column's height. The high level of agreement underscores the model's utility for process design, scale-up, and real-time control applications, positioning AVEVA Process Simulation as a robust tool that can be used for accelerating the deployment of advanced carbon capture solvents.

Keywords: Carbon capture, thermodynamics model, Rate-based column, Pilot plant validation

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1. Introduction

Carbon Capture, Utilization, and Storage (CCUS) is a critical technology for achieving net-zero emissions, particularly in sectors like industry and power. It also enables negative emissions and supports low-carbon hydrogen production, complementing other decarbonization strategies. Carbon capture technologies encompass a range of approaches, including solvent absorption, membrane separation, and cryogenic processes. Amine-based CO_2 absorption plays a pivotal role in post-combustion carbon capture due to its high efficiency and established technological foundation. This process enables scalable decarbonization of existing industrial and power generation infrastructure within CCUS frameworks [1].

The conventional solvents used in amine-based CO_2 absorption processes suffer from several drawbacks, including high regeneration energy demand, solvent degradation, and equipment corrosion. These challenges can be overcome by developing new solvent systems with enhanced CO_2 absorption capacity, faster reaction kinetics, improved thermal and chemical stability, and reduced energy requirements, to achieve more efficient and cost-effective carbon capture in post-combustion applications.

Process simulation plays a crucial role in the study of carbon capture by enabling detailed evaluation of process behavior and performance under varying conditions. It facilitates the optimization of system design and energy integration, ensuring efficient and cost-effective CO_2 capture. Moreover, simulation reduces reliance on extensive experimental trials, thereby accelerating the development and deployment of carbon capture technologies. Accurate thermodynamic modeling is fundamental to understanding phase equilibria, chemical reaction equilibrium, reaction kinetics, and energy requirements in carbon capture systems. This is especially critical when working with novel or advanced solvents, which often exhibit non-ideal and complex behavior. Reliable models enable precise prediction of process performance, aiding in the design, optimization, and scale-up of efficient capture technologies.

Modeling CO_2 absorption using amine-based solvents requires an accurate representation of a solvent's thermodynamic behavior, mass transfer, and reaction kinetics occurring within the absorption column. Traditional equilibrium-stage models assume instantaneous phase equilibrium, which fails to capture the complex dynamics between chemical reactions and diffusion in reactive systems. In contrast, rate-based models account for the rigorous mass transfer rates, reaction kinetics, and temperature gradients along the column, providing a more realistic and predictive description of the absorption and regeneration processes. Consequently, rate-based modeling is essential for reliable design, optimization, and scale-up of post-combustion carbon capture systems using amine solvents [2].

In this work, the thermodynamic and process model is developed in AVEVA Process Simulation (APS) for a proprietary amine-based solvent from ION Clean Energy (ION) designed for post-combustion CO_2 capture and related gas treating applications. The thermodynamic model is parameterized using the experimental data provided by ION to accurately represent the behavior of ION's solvent system by incorporating both laboratory and pilot plant data. Parameterization is performed through a combination of laboratory measurements and regression against a curated dataset that includes vapor–liquid equilibrium (VLE), calorimetric, and thermophysical property data. The system studied consists of amine solvent, Am in aqueous solution, with CO_2 as the target acid gas. Liquid-phase non-idealities are described using the electrolyte Non-Random Two-Liquid (eNRTL) model, while the vapor phase is represented by the Redlich–Kwong (RK) equation of state. The VLE and calorimetric data are primarily used to define and calibrate the thermodynamic model of the proprietary solvent, whereas pilot plant data is employed to validate the carbon capture process simulated in APS.

The structure of this paper is as follows: Section 2 outlines the methodology used to develop the thermodynamic framework in APS for modeling the amine-based solvent system. Section 3 describes the parameterization of the model using experimental data and estimation of the properties to capture the specific behavior of the proprietary solvent within APS framework. Section 4 details the development of the process simulation of the CO_2 capture system using a rate-based column in APS and the subsequent validation of model predictions against pilot plant data. Finally, Section 5 presents the conclusions drawn regarding the robustness and applicability of the developed thermodynamic and process model for simulating amine-based carbon capture processes. The APS framework is thermodynamically and kinetically rigorous such that the proprietary amine solvent may be combined with other amines to simulate solvent blends.

2. Thermodynamic Framework

Electrolyte systems involved in CO_2 capture processes exhibit highly non-ideal behavior, necessitating robust thermodynamic models for accurate representation. The eNRTL activity coefficient model [3] is widely employed for such systems due to its ability to account for complex molecular interactions including ions and reliability in the thermodynamic analysis of CO_2 capture solvents.

The equilibrium reactions characterizing the Am–H_2O–CO_2 system, which occur in the liquid phase, are shown in Eq 1 - 5.

$$2\,H_2O \leftrightarrow OH^- + H_3O^+ \qquad (1)$$

$$CO_2 + 2\,H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad (2)$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad (3)$$

$$AmH^+ + H_2O \leftrightarrow Am + H_3O^+ \qquad (4)$$

$$AmCOO^- + H_2O \leftrightarrow Am + HCO_3^- \qquad (5)$$

Equation (1) represents the autoionization of water, while Equations (2) and (3) describe the formation of bicarbonate and carbonate ions, respectively. Equation (4) corresponds to the protonation equilibria of the amine, and Equation (5) describes the formation of amine carbamate ions. The complete reaction chemistry of the system, along with the corresponding equilibrium constants and speciation data, was provided by ION.

The reference state for the molecular solvents is defined as symmetric, corresponding to the pure liquid phase under operating conditions, while an unsymmetric reference state representing infinite dilution in aqueous solution is applied for the ionic species. The components Am, and H_2O are treated as solvent species.

The physical solubility of CO_2 is represented using Henry's Law. Molecular solutes such as CO_2 and H_2S exhibit significantly higher solubility than non-reactive gases like N_2 or CO, particularly due to their participation in liquid-phase reactions. To account for non-ideal behavior in the liquid phase, activity coefficients are incorporated. Under the system conditions, these gases are treated as supercritical, with their unsymmetric reference state defined as infinite dilution in aqueous solution and modeled using gamma-phi methods represented by Equation 6,

$$y_i \varphi_i P = x_i \gamma_i^* H_i(T,P) \tag{6}$$

where x_i and y_i represent the mole fractions of component i in the liquid and vapor phases respectively, φ_i is the gas-phase fugacity coefficient of component i at the system temperature and pressure, P is the system pressure (kPa); γ_i^* denotes the activity coefficient of component i using infinite dilution reference state, and H_i is the Henry's constant of component i in the liquid mixture. The activity coefficient with an aqueous infinite dilution reference state for electrolyte Henry solutes is defined in Equation 7,

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^\infty} \tag{7}$$

A rigorous mixing rule is used to calculate H_i in the mixed solvent system, which uses the activity coefficient and critical volume to account for the non-ideality of the Am–H_2O–CO_2 system as shown in Equations 8-9,

$$ln\left(\frac{H_i(T,P)}{\gamma_i^\infty}\right) = \sum_A w_A \, ln\left(\frac{H_{iA}(T,P)}{\gamma_{iA}^\infty}\right) \tag{8}$$

$$\mathrm{w}_A = \frac{x_A (V_{cA})^{2/3}}{\sum_B x_B (V_{cB})^{2/3}} \tag{9}$$

Where V_{cA} and V_{cB} are the critical volumes of solvent A and solvent B, respectively.

For a given solute-solvent pair, the Henry's Law constant is calculated using Equation 10,

$$\ln(H_i(T,P)) = c1 + \frac{c2}{T} + c3\ln(T) + c4\,P + c5\,T \tag{10}$$

Where T is temperature in K, P is pressure in kPa and H is Henry's constant in kPa/mole fraction. For accurate estimation of solubility at high pressures, a pressure correction term is included using the Brelvi O'Connell Model [4] as shown in Equation 11,

$$H_{iA}(T,P) = H_{iA}(T,P_A^0)\ exp\left(\frac{v_{iA}^{\infty}(P-P_A^0)}{RT}\right) \tag{11}$$

Where P_A^0 is the saturation pressure of solvent, and v_{iA}^{∞} is the partial molar volume of molecular solute at infinite dilution in pure solvent, calculated using Brelvi-O'Connell method as a function of characteristic volumes as shown in Equation 12,

$$v_{iA}^{\infty} = f(v_{Ci}, v_{CA}, v_A^0) \tag{12}$$

Where v_{Ci} is characteristic volume of the component, v_{CA} is the characteristic volume of the solvent and v_A^0 is the liquid molar volume of the pure solvent.

With pressure correction applied to eNRTL, the activity coefficients of Henry solutes in the reactions are based on infinite dilution in aqueous solution and the Henry constant used in VLE calculations are based on infinite dilution in mixed solvents.

In the Liquid Activity Coefficient (LACT) method like eNRTL, the activity coefficients of all components (solvents, Henry solute, ions) are determined by a set of interaction parameters between components. APS employs a true-component approach to represent the system. Three categories of model-adjustable interaction parameters are defined: molecule–molecule, molecule–electrolyte, and electrolyte–electrolyte interactions. In this context, an "electrolyte" refers to a cation (c) –anion (a) pair. Molecule–molecule interactions are referred to as binary interactions, molecule–electrolyte interactions as ternary interactions, and electrolyte–electrolyte interactions as quaternary interactions. The eNRTL thermodynamic method is modeled using two kinds of parameters such as the symmetric non-randomness parameter (α_{ij}) and the unsymmetric binary interaction energy parameters (τ_{ij}). The non-randomness parameter, α_{ij}, is assigned default values as follows: 0.2 for molecule – molecule pairs, 0.2 for water – electrolyte pairs, 0.1 for non-water (amine & CO_2) – electrolyte pairs, and 0.2 for electrolyte – electrolyte pairs. For all three types of eNRTL interactions, the interaction energy parameters (τ_{ij}) is defined as a function of the temperature as shown in Equation 13[1], 14 [3].

$$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} + \frac{C_{ij}}{T^2} + D_{ij}ln(T) + E_{ij}T + F_{ij}Tln(T) \tag{13}$$

$$\tau_{ij} = -\frac{\ln(G_{ij})}{\alpha_{ij}} \tag{14}$$

Where, T is temperature in K, A_{ij}, B_{ij}, C_{ij}, D_{ij}, E_{ij}, and F_{ij} are the eNRTL interaction parameters. These interaction parameters are regressed using experimental data provided by ION as discussed in Section 3.

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[1] The format of τ_{ij} implemented in APS is different from the eNRTL format found in the literature

3. Property Estimation & Model Parametrization:

The APS thermodynamic model developed in Section 2 is parameterized using laboratory experimental data to capture the specific behavior of the proprietary amine solvent. The properties of the amine solvent and its corresponding ionic species, along with eNRTL interaction parameters and mixture properties, are regressed against experimental data within APS. Furthermore, the open platform architecture of APS allows seamless integration with built-in Python scripting, enabling enhanced process analysis, parameter regression, and workflow automation.

3.1 Pure component properties

The known components (CO_2, H_2O, H_3O^+, OH^-, CO_3^{2-}, HCO_3^-) of the system Am–H_2O–CO_2 are added from the SIMSCI and ELECTRL data bank available within APS framework. The amine solvent and associated ionic species within the Am–H_2O–CO_2 system are incorporated as user-defined components using the Library Generation tool in APS. The basic properties such as molecular weight, normal boiling point, and critical properties like critical temperature, critical pressure, critical volume, and acentric factor for the solvent is provided by ION. Temperature-dependent coefficients for these components (solvent and ions) are determined either through regression of experimental data provided by ION or estimation via the property synthesis method in the APS Thermodynamic Data Manager (TDM). Table 1 summarizes the temperature-dependent properties that are regressed or estimated for solvent and ions. The regression of temperature-dependent coefficients of the solvent and ions was performed using the native regression library in APS and validated over an extensive range of operating temperatures.

Table 1 - The list of temperature dependent properties regressed for solvent and ion components

Components	Temperature dependent properties
Solvent (Am)	Vapor Pressure, Latent heat, Ideal Gas heat capacity, Liquid heat capacity, Liquid density, Liquid viscosity, Liquid thermal conductivity, Surface tension, Dielectric constant
Ions	Liquid density, Liquid viscosity, Liquid heat capacity

3.2 Estimation of ion properties

Ions are modeled as non-volatile species within APS and exist only in the liquid phase. Their unsymmetric reference state corresponds to infinite dilution in the aqueous phase. The molecular weight, and charge of the ions are provided by ION. The reaction chemistry and equilibrium rate constant data are used to calculate the Heat of formation and Gibbs free energy of formation as shown in Equation 15 and 16. Then the heat capacity of the ions is calculated based on the reaction heat of formation and Gibbs free energy of formation as shown in Equation 17, thereby ensuring thermodynamic consistency within the model framework.

$$-RT\,ln\,K = \Delta G^o(T) \qquad (15)$$

$$\frac{d(ln\,K)}{dT} = \frac{\Delta H^o}{RT^2} \qquad (16)$$

$$\frac{-\Delta G^{\circ}(T)}{RT} = -\frac{\Delta G^{\circ}(T_{ref})}{RT_{ref}} + \frac{\Delta H^{\circ}(T_{ref})}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) + \frac{\Delta C_p(T_{ref})}{R}\left(\frac{T_{ref} - T}{T} + ln\frac{T}{T_{ref}}\right) \tag{17}$$

Where ΔH^o, ΔG^o, ΔC_p are change of properties based on the reaction, K is the equilibrium constant of the reaction, R is the universal gas constant, T is the system temperature and T_{ref} is the reference temperature.

3.3 Estimation of Equilibrium reaction constants

The chemical reaction equilibrium is solved simultaneously with the phase equilibrium in APS. The equilibrium constants are calculated using the temperature dependent equation shown in Equation 18.

$$ln(K_{eq}) = A + \frac{B}{T} + CT + Dln(T) \tag{18}$$

Where A, B, C and D are regressed using experimental data (Keq vs T) provided by ION. The equilibrium constants are expressed on a mole-fraction basis in APS, so the provided equilibrium constants are converted to mole-fraction basis to match the reference state in APS.

3.4 Estimation of eNRTL Interaction parameters

Key interaction parameters of the eNRTL model are determined using a sequential regression approach based on experimental vapor–liquid equilibrium (VLE) and calorimetric data. In this method, the binary interaction parameters are first regressed for the Am–H_2O system, followed by the ternary interaction parameters corresponding to the Am–CO_2–H_2O system.

The schematic representation of regression of interaction parameters in APS is shown in Figure 1. The regression procedure begins with the collection of relevant data (such as CO_2 partial pressure, P_{exp}), obtained either from experimental measurements or from literature sources. The APS electrolyte model is then employed to calculate the same thermodynamic property (P_{APS}), which is subsequently compared against the experimental data. The relative deviation between the calculated and experimental values is quantified, and regression is performed iteratively to minimize this error by adjusting the interaction parameters. This iterative optimization ensures that the model accurately reproduces the behavior of the proprietary solvent system.

The regression of the interaction parameters is carried out through the APS Python scripting interface, which enables a bidirectional integration between APS and external Python packages. The regression workflow is fully automated in APS, which facilitates the generation of simulation inputs, execution of regression routines, and real-time updating of model parameters. Following regression, the model is validated to ensure model accuracy and consistency across the full range of operating conditions.

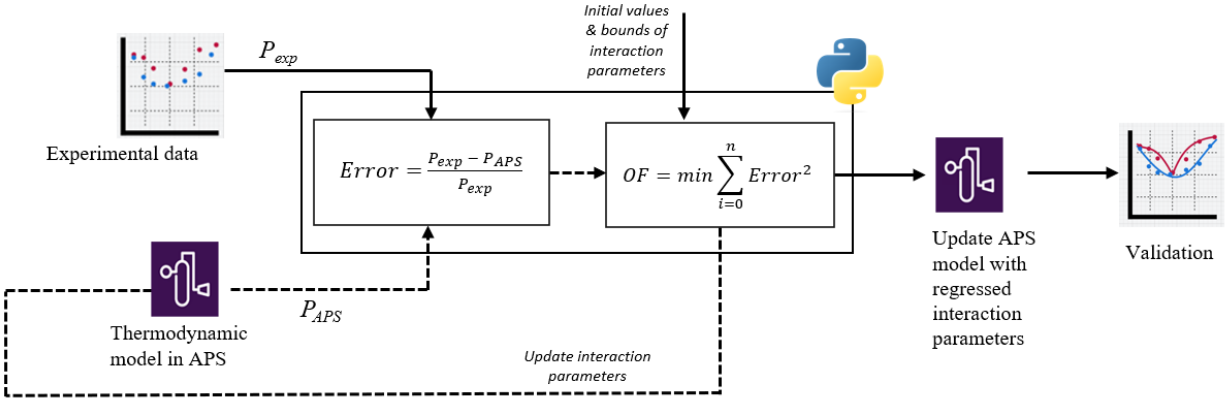

Figure 1 – The schematic representation of regression of ternary interaction parameters of the system Am-H_2O-CO_2 using CO_2 partial pressure data in APS.

To prevent overfitting and streamline the regression process, only the interaction parameters that have a significant influence on the solution thermodynamics are regressed. The regression is therefore limited to the principal ternary (molecule–electrolyte) interaction parameters and binary (molecule–molecule) interaction parameters of component pairs listed in Table 2 and default values are used for the remaining component pairs, also reported in Table 2.

Table 2 - List of component pairs for which binary and ternary interaction eNRTL parameters are regressed and updated in the model, along with default values assigned to non-sensitive pairs that are not regressed.

Interaction Parameters	**Component Pairs**	**Default values**
Binary System	Am – H_2O	$A_{ij}=B_{ij}=C_{ij}=D_{ij}=E_{ij}=F_{ij}= 0$ $\alpha_{ij}= 0$
Ternary System	Am – AmH^+ – HCO_3^- Am – AmH^+ – CO_3^{2-} Am – AmH^+ – $AmCOO^-$	$A_{ij}=15$, $A_{ji}=-8$ $B_{ij}=C_{ij}=D_{ij}=E_{ij}=F_{ij}= 0$ $\alpha_{ij}= 0.1$
	H_2O – AmH^+ – HCO_3^- H_2O – AmH^+ – CO_3^{2-} H_2O – AmH^+ – $AmCOO^-$	$A_{ij}=8$, $A_{ji}=-4$ $B_{ij}=C_{ij}=D_{ij}=E_{ij}=F_{ij}= 0$ $\alpha_{ij}= 0.2$

The binary interaction parameters are regressed against the binary system's amine volatility and excess enthalpy data. The regression of the ternary interaction parameters within the eNRTL model and Henry parameters (Am – CO_2) are done utilizing two primary types of experimental data: CO_2 partial pressure and speciation measurements at a temperature range of 40 – 120 ˚ C and a CO_2 loading (moles CO_2 / moles amine) range of 1 – 20 wt%. Accurate fitting of CO_2 partial pressure is essential, as it directly influences key performance metrics of the carbon capture process, including capture efficiency and energy consumption for solvent regeneration. Figure 2 demonstrates close agreement between APS model predictions and experimental CO_2 partial pressures over a representative temperature range and varying CO_2 loading conditions with an average error of 10%. This strong correlation validates the regression quality and supports the model's capability to reliably represent the thermodynamic behavior of the proprietary solvent system.

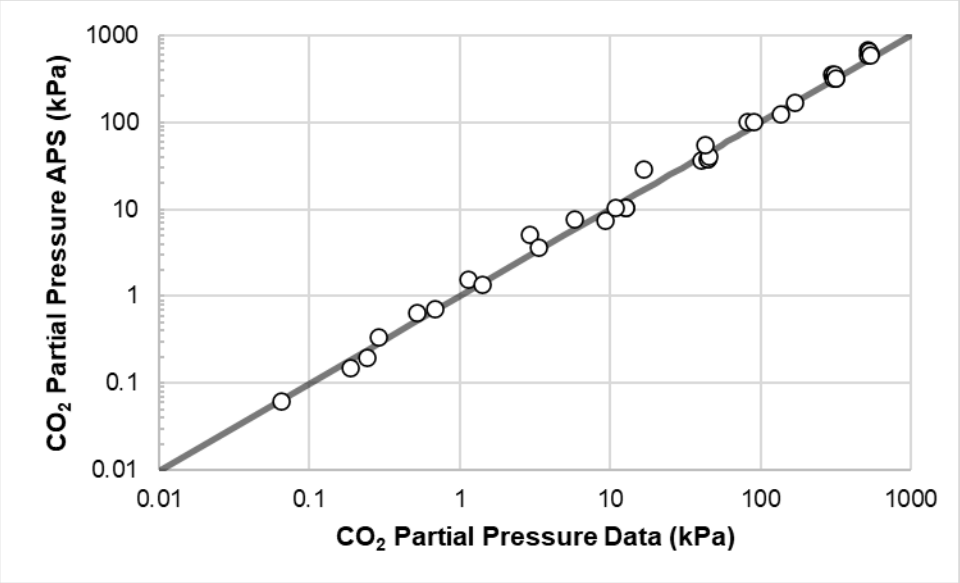

Figure 2 - Parity plot comparing APS-predicted and experimental CO_2 partial pressures after regression of eNRTL model interaction parameters across a wide range of temperatures and CO_2 loadings. The solid line is the 45° line (line of parity). The model matches experimental CO_2 partial pressures with an average error of ~ 10 %

3.5 Estimation of Differential Heat of absorption of CO_2

The heat of CO_2 absorption represents a substantial component of the energy consumption in the CO_2 regeneration process and serves as a critical parameter for validating the thermodynamic model. The differential enthalpy of absorption of the Am-H_2O-CO_2 system is defined as the heat released or absorbed per unit mole of CO_2 when an infinitesimal amount of CO_2 is added to the system. The differential enthalpy of absorption can also be determined using the estimated partial pressure and the Gibbs–Helmholtz equation as shown in Equation 19. In this study, the heat of absorption values predicted by these two independent methods are compared against each other and validated against experimentally measured calorimetric data, thereby confirming the thermodynamic consistency of the regressed models.

$$\left[\frac{\partial\, ln\, P_{CO_2}}{\partial\, (\frac{1}{T})}\right]_{\alpha CO_2} = -\frac{\Delta H_{CO_2}}{R} \qquad (19)$$

Where P_{CO_2} is partial pressure estimated using the thermodynamic model, and ΔH_{CO_2} is heat of CO_2 absorption. Due to the proprietary nature of the data, the comparison plot of the heat of absorption calculated using the regressed thermodynamics model, the Gibbs–Helmholtz equation, and experimental measurements is not included in this paper.

3.6 Estimation of mixture properties

Mixture properties such as liquid density and viscosity of the solvent are essential thermophysical parameters in the carbon capture process, as they influence mass transfer efficiency, column, and overall process performance. The liquid molar density of the mixture is calculated using the Quadratic Mixing Rule (VLQMR) implemented in APS, while the liquid viscosity is determined using the Power Molar Average method as defined in APS. The data used to regress the mixture properties, and the range of temperature and CO_2 loadings to characterize the proprietary solvent is summarized in Table 3.

Table 3 - Summary of experimental data employed in regressing mixture properties of the proprietary solvent.

Property: Mixing Rule	**System**	**Data Range**	**Regressed Parameters**
Liquid density: Quadratic Mixing Rule	$Am - H_2O$ $Am - H_2O - CO_2$	Temperature: 20 – 60 °C CO_2 Loading: 0.00 – 0.14 (wt basis)	Liquid density - temperature dependent coefficients of Ions & VLQMR data between component pairs
Liquid viscosity: Power Molar Average			Liquid Viscosity temperature dependent coefficients of Ions

Regression of mixture properties such as liquid density and viscosity is conducted using the APS Python thermo access interface, which provides access to the thermodynamic calculation engine for data analysis and parameter estimation. Table 4 lists the component pairs for which binary VLQMR interaction parameters are regressed and updated to match density data.

Table 4 - List of component pairs for which binary VLQMR interaction parameters are regressed and updated in the model to fit density data

Interaction Parameters	**System**	**Component Pairs**
Liquid Density	$Am - H_2O - CO_2$	$Am - H_2O$ $AmH^+ - H_2O$ $HCO_3^- - H_2O$

The data indicates that the mixture properties are composition-dependent and must be updated for different $Am–H_2O–CO_2$ mixtures. Moreover, these properties are influenced by the solvent's operating conditions within the rate-based column.

Temperature-dependent parameters and quadratic mixing rule parameters for liquid density and temperature-dependent parameters for liquid viscosity are regressed using both CO_2-loaded ($Am–CO_2–H_2O$) and CO_2-free ($Am–H_2O$) amine solutions. Validation results, presented in Figures 3 and 4, demonstrate strong agreement between APS-predicted and experimental values for density and viscosity over a temperature range of 20–60 °C and CO_2 loading range of 0 to 14 wt%. The average prediction error remains within 3%, providing high confidence in the model's accuracy to develop carbon capture process. The same methodology can be applied to parameterize any additional amine when modeling a proprietary amine solvent blend.

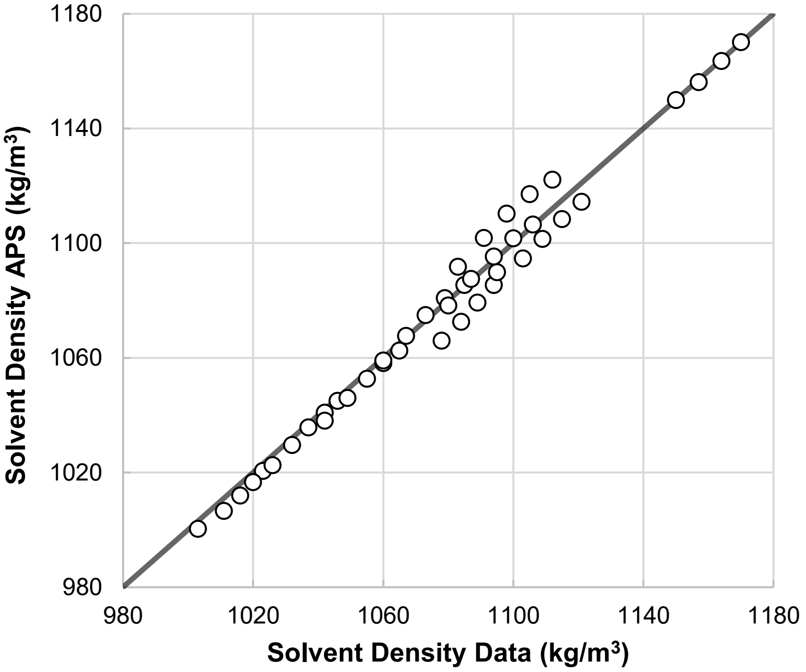

Figure 3 - Parity plot of APS-predicted versus experimental CO_2 solvent densities following regression of temperature-dependent liquid density coefficients and VLQMR parameters over varying temperatures and CO_2 loadings. The solid line is the 45° line (line of parity). The model matches experimental CO_2 partial pressures with an average error of ~ 3 %

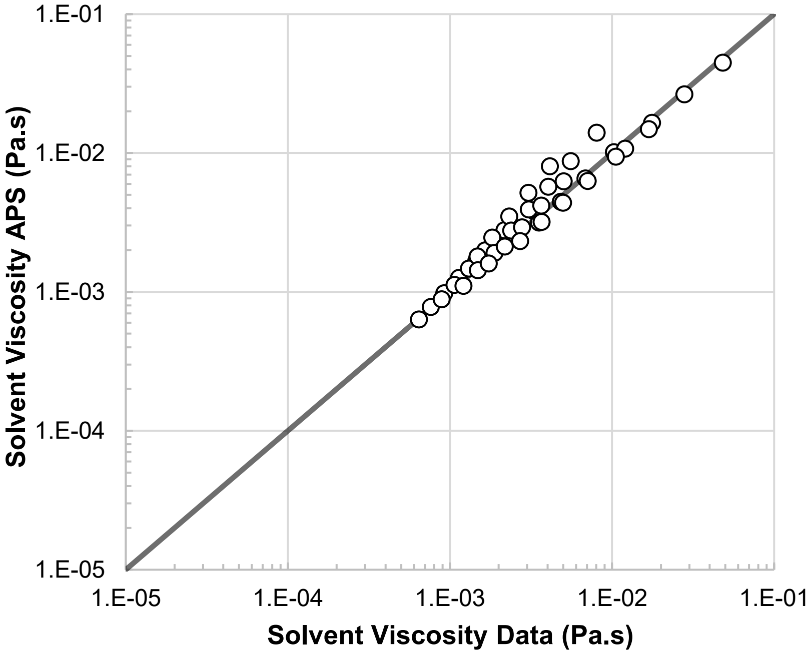

Figure 4 - Parity plot of APS-predicted versus experimental CO_2 solvent viscosities following regression of temperature-dependent liquid viscosity coefficients over varying temperatures and CO_2 loadings. The solid line is the 45° line (line of parity). The model matches experimental CO_2 partial pressures with an average error of ~ 3 %

3.7 Fluid Definition in APS

The regressed pure-component properties, eNRTL interaction parameters, mixture properties, and reaction chemistry are integrated to define the system, referred to as a *Fluid* within APS. This fluid represents the proprietary amine solvent developed by ION and can be applied across all unit operations within the simulation environment. The equation-oriented solver in APS simultaneously solves chemical and phase equilibria. The defined fluid is subsequently used to model CO_2 absorption in a rate-based column, as discussed in Section 4.

4. Process Modeling of Carbon capture using proprietary solvent

The absorption of CO_2 from a flue gas stream is simulated using a rate-based column from the APS rate-based modeling library, combined with the thermodynamic model of the proprietary solvent. Non-equilibrium separations in APS are addressed through rigorous stage-wise models that incorporate both mass and heat transfer, enabling accurate representation of absorption and regeneration processes. It is assumed that the system operates at a steady state condition. In an equilibrium model, the mass and energy transfer rates are determined solely by phase equilibria. Conversely, in a non-equilibrium model, the approach to equilibrium compositions and temperatures for each phase are influenced by resistances within the interfacial film layers. The rate-based stage model incorporates these resistances by expressing the transfer rates as functions of diffusional mass and heat fluxes. Mass fluxes are calculated using estimates of binary diffusion and mass-transfer coefficients within each phase's film layer, while energy flux is determined based on heat-transfer coefficients in the corresponding film layers. The reactions occur simultaneously with diffusion in the liquid film as shown in Figure 5. In the case of mass transfer coupled with a chemical reaction in the liquid phase, the reaction will enhance mass transfer [5], and this is modeled using Enhancement factor in APS.

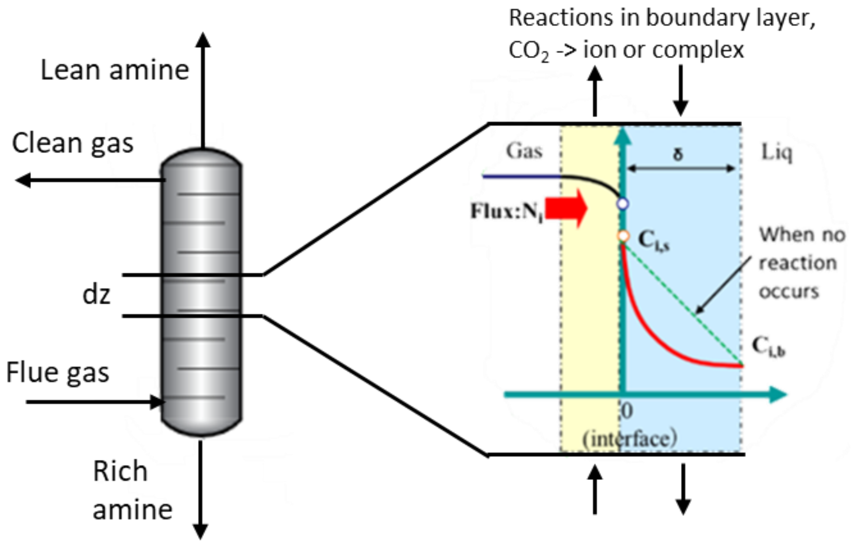

Figure 5 - Schematic representation of the Enhancement factor in absorption of CO_2

4.1 Enhancement factor

The Enhancement model accounts for the increased mass transfer of CO_2 within the diffusive film layer of an aqueous amine solution. The rapid chemical reactions between the CO_2 and the amine solvent accelerate mass transfer that would otherwise be limited by diffusion. The Enhancement factor (E) derived from the model is applied as a scaling factor in the rate-based column calculations to represent the effect of chemical reactions on mass transfer. These models account for the increased mass transfer due to rapid chemical reactions within the liquid phase. It is assumed that one mole of amine reacts with one mole of CO_2 according to Equation 20.

$$\text{Am} + \text{CO}_2 \leftrightarrow \text{AmCO}_2 \qquad (20)$$

The reaction in Equation 20 is considered for the formulation of the CO_2 Enhancement factor. The Enhancement factor is a ratio of mass transfer rates with reaction enhancement ($k_{CO_2,L}$) to those without reaction ($k^0_{CO_2,L}$) as shown in Equation 21.

$$E_{CO_2} = \frac{k_{CO_2,L}}{k^0_{CO_2,L}} \qquad (21)$$

In APS, the analytical expression for the enhancement factor in the enhancement model is determined by solving a set of differential equations, describing diffusion, reaction, and material balance in the boundary film [6]. The enhancement models in APS can simulate both simultaneous and selective absorption of CO_2 and H_2S and are compatible with single amine and amine blends. These correlations are applied in both the absorber and stripper columns, requiring only the overall kinetic rate constant expression (Equation 22) as input, thereby simplifying implementation while preserving model accuracy.

$$kov_{CO2\_Am} = A_r \, exp\left(-\frac{E_r/R}{T}\right)\frac{1}{v} \qquad (22)$$

Where A_r is the pre-exponential factor (m^3/kmol-s), E_r/R is the ratio of activation energy to gas constant (K), v is the molar volume of solute (m^3/kmol) and T is the reaction temperature (K). The kinetic data for the reaction (Equation 20) is provided by ION. The same enhancement model can be extended to incorporate the appropriate kinetic rate expression for any additional amine when modeling solvent blends.

4.2 Data Requirements for Process Modeling

In the rate-based column model, APS incorporates a range of standard structured and random packing types, along with built-in mass and heat transfer correlations from the literature. For this study, pilot-plant-specific packing characteristics are implemented to more accurately represent the actual column configuration. Chilton Colburn analogy is used for heat transfer coefficient models [7]. In addition, the mass transfer models are adapted from literature data to ensure closer alignment with system behavior [8] [9]. A major advantage of APS is its customizable modeling framework, which allows users to access and modify the underlying equations, providing the flexibility required for this work.

Modeling of the CO_2 capture process using a rate-based column requires information on the packing type, packing-specific parameters (including specific surface area, crimp height, channel base length, channel side length, bed void fraction, channel flow angle), and column geometry such as column height and diameter. All necessary data was provided by ION based on pilot plant measurements to use in the CO_2 capture process simulated in APS. The flue gas and lean amine stream conditions, temperature, pressure, composition, and mass flow rate obtained from pilot plant data are used as inputs for modeling the absorber section of the process. The predicted CO_2 loading in the rich amine stream and the treated gas flow rate are used to validate the absorber model. Similarly, the temperature, pressure, composition, and mass flow rate of the rich amine stream served as inputs for modeling the stripper section. The predicted lean amine and CO_2 product gas flow rates and compositions are then compared with pilot plant data for model validation.

4.3 Process Simulation and Validation of post combustion carbon capture

A typical simulation of CO_2 removal from flue gas is shown in Figure 6. The flue gas exits the post combustion process unit at temperatures exceeding 100 °C and is first cooled to approximately 40 °C using a direct contact cooler. The cooled gas then enters a rate-based absorber column, where CO_2 is absorbed counter currently into the solvent within a packed section. To minimize solvent losses and enhance recovery, a water wash section is incorporated at the top of the absorber to remove volatile organic components and restore water balance.

The CO_2-rich amine leaving the bottom of the absorber passes through a lean-rich cross-exchanger for energy recovery before entering the stripper column, where CO_2 is desorbed and collected. The regenerated lean amine is then recycled to the absorber, enabling continuous operation. CO_2 enhancement factors are implemented in both the absorber and stripper columns to accurately represent the coupled mass transfer and reaction kinetics.

The simulation results from APS were validated against ION's pilot project at Los Medanos Energy Center [10]. The pilot has run continuously for one year, and a wide range of process conditions were tested. The setpoints used to validate the APS model encompass all of these process conditions, furthering ION's confidence in the accurate modeling of thermodynamics and kinetics of the system within APS.

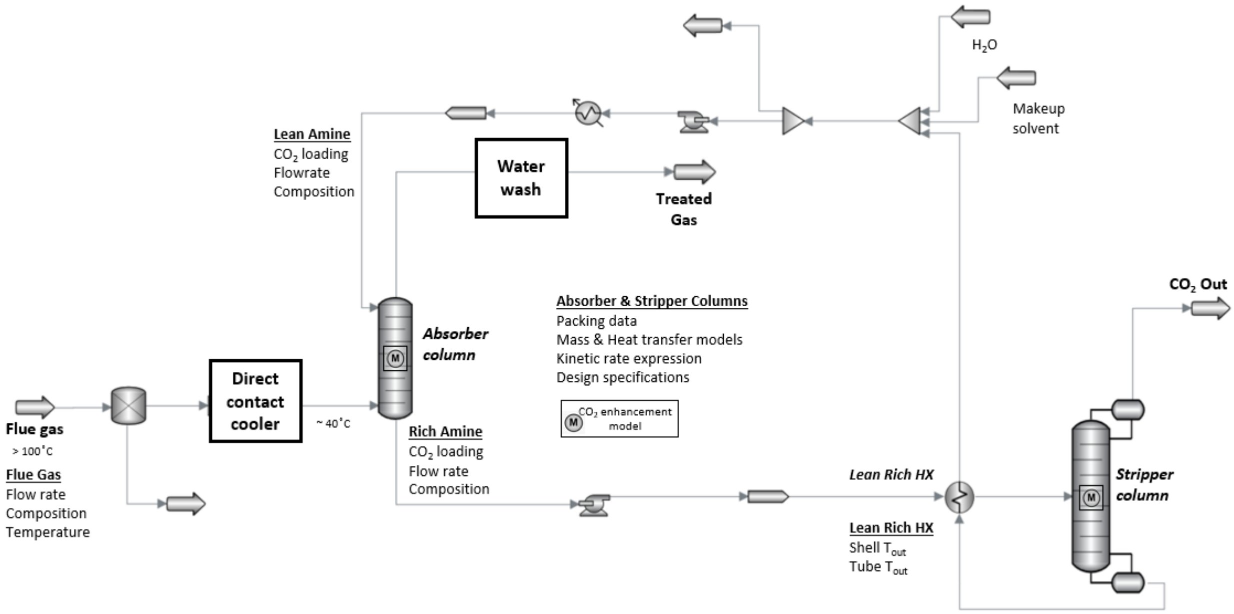

Figure 6 – Typical simulation of CO_2 removal from flue gas in APS with key stream variables highlighted

Key performance indicators (KPIs) for the process include CO_2 capture efficiency (CE) and specific reboiler duty (SRD). The CO_2 capture efficiency quantifies the fraction of CO_2 removed from the flue gas stream in the absorber as shown in Equation 23.

$$CE\ (\%) = \frac{FlueGas.F[CO_2] - TreatedGas.F[CO_2]}{FlueGas.F[CO_2]} \tag{23}$$

where FlueGas.F[CO_2] and TreatedGas.F[CO_2] represent the molar flow rates of CO_2 in the inlet (flue gas) and outlet (treated gas) streams, respectively. A higher CE value indicates a greater proportion of CO_2 captured by the amine solvent.

The specific reboiler duty (SRD) represents the thermal energy required in the stripper column per unit mass of CO_2 captured as shown in Equation 24.

$$SRD\ \left(\frac{GJ}{tonne}\, of\ CO_2\right) = \frac{StripperCol.ReboilerDuty}{1000\ * CO_2Out.W[CO_2]} \tag{24}$$

where StripperCol.ReboilerDuty denotes the reboiler duty of the stripper column (in kJ/h), and CO_2Out.W[CO_2] is the mass flow rate of CO_2 in the product stream (in kg/h). The factor of 1000 converts the units to gigajoules per tonne of CO_2. A lower SRD indicates better energy efficiency of the solvent regeneration process.

The developed APS model was validated against pilot plant operating setpoints to assess its predictive accuracy. The study presents results for one representative validation setpoint. Figure 7 shows the comparison of predicted absorber temperature and pilot plant data from ION along the absorber column. The model accurately predicts the temperature distribution across the column height with a maximum deviation of 2 °C and this demonstrates the reliability of the thermodynamic and kinetic representations. A minor deviation observed at the midpoint location in the absorber— indicated by marker x —was traced back to a faulty temperature probe, a trend also identified in other setpoints. This shows the model's ability to help diagnose problems with equipment and further proves the robustness of the developed thermodynamic and process model in APS.

Figure 8 shows the comparison of predicted stripper column temperature and pilot plant data from ION. The model gives a good representation of the temperature along the stripper column with a maximum deviation of 4 °C. The overall process model demonstrates no systematic bias under the different operative conditions investigated in this study.

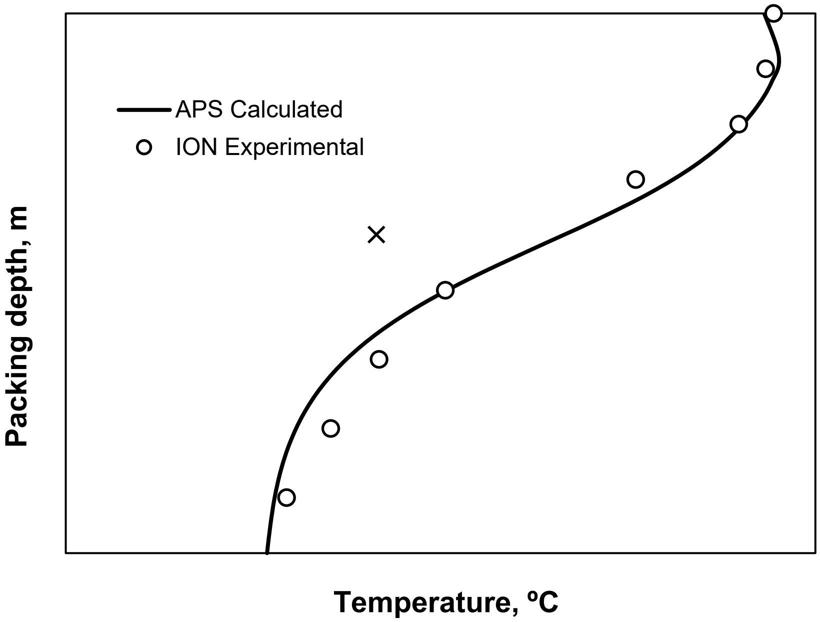

Figure 7 - Comparison of absorber column temperature profiles[2] between pilot plant data from ION and APS model predictions. The temperature profile in the absorber column aligns with the pilot plant data, with a maximum deviation of 2 °C throughout the column's height.

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[2] The temperature values on the x-axis are not disclosed due to the proprietary nature of the data.

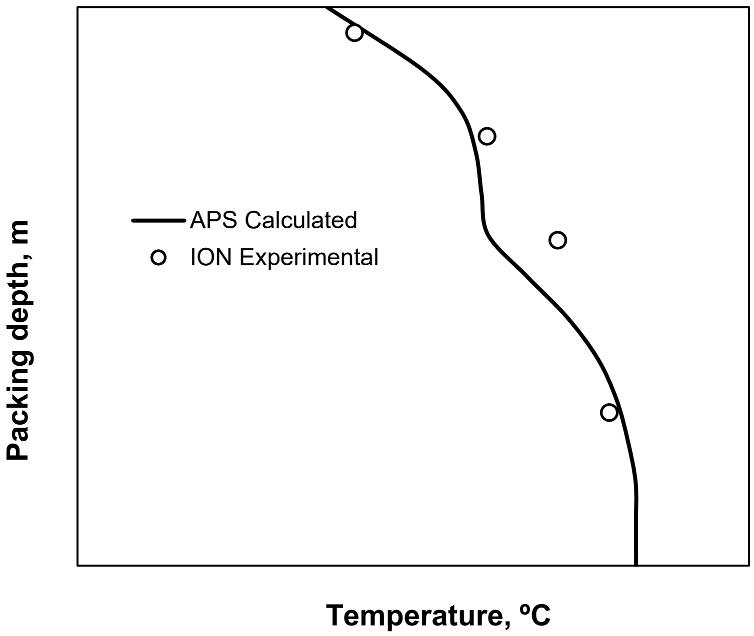

Figure 8 - Comparison of stripper column temperature profiles[2] between pilot plant data from ION and APS model predictions. The temperature profile in the stripper (regenerator) column aligns with the pilot plant data, with a maximum deviation of 4 °C throughout the column's height

Table 5 presents a quantitative comparison of carbon capture efficiency, specific reboiler duty, and CO_2 loading in the rich stream leaving the absorber column between the APS model predictions and pilot plant data. Due to the confidentiality restrictions, the comparison of specific reboiler duty and rich loading is shown on an arbitrary (relative) basis. The strong consistency between the model and experimental results highlights the reliability and accuracy of the CO_2 enhancement model and the associated thermodynamic framework. Furthermore, the model provides diagnostic and interpretive capabilities that are beneficial for performance assessment and troubleshooting of pilot-scale operations.

Table 5 - The quantitative comparison of Process KPI’s between Pilot plant data and APS model predictions.

KPI	Pilot plant data	APS Prediction
Capture Efficiency [%]	95.08	95.00
Specific Reboiler Duty [arbitrary]	1.00	1.003
Rich Loading [arbitrary]	1.00	1.058

5. Conclusion

This study presents the development and validation of a comprehensive thermodynamic and rate-based model for a proprietary amine-based CO_2 capture system using APS. Pure component and interaction parameters were regressed through automated regression workflows using Python-based scripting, facilitating efficient and reproducible parameter estimation. The model was parameterized using experimental vapor–liquid equilibrium, calorimetric, and thermophysical property data to ensure accurate representation of solvent behavior over a wide operating range. The proposed eNRTL Am-H_2O-CO_2 model predicts partial pressures of CO_2 with an average error value of 10%. Thermodynamic consistency was verified by validating the heat of absorption through eNRTL framework, Gibbs–Helmholtz approach and the experimental data. Mixture properties such as liquid density and viscosity were regressed against experimental measurements, and the model predicts mixture density and viscosity at an average error of 3%.

The rate-based column model in APS, incorporating a generalized CO_2 enhancement factor formulation, successfully captured the combined effects of mass transfer and chemical reaction kinetics. The process model, validated against pilot plant setpoints, demonstrated close agreement between predicted and experimental results for key performance indicators, including CO_2 capture efficiency, specific reboiler duty, and temperature profiles. The temperature profile in the absorber column aligns with the pilot plant data, with a maximum deviation of 2 °C throughout the column's height. Based on the validation results, the absorber and stripper models show no systematic bias to the main process variables. The strong correlation confirms the robustness and predictive capability of the developed model.

Overall, the integrated modeling framework developed in this study provides a reliable and flexible approach for developing thermodynamic models of proprietary solvent in APS using experimental data and for developing process models of amine-based CO_2 capture systems based on pilot plant data. This framework offers a robust foundation for future work on process optimization, solvent screening, and scale-up analysis.

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